Enhancement of the Stability of Mordenite for use in Dimethyl Ether Carbonylation

by

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Abstract

Recently, considerable research has been conducted into solid-acid catalyzed carbonylation of dimethyl ether (DME) to methyl acetate (MeOAc), which can be further used for the iodine-free production of ethanol or acetic acid. The zeolite mordenite (H-MOR) is known as a potential catalyst but is subject to a rapid deactivation that so far hinders the process commercialization. The objective of the current study is to find a simple and effective means by which H-MOR can be stabilized for DME carbonylation.

The bimetallic liquid-based ion-exchange (IE) of Cu^{2+} and Zn^{2+} onto MOR was used to enhance its stability. Compared to the original H-MOR (Si/Al ratio of 6.5), 1Cu-4Zn/H-MOR (Cu:Zn ratio of 0.25) had 3 times the lifetime and produced 4 times the total MeOAc before deactivation at 438 K. High selectivity to MeOAc was also maintained on catalyst deactivation. Cu and Zn occupied around 55% of the acid sites on MOR but there was no decrease in activity compared to the H-MOR. Despite Cu being a known carbonylation catalyst, it did not enhance the catalyst activity. It was determined that, due to the competitive IE of Cu^{2+} and Zn^{2+} over MOR, the two metals were forced into blocking different unselective acid sites that would normally have contributed to coking reactions. This was shown by quantum chemical modeling of the potential IE locations for Cu^{2+} and Zn^{2+} , which was in agreement with catalyst characterization results. Specifically, competitive IE at the T1 acid site was responsible for the unique behaviour of the 1Cu-4Zn/H-MOR. The use of Zn also stabilized Cu in its monovalent state and prevented any sintering from occurring. Thus, it is shown that the selectivity and stability of H-MOR can be substantially improved by selective poisoning of acid sites. This has important implications for Cu/H-MOR catalysts that have found increasing use, such as in methane-to-methanol processes.

Dealumination of MOR via acid leaching was also used in an attempt to increase its stability and to understand the relative contributions of different acid sites. Gradual

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dealumination from the original Si/Al ratio of 6.5 resulted in activity loss, but also increased H-MOR's selectivity to MeOAc during deactivation. At a Si/Al ratio of 15.4, the H-MOR was substantially deactivated by the dealumination. The catalyst characterization showed that the acid leaching was preferably removing the T3 acid site. This acid site had been previously theorized to be the only site at which DME carbonylation selectively occurred. This work provided substantial experimental evidence supporting this theory. Mild dealumination to a Si/Al ratio of 8.6 did improve H-MOR performance and it was determined that, while the other acid sites may contribute to coking, they were not solely responsible for the catalyst deactivation. Too high an acid site density near to the T3 acid site is also detrimental to the performance of the catalyst.

Applying the principle of selective site poisoning derived from the bimetallic Cu²⁺-Zn²⁺ IE study, Fe²⁺ was placed onto MOR via oxidative solid-state IE (Fe(II)/H-MOR). The resultant catalyst had 2 times the lifetime and produced over 3 times the MeOAc compared to acidic MOR. High selectivity to MeOAc was maintained even with catalyst deactivation. The use of monometallic Fe²⁺ on MOR is preferable to the use of monometallic Cu²⁺ or Zn²⁺ placed onto mordenite via IE. When combined with Zn²⁺, the bimetallic 3Fe(II)-1Zn/H-MOR catalyst (Fe:Zn ratio of 3) had very similar performance to the bimetallic 1Cu-4Zn/H-MOR catalyst.

Thus, three potential catalysts were identified for possible use in industrial DME carbonylation: Fe(II)/H-MOR, 1Cu-4Zn/H-MOR, and 3Fe(II)-1Zn/H-MOR. All of these catalysts have high peak activity levels and maintain high selectivity to MeOAc for the entirety of the catalyst lifetime, and are significant improvements over H-MOR alone. It is still required that the reaction conditions be optimized as well as suitable regeneration procedures put in place to restore the catalysts after deactivation.

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Preface

Parts of Chapter 4 of this thesis have been published as A.A.C. Reule, N. Semagina, "Zinc Hinders Deactivation of Copper-Mordenite: Dimethyl Ether Carbonylation", *ACS Catalysis*, 6 (8), 2016, 4972-4975. I was responsible for the majority of the collection and analysis of the data and wrote the entirety of the first draft of the paper. N. Semagina was the supervisory author and edited the first drafts of the paper.

A variation of Chapter 5 of this thesis has been submitted for publication to *Journal of Catalysis* as A.A.C. Reule, J. Sawada, N. Semagina, "Effect of selective 4-membered ring dealumination on mordenite-catalyzed dimethyl ether carbonylation". I was responsible for the majority of the data collection and analysis and wrote the entirety of the first draft of the paper. J. Sawada provided training and insights into the results. N. Semagina was the supervisory author and edited the first drafts of the paper.

The chapters related to these publications have been written solely by myself and present a significantly extended version of the publications.

In all of the work, there were several technicians who helped to collect data. Diane Caird collected XRD data, Dr. Guy Bernard collected ²⁷Al MAS NMR data, Dr. Jing Shen collected DRIFTS and took TEM images, Dr. Dimitre Karpuzov and Dr. Anqiang He collected XPS data, and Dr. Mike Xia collected UV-Vis data. Dr. Jing Shen also assisted in the analysis of XPS and DRIFTS data. Unless someone like you cares a whole awful lot, nothing is going to get better. It's not.

--Dr. Seuss, The Lorax

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List of Symbols and Abbreviations

| AcOH | Acetic acid |
|---------|---|
| AIPO | Aluminophosphate |
| BAS | Brønsted acid sites |
| С | Cation |
| CEC | Cation exchange capacity |
| DFT | Density Functional Theory |
| DME | Dimethyl ether |
| DRIFTS | Diffuse reflectance infrared Fourier transform spectroscopy |
| EDX | Energy-dispersive X-ray analysis |
| EPA | Environmental Protection Agency |
| ETS | Engelhard titanosilicate |
| EXAFS | Extended x-ray absorption fine structure |
| F | Molar gas flow |
| FER | Ferrierite |
| H-MOR | Acidic mordenite |
| НК | Horvath-Kawazoe |
| HF | Hartree-Fock |
| ICP-OES | Inductively coupled plasma optical emission spectroscopy |
| IR | Infrared |
| LAS | Lewis acid sites |
| М | Metal |
| MAS NMR | Magic angle spinning nuclear magnetic resonance |
| MCM | Mixed coordination material |
| MeAPO | Metal-aluminophosphate |
| MeOAc | Methyl acetate |
| MeOH | Methanol |
| MOR | Mordenite |
| MR | Membered-ring |
| PDA | Pore directing agent |
| S | Selectivity |

| Sa | Adsorption site A |
|--------|--------------------------------------|
| Sb | Adsorption site B |
| SAPO | Silicoaluminophosphates |
| SBU | Secondary building unit |
| SDA | Structure-directing agent |
| SEM | Secondary electron microscopy |
| х | Conversion |
| т | Temperature |
| t | time |
| TEM | Transmission electron microscopy |
| TPD | Temperature-programmed desorption |
| TPO | Temperature-programmed oxidation |
| TPR | Temperature-programmed reduction |
| TS | Titanosilicate |
| UV-Vis | Ultraviolet-visible |
| XANES | X-ray absorption near-edge structure |
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray diffraction |
| Z | Zeolite |

Chapter 1

Introduction

Education is not training but rather the process that equips you to entertain yourself, a friend, or an idea.

--Wallace Sterling

1.1 Green Chemistry and Sustainable Development

Modern chemistry and chemical engineering have evolved from the idea of "can it be done?" to "can it be done *better*, *safer*, and more *efficiently*?". While industrial companies have always been interested in the minimization of costs, attention towards the reduction of pollution and hazardous substances is a more recent development. It could be argued that this move began in 1990, with the implementation of the Pollution Prevention Act in the United States (U.S.) [1,2]. Instead of waiting for incidents with pollution and waste to happen, the intent of the act was to prevent this waste from being formed in the first place. While many fields of study were involved and initiatives set up in the decade after the Pollution Prevention Act, the most relevant to the subject at hand would be the Alternative Synthetic Pathways research solicitation, set up by the U.S. Environmental Protection Agency (EPA) in 1991 [2–4]. Two years later, the EPA changed the name of the program to the "U.S. Green Chemistry Program," which resulted in the term "green chemistry" becoming official [4,5].

Green chemistry came to be formally defined as the development of chemical products and processes that either reduce or completely eliminate the use or generation of

hazardous substances. It is framed by 12 guiding principles [6]. These principles are easily found online or in literature and will not be listed in detail here [7,8]. Even at the time the 12 principles were finalized, none of them was new individually, but together gave researchers a more formalized approach for developing inherently safer products and processes. Many of the principles involve the minimization of waste and the avoidance of the use of feed stocks that do not end up in the final product, which is commonly referred to as the atom economy [9]. The seventh principle of green chemistry states that the raw material or feedstock should be renewable, which is the principle that most directly addresses the issue of sustainable development.

The idea of sustainable development was introduced in 1987 by G.H. Brundtland in a report to the United Nations [10]. In this document, it was stated that "sustainable is the development that meets the needs of the present without compromising the ability of future generations to meet their own needs." Like green chemistry, sustainability had its own key concepts. The most notable of these concepts was that no impact to the environment should be irreversible, the most recent scientific knowledge should be used when designing new processes, and it is a scientist's duty to aid in development of environmental knowledge [5]. Strictly speaking, green chemistry and sustainable chemistry are not the same. Green chemistry focuses on ways to make products in a way that is less harmful to human health and the environment, and it does this through changes to feedstocks, solvents, synthesis and processing. Green chemistry principles are focused more on syntheses as opposed to industrial processes [5,11]. Sustainable chemistry takes a more comprehensive approach. It includes green chemistry and engineering concepts but strives to strike a balance between economic growth and development, promotion of society, and environmental preservation [12].

Regardless of which term is used, catalysis is fundamentally important to both green and sustainable chemistry. Catalysis is directly included in the 12 principles of green chemistry as the ninth principle, which states that catalytic reagents are superior to stoichiometric reagents [7,8]. This thought is shared by advocates of sustainable chemistry and, going along with their more holistic approach, also state that catalysis allows for intensification of a reaction. Through reaction intensification, catalysis can allow for the development of continuous processes with smaller reactors and less severe reaction conditions. Catalysts will also allow for the maximization of the desired product, reducing the need for downstream separation. This lowers costs, minimizes the environmental impact, and reduces waste [5,8,13,14]. Catalysts are absolutely fundamental from the point of view of industry not only for the above reasons, but also just to make some reactions even feasible at an industrial scale. As a point of reference, more than 90% of industrial processes use a catalyst [15].

The principles of green chemistry and general concepts of sustainable chemistry have permeated most areas of industrial manufacture. These principles are not necessarily forced on producers. Producers embrace them, as abiding by these concepts usually results in a reduction of overall costs as well as providing opportunities for improvement of public relations.

1.2 Using every last little bit – gasification and pyrolysis

One of the more difficult principles of green chemistry to adhere to is principle seven, which states that feedstocks should come from renewable sources rather than depleting natural resources. Of course, this principle does also state that this should be accomplished only whenever technically and economically practicable [7,8,11]. Any renewable source must be highly available if it is ever to have any hope of industrial implementation. Of the resources available now, biomass is one of the few showing great potential for green chemistry, and is even considered as a candidate for the replacement of crude oil [16]. The U.S. Department of Energy (DOE) set the goal of deriving 20% of transportation fuel from biomass by the year 2030 [17]. Biomass is a rather broad term, and includes any organic matter (specifically cellulosic or lingo-cellulosic) that is available on a recurring basis. This includes wood and wood residues, plant fiber, aquatic plants, other plants and their associated residues, animal wastes, some industrial waste, and dedicated energy crops [17,18].

Obviously the use of biomass raises some ethical and environmental issues. The first generation of biofuels was derived from sugars, grains, or seeds [19]. This created the food-versus-fuel debate, considered to be the primary disadvantage of the first generation biofuels [20]. Issues such as rising food costs and land use were raised. Of the grown crops, only a small fraction of the total plant biomass was used to produce the biofuel, which significantly reduced land use efficiency [19,21]. The goal of the second generation of biofuels was to utilize the residual non-food parts of current crops as well as to expand the feedstock sources to municipal, industrial, and construction waste [19,22]. Despite resolving the food-versus-fuel debate, second generation biofuels introduced challenges not present with the first generation biofuels. While the feedstock is less costly and highly available, the cost of processing the materials is significantly higher [19,22,23]. It is noted

here that research is also being conducted into third and fourth generation biofuels. The third generation uses algae and cyano-bacteria as feedstock, whereas the fourth generation attempts to make biohydrogen and bioelectricity by photosynthetic mechanisms [19,22].

The advantage to second generation biofuels is that they use waste materials that are already produced and normally just disposed of in a landfill or by some other means. Unfortunately, there was a reason these feedstocks were normally just tossed aside: they were difficult to process. Second generation biofuels are usually processed by thermochemical methods. While thermochemical methods are far more flexible with feedstock accommodation as opposed to biochemical methods, it comes at the cost of more extreme operating conditions. Thermochemical methods require extreme temperatures and pressures and include combustion, gasification, pyrolysis, liquefaction, and hydrothermal upgrading [19,22,23]. Of these methods, the two primary approaches used today are gasification and pyrolysis [24].

Both gasification and pyrolysis involve the thermal destruction of biomass into more basic molecules. Pyrolysis is conducted in the absence of oxygen, usually starts at 350-550°C but can go as high as 1000°C, and has potentially very short reaction times [25–27]. Pyrolysis always produces three products: char, bio-oil, and fuel gas. The proportions of these products can be altered by adjusting the process conditions [26]. Three different sets of process conditions have been established, and have come to be known as slow pyrolysis, fast pyrolysis, and flash pyrolysis. Slow pyrolysis occurs at 5-7°C/min, and usually results in the production of more char. Fast pyrolysis occurs at 10-200°C/s and favours the formation of bio-oil. Flash pyrolysis involves very high heating rate (<1000°C/s), only a few seconds reaction time, and favours the formation of fuel gas, which is primarily comprised of CO, CO₂, and CH₄. Many other components may also be present, including H₂ [25–27]. Consequently, the reaction schemes for the pyrolysis of biomass are extremely complex since there may be over a hundred intermediate products [27].

One of the biggest differences between gasification and pyrolysis is that gasification is conducted in the presence of a gasifying agent that promotes partial oxidation. The gasifying agent used is commonly oxygen, but may also be air, steam, CO_2 , or a mixture of all of them. Gasification of biomass results in the formation of a gaseous product called synthesis gas, which is more concisely referred to as syngas. Syngas consists largely of H₂ and CO, but may also contain some CO_2 , N₂, CH₄, H₂O, other ashes, tars, and oils [28–30]. Gasification takes place between 500 and 1400°C and at pressures anywhere between atmospheric and 33 bar [28]. Gasification likely takes places in several stages. Firstly, the solids are heated and dried, followed by a pyrolysis step. This pyrolysis step occurs between 150 and 400°C, resulting in char. The pyrolysis step is followed by oxidation or partial combustion of some gases, steam, and char by the gasification agent. The final step is reduction or gasification of the char to produce CO, CH_4 , and H_2 [31]. Interestingly, although many view gasification and pyrolysis as competing technologies, they are not necessarily. The bio-oil from fast pyrolysis can be gasified to produce syngas for further use in Fischer-Tropsch synthesis or alcohol synthesis [24,26].

Both gasification and pyrolysis processes can be modified to use a catalyst. Pyrolysis catalysts are usually zeolites used for the cracking of biomass and bio-oil [24]. Of all zeolites, ZSM-5 is used most often as it provides a balance between activity, limited deactivation by coking, and high thermal stability. ZSM-5 also has reasonable selectivity to $<C_{12}$ hydrocarbons [32]. The use of catalysts, zeolites or otherwise, in pyrolysis is mostly to assist in the change of composition of the products. The purpose of catalysts in gasification is to mostly assist in the clean-up of the tars or methane that is formed. These catalysts also need to be resistant to deactivation, simple to regenerate, and be inexpensive [33]. The minerals dolomite and olivine have been used extensively for gasification [34–36], along with alkali salts, which may be added directly, [37] and nickel-based catalysts [33,38].

1.3 Syngas to methanol and dimethyl ether

The syngas from either direct gasification of biomass or gasification of bio-oil from fast pyrolysis must be valorized by upgrading. There a few means by which syngas is upgraded. Syngas is often converted to methanol, ethanol, and other alcohols [26,39]. Alcohols, specifically ethanol, possess considerable value as biofuels. Even though ethanol does not possess the same energy equivalence as petroleum fuel, the combustion of ethanol is cleaner [40]. Methanol is often further upgraded to other products, some of which are biofuels. Rather than going through a multi-step process, syngas can also be converted more directly to methane, gasoline, diesel, and kerosene via Fischer-Tropsch synthesis [26]. Fischer-Tropsch synthesis is instrumental in the biomass-to-liquids process, utilizing either Co- or Fe-based catalysts [41]. While on the surface Fischer-Tropsch syntheses sound ideal for upgrading of biomass to liquid fuels, there are many challenges. Catalyst performance remains an issue, with catalysts being highly vulnerable to impurities and deactivation. This means that Fischer-Tropsch processes typically involve a large, costly cleaning section for purification of the synthesis gas before upgrading it in the presence of the catalyst [42]. The conversion of syngas to methanol is already a very old technology and has been implemented at an industrial scale for some time now. Syngas to methanol (known as hydrogenation of CO) is performed typically using a Cu-ZnO/Al₂O₃ catalyst (though some variants exist) which gives over 99% yield and very high production rate [43–45]. The dehydration of methanol to dimethyl ether is also very well understood. This is typically done using γ -Al₂O₃ catalyst, or, much more recently, solid-acid catalysts in the form of zeolites and related materials [46–49].

Dimethyl ether synthesis directly from syngas has received much attention in the past decade. As far as feedstocks go, methanol is quite expensive and adds substantially to the cost of manufacturing dimethyl ether [50,51]. Removing dependence on methanol as a feedstock can greatly increase the viability of dimethyl ether synthesis. There are two types of catalysts for direct dimethyl ether synthesis from methanol: hybrid catalysts and bifunctional catalysts [51]. Both types of catalysts involve the presence of two different active sites. These sites allow for the formation of methanol from CO and H_2 and the immediate dehydration of methanol to dimethyl ether. Hybrid catalysts typically consist of a physical mixture of the well-known Cu-ZnO/Al₂O₃ catalyst for methanol synthesis and an acidic zeolite for the dehydration step [52–54]. It has been found by researchers that the mechanical mixture of the two catalysts is not stable, with methanol synthesis activity gradually deteriorating with reaction time. This is thought to be due to the interaction between Al and Cu [50,55,56]. This catalyst deactivation issue has spurred on research into bifunctional catalysts [51]. A bifunctional catalyst is one where, instead of a mechanical mixture of the two catalysts, the Cu and ZnO are the supported metals and the solid-acid is used as a support (though sometimes γ -Al₂O₃ is still used), making one catalyst with two catalytically different active sites. While some investigation has been performed into metal precursor selection and synthesis technique [57–59], there is still a considerable amount of work to be done before these catalysts are considered for industrial implementation.

Dimethyl ether has become quite a valuable commodity. From the perspective of green chemistry, it is a great feedstock as it is non-toxic, non-corrosive, non-carcinogenic, environmentally friendly and, unlike other homologous ethers, does not form explosive peroxides [60]. Dimethyl ether can be used directly as a diesel fuel substitute or for domestic heating. Like methanol, dimethyl ether is also used as a feedstock for the production of other valuable olefins, such as ethylene, propylene, methyl acetate, formaldehyde, and ethanol [51,60]. Dimethyl ether is also normally an intermediate in the

methanol to gasoline process for producing gasoline, diesel fuel, and aromatics, and can be used directly in place of methanol for producing these highly valuable commodities [61,62]. The process therefore exists, albeit with some complexity, to convert inedible and waste biomass to syngas and highly valuable dimethyl ether, shown in Figure 1.1.



Figure 1.1. Processes for conversion of inedible biomass to valorized products.

1.4 Current methods for producing acetic acid

Acetic acid is used primarily in the production of polymers but is also used in foods, pharmaceuticals, detergents, and other organic syntheses. Total world production of acetic acid currently exceeds 12×10^6 t/a [63,64]. Of all the processes for synthesizing acetic acid, methanol carbonylation is the dominant technology and accounts for over 65% of global capacity [65]. The two leading processes in methanol carbonylation at present are

the Monsanto and BP Cativa[™] processes [63]. Monsanto commercialized their process in 1970, utilizing a rhodium-based homogeneous catalyst which required an iodide promoter. The process operated at a temperature of 150-200°C and pressure of 30-60 atm. These conditions were much milder as compared to the previously widely used BASF process and gave a selectivity of 99% to acetic acid based on methanol consumption [66,67]. However, the process did not come without some disadvantages. The rhodium catalyst was unstable when in CO-deficient areas of the process and could form inactive and insoluble RhI₃, which had to be removed from the process. Conditions in the reactor had to be maintained within certain narrow limits to prevent catalyst precipitation. Limits were placed on water, methyl acetate, methyl iodide, and rhodium concentrations [68,69]. After acquiring the licensing rights to the Monsanto process in 1986, BP Chemicals Ltd. further developed the process and in 1996 announced their new BP Cativa[™] process. This new process was based on the use of an iridium homogeneous catalyst with iodide promoter [69]. Researchers at Monsanto had known iridium was an alternative to rhodium for the catalyst, but chose to develop the rhodium-based catalyst as it gave higher activity under the conditions used [70]. The advantage to using iridium was that it had much higher stability as compared to the rhodium-based catalyst, allowing for a much broader range of process conditions without having to worry about the precipitation of IrI_3 [67,69,70]. At the time, iridium was also much cheaper than rhodium. Due to the stability of the iridium catalyst, much less water was required in the process, which translated into reduced stress on the distillation columns and decreased separation and purification costs [68,69]. The temperature and pressure of the reaction was not changed significantly with the development of the iridium catalyst. Detailed mechanistic studies were conducted with both the iridium and rhodiumbased catalysts and the main reaction mechanism was theorized to be the same for both cases, shown in scheme 1.1 for the Ir-based catalyst [69,71]. As shown in the mechanism, the methanol reacts with hydrogen iodide to form methyl iodide, which interacts with the Irbased catalyst.



Scheme 1.1. Proposed reaction mechanism for homogeneous Ir-catalyzed methanol carbonylation.¹

Both the Monsanto and BP CativaTM processes share several disadvantages. Hydrogen iodide is very corrosive in the presence of moisture and requires special materials of construction so as to prevent excessive corrosion. Rhodium and iridium are also expensive metals. In the past three months, the average prices of rhodium and iridium were \$709.05 and \$520.00 per ounce respectively [72]. The use of a homogeneous catalyst also brings with it several disadvantages. While homogeneous catalysts do provide an increased area of contact and more intimate mixing as opposed to heterogeneous catalysts, homogeneous catalysts (especially those synthesized from expensive precious metals) need to be separated from the rest of the solution, and this may require expensive distillation columns as in the case of the Monsanto and BP Cativa[™] processes [69,73]. Distillation columns introduce additional capital and operational expenditures and may not provide for complete reclamation of the catalysts. The separation process may also harm the catalyst, as was the case of the Monsanto process where excess removal of water resulted in the formation of RhI_3 . From an industrial perspective, it is much simpler to separate a solid catalyst from gaseous or liquid reactants and products, whether it is by filtration or by keeping the catalyst in a packed bed or floating bed reactor.

The Monsanto and BP Cativa[™] processes are both in violation of some of the principles of green chemistry. Specifically, the synthesis of acetic acid by both the processes is quite hazardous due to the use of a halide co-catalyst, which violates the third

¹ Reprinted from Catalysis Today, Vol. 58 Issue 4, G.J. Sunley, D.J. Watson, High productivity methanol carbonylation catalysis using iridium: The Cativa[™] process for the manufacture of acetic acid, 293-307, 2000, with permission from Elsevier.

principle. The use of a homogeneous catalyst inevitably creates additional energy requirements due to the operation of distillation columns and separation vessels, violating the sixth principle. The halide co-catalyst also brings with it various safety concerns, violating the twelfth principle.

1.5 Methanol carbonylation on heterogeneous catalysts

Though sporadic, there have been groups that have attempted to perform vaporphase methanol carbonylation over a heterogeneous catalyst, with most of the research resulting in the same issues. In the case of using a rhodium-based heterogeneous catalyst, dependent on the support used, metal leaching led to rapid catalyst deactivation. Even if a support more capable of affixing rhodium in place was used, it was found that to obtain reasonable rates, methyl iodide still had to be used [74]. Without methyl iodide, it was found that hardly any acetic acid was produced. With increasing partial pressure of methyl iodide, acetic acid slowly became the most selectively produced product [75]. The selectivity towards acetic acid was not very high in this scenario, with more dimethyl ether and methyl acetate produced. Nickel catalysts were also used with activated carbon as a support. Many of these studies still used methyl iodide as a catalyst promoter, and selectivity towards acetic acid was again poor, with the most produced product being methyl acetate [76,77]. The nickel catalysts were also found to rapidly deactivate, likely due to strongly adsorbed species, sintering of nickel, or potentially even nickel leaching [77,78]. The formation of methyl acetate also implies that water is also produced, which is known to promote the sintering of metal nanoparticles and subsequently lead to faster catalyst deactivation [79,80]. Metal ion-exchanged heteropoly acids have also been used for vapour-phase carbonylation of methanol, giving mostly dimethyl ether with some methyl acetate as products [81].

The research into methanol carbonylation over heterogeneous Rh or Ni catalysts (or variants thereof) has shown that, regardless of support, methyl iodide is necessary for both increased activity and increased selectivity towards acetic acid. Otherwise, mostly dimethyl ether or methyl acetate is produced. In abiding by the principles of green chemistry, the use of methyl iodide is discouraged. However, the studies have shown the importance of having an activated methyl group present for the reaction to occur. Fujimoto et al. [82] performed methanol carbonylation over solid-acids Y, mordenite, and ZSM-5. While again finding that dimethyl ether was the most produced product (due to acid catalyzed dehydration of methanol), some methyl acetate and acetic acid were produced. However, Fujimoto et al. [82] results seemed to confirm earlier results from Ono et al. [83] that

active methyl groups would form at acid sites on zeolites without an iodide promoter. Water formation was also observed with methanol carbonylation over zeolites and was hypothesized to be a probable reason for the low activity of the zeolites. Zeolites with a high Al content are inherently hydrophilic and have high capacity for water adsorption. Adsorbed water can block acid sites and cover the surface of the zeolite, preventing reaction [84].

Fujimoto et al. [82] hypothesized that, to resolve the issue of adsorbed water, dimethyl ether should be used as a reactant, instead of methanol, for carbonylation using zeolite catalysts.

1.6 Carbonylation of dimethyl ether

As shown in Equation 1.1, the carbonylation of dimethyl ether produces methyl acetate. Methyl acetate can be converted to acetic acid and methanol via hydrolysis and is known to occur over acidic catalysts, specifically Amberlyst, and most research these days is focused on the determination of kinetics and equilibrium as well as developing technologies for the efficient separation of the products [85–88].



The reaction is mildly exothermic with ΔH° of -115.4 kJ mol⁻¹, ΔS° of -140.4 J mol⁻¹ K⁻¹, and ΔG° of -73.6 kJ mol⁻¹ (evaluated at 25°C). This indicates that the reaction should be spontaneous and equilibrium highly favours the products, and for all intents and purposes the reaction can be considered irreversible at the temperatures of interest in this study. In an ideal scenario, there should be no water produced during this reaction and no other products formed, minimizing the need for regeneration of a zeolite catalyst and purification of the products.

The carbonylation of dimethyl ether to methyl acetate, despite the thermodynamics, does not occur without a catalyst present, indicating high activation energy.

1.7 Objectives of the current study

There has been a considerable amount of research in the past decade regarding dimethyl ether carbonylation. Approximately 10 years ago, the zeolite mordenite was shown to have both high activity and very high peak selectivity (>99%) towards the desired methyl acetate product [89]. Aside from the high peak activity and selectivity, the mordenite catalyst does not require an iodide co-catalyst for promotion. Therefore, the use of mordenite removes the need for expensive distillation as a means to separating the catalyst from the products. It also removes the need for special materials of construction for the process that were required in the past to deal with the iodide co-catalyst. With high selectivity, it also means the need for separation and purification of the product is minimized. This again provides economic benefit over current technologies for producing methyl acetate and its subsequent conversion to acetic acid. These improvements over the Monsanto and BP Cativa[™] processes make it quite an attractive idea from an economic perspective, never mind that the developed process would be in line with all 12 of the principles of green chemistry. Despite the many advantages to using mordenite as a means of producing methyl acetate, the disadvantage is that it is unstable. Within the first 10 hours of reaction, dependent on the conditions used, the mordenite catalyst already shows signs of deactivation [90–92]. The mordenite would have to be regenerated after deactivation, which adds to the cost and complexity of the process and makes industrial implementation unattractive. There has been a considerable amount of research by various groups around the world attempting to find a solution to the deactivation issue, but a simple solution that is easily scalable to an industrial level while being cost-effective remains elusive. It is the objective of the current study to find a simple and effective means for stabilizing mordenite for the carbonylation of dimethyl ether to methyl acetate and make its use industrially a more attractive venture.

Two methods were employed in to accomplish this objective. The first was to attempt to use partial bimetallic liquid-based or solid-state ion-exchange as a means to increasing the activity of the mordenite and reducing the probability of side reactions which may lead to catalyst poisoning. The second method was to remove some of the Al present in the zeolite via an acid leaching procedure. While potentially decreasing the activity of the catalyst, it may also reduce the likelihood of side reactions that lead to deactivation, as well as introduce additional pathways for reactants to get to active sites. The increase in accessibility of active sites also means the formed products can leave the mordenite crystal more easily, preventing successive reactions of the products.
Chapter 2

State of the Art

A great many people think they are thinking when they are merely rearranging their prejudices.

--William James

2.1 Zeolites and Zeotypes

2.1.1 What are zeolites?

Zeolites are naturally occurring crystalline materials that have been known for nearly 250 years as aluminosilicate minerals. The natural forms are not commonly used as they usually contain undesired impurity phases, the chemical compositions vary too widely, and they are not optimized for use as adsorbents or catalysts [93]. For this reason, aside from the over 50 natural zeolite forms, there are over 140 synthesized zeolites, making for a total of 176 unique zeolite frameworks (as of February 2007) [94,95]. One of the first applications of a synthesized zeolite was in 1962 when zeolites X and Y (of the faujasite framework) were used in fluid catalytic cracking of heavy petroleum distillates [93]. The framework and pore diameter are shown in Figure 2.1 for these two very important zeolites. Zeolites X and Y were orders of magnitude more catalytically active than the previously used amorphous silica-alumina catalysts. They also brought about substantial improvements in the process design and increased the overall yield of gasoline [96].



Figure 2.1. The a) framework, and b) 12-MR pore size (dimensions shown in Å) viewed along the (111) of Zeolite X and Y, one of the first zeolites to be used industrially.²

Zeolites are composed of Si and Al tetrahedra connected by O atoms to adjacent tetrahedra to form a structurally distinct, three-dimensional microporous framework, with channels and interconnected cavities that have dimensions ranging from 2 - 12 Å. This results in net formulae for the tetrahedra of SiO_2 and AIO_2^{-1} [93–95]. During the synthesis of a zeolite, individual tetrahedra combine to form different secondary building units (SBU's). There are currently 23 unique SBU's known [95]. These SBU's combine to form 6, 8, 9, 10, 12, 14, 18, or 20-membered ring (MR) cages or cavities which further connect with other SBU's to form the unit cell of the zeolite. The unit cell is the smallest repeating unit of a zeolite that defines the structure. Unit cells assemble into the crystalline lattice, which grows into recognizable crystals [94]. A purely siliceous zeolite (otherwise known as silica) possesses no charge and is unsuitable for applications such as ion-exchange, though may still find some use as an adsorbent. The introduction of Al into the siliceous zeolite makes the framework negatively charged, and extraframework cations (either inorganic or organic) are required to balance the charge and keep the overall framework neutral [97]. The composition of the zeolite can therefore be described by the chemical structure shown in 2.1 below (from Payra and Dutta [97]):



² Atlas of Zeolite Framework Types by Baerlocher, CH.; McCusker, L.B.; Olson, D.H.; Sixth Revised Edition, 2007; with permission of Elsevier in the format Thesis/Dissertation via Copyright Clearance Center, Inc.

The extraframework cations can be removed and replaced with other cations. This is referred to as ion-exchange, and can result in the formation of Brønsted acid sites. This will be discussed in further detail in a later section.

The quantity of AI in the framework can vary significantly, between Si/AI of 1 to ∞ . The lower Si/Al limit of 1 is due to Löwenstein's rule, which states that tetrahedral Al bound together through an O atom (AI - O - AI) are extremely unlikely in a zeolite framework due to the electrostatic repulsion between the negative charges. If two Al ions did share the same O anion, one of those AI must have a coordination number larger than 4 (5 or 6) towards oxygen [98,99]. Ab initio calculations have shown that the Al – O – Al framework bond is less stable as compared to AI - O - Si, partly due to the AI - O - AI bond angle being 180°, which is not easily accommodated in the zeolite framework [100]. There is also Dempsey's rule, which states that for zeolites with Si/Al > 1, the framework Al ions will try to maximize the distance between themselves due to electrostatic repulsion [101]. Therefore, AI - O - Si - O - AI linkages should be minimized. Dempsey's rule is not considered universally applicable, as there is evidence that such a linkage does provide for a minimization of energy in the framework [99]. In addition to these rules, Takaishi et al. [102] theorized that a 5-MR could not contain more than two Al atoms, and in applying this rule they were able to accurately predict the correct values for the maximum Al amounts in ferrierite and mordenite. This rule may only be applicable to highly siliceous zeolites and may not be universally applicable. It may also be considered to be just another iteration of Löwenstein's rule. Though the discussion about the exact locations of Al in zeolite frameworks is ongoing and many new frameworks have been synthesized, Löwenstein's rule is still held to be true.

Based on Al content, zeolites can be divided into different classifications. Low silica zeolites generally have Si/Al ratios of 1-1.5. Intermediate Si/Al zeolites are classified as having Si/Al ratios of ~2–5. High Si/Al zeolites have Si/Al ratios of ~10-100 [103]. Early assynthesized zeolites rarely had high Si/Al ratios. Out of the desire to have a zeolite with both a wider pore opening (to serve as a better cracking catalyst in the petroleum industry) and a higher Si/Al ratio, ZSM-5 (and, subsequently, the ZSM line of zeolites, sometimes referred to as templated aluminosilicates) was developed [104]. Zeolites with a higher Si/Al ratio also have increased thermal, hydrothermal, and acidic stability. To synthesize these materials successfully, an organic cation, usually an alkylammonium cation or other organic complex, was added to the synthesis mixture. It was found that the incorporation of an organic cation into the synthesis gel led to a more open crystal structure and could also

enhance the siliceous nature of the zeolites [105]. The template molecule could be later burnt out by calcination at high temperatures (~500°C), leaving an open framework.

Aluminum is not the only element that can be integrated into a framework with Si. The general rule would be that the metal needs to be stable in a tetrahedral orientation. In early literature, it was accepted that only Ga, P, and Ge ions could be potentially incorporated into a zeolite framework [106]. It was later theorized that the metal cations that could be included in a zeolite framework were Al³⁺, Mn⁴⁺, Ge⁴⁺, V⁵⁺, Cr⁶⁺, Si⁴⁺, P⁵⁺, Se⁶⁺, and Be²⁺. This list was made based on Pauling criteria and was only considered to be an estimate since other metals, such as B³⁺, had been previously included in a tetrahedral oxygen environment. However, these other metals may have greater instability in that coordination compared to those included in the list [107]. The term "zeolite" is often restricted to describing conventional aluminosilicates. Others may be referred to as "zeotypes", acknowledging that they have a repeating framework but are distinct [108].

Before proceeding, it is worthwhile to mention the definition of micropores, mesopores, and macropores. As referred to in this work, these terms will follow the definition outlined by the International Union of Pure and Applied Chemistry [109], which is:

| micropores: | 20 Å $\ge d_p$ |
|-------------|-------------------------|
| mesopores: | 20 Å < $d_p \leq$ 500 Å |
| macropores: | d _p > 500 Å |

2.1.2 AIPOs and SAPOs

In 1982, Wilson et al. [110] introduced the first family of molecular sieves that were synthesized without silica. Aluminophosphates (AlPOs) consisted entirely of Al and P tetrahedra connected by neighbouring O atoms. As was with zeolites, the aluminum centres carry a negative charge (AlO_2^{-}), but the phosphorous centres carry a positive charge (PO_2^{+}). In AlPOs, the Al and P tetrahedral centres strictly alternate, meaning that the Al/P ratio is always 1. This results in an overall neutral framework charge [111]. The chemical equation representing their composition is given below (from Flanigen et al. [111]):

| | | 2.2 | | |
|----------|---|------------------------|---|---------------------------------|
| template | | framework | | sorbed phase |
| xR | • | $Al_2O_3 \cdot P_2O_5$ | • | <i>yH</i> ₂ <i>0</i> |

In the above chemical formula, R represents a template molecule that is used during synthesis (usually an amine or quaternary ammonium template) while x and y represent the amounts of each required to fill the microporous voids of the AIPO. The template molecule is used as a structure-directing agent (SDA) and is required for successful synthesis of AIPOs. The template and adsorbed water can be removed with calcination at high temperature. While having high thermal and hydrothermal stability comparable with the more stable zeolites, AIPOs have no framework charge, no ion-exchange capacity, and only weakly acidic catalytic properties [111].

To add more functionality to the AIPOs, silicon was added to form a silicoaluminophosphate (SAPO), which was first reported on in 1984 [112]. The molar fraction of silicon in these materials varied between 0.04 and 0.20, dependent on the conditions of synthesis and the structure type [111]. It was determined that the silicon was introduced into the structure by two primary mechanisms. The first mechanism is replacement of a phosphorous atom with a silicon atom. The second is where two silicon atoms would simultaneously substitute for an aluminum and phosphorous atom. In the first mechanism, this would result in a negative framework charge, while the second mechanism would again result in a neutral framework. The first mechanism was found to be the predominant method of substitution [111]. SAPOs share many of the same properties as AIPOs, having similar pore sizes, adsorptive properties, and thermal and hydrothermal stability. With the introduction of a negative framework charge, which requires a cation to compensate for it, ion-exchange capability is added and the potential for Brønsted acid sites. Among the 13 different three-dimensional framework structures introduced in 1984 for SAPOs, some were completely new, such as SAPO-41 which has an AFR framework and is shown in Figure 2.2. SAPO-34 was also introduced at the time, which was structurally similar to chabazite and today is a popular methanol-to-olefins catalyst [112,113].



Figure 2.2. The a) framework, b) 8-MR (viewed along (010)) and c) 12-MR (viewed along (010)) of SAPO-41 with the AFR type framework (dimensions shown in Å).³

Silicon was not the only metal which could be substituted into the AIPO framework. AIPOs appear to be much more accepting of other metals into their framework, as in the original report it was shown that Li, Be, B, Mg, Ga, Ge, As, Ti, Mn, Fe, Co, and Zn could all be integrated into the framework [111]. The list was later expanded to include V, Cr, Ni, and Cu [114]. AIPOs with metals aside from silicon in their framework were called metal aluminophosphates (MeAPOs). The molar fraction of metal in these MeAPOs varied between 0.01 and 0.25.

Some of the frameworks of AIPOs and SAPOs were identical to that of zeolites while several new frameworks were introduced with them. The number of different compositions for these materials is incredibly large, due simply to the number of different metals that could be included in the framework. This also meant that there were many new opportunities for catalysis with these materials.

2.1.3 Other zeotypes

In 1983, the successful isomorphous substitution of Ti⁴⁺ for Si⁴⁺ in a zeolite framework was shown by Enichem in Italy. The material was labelled as TS-1 (titanosiliciate-1) and had an MFI topology [115–117]. As the Ti was tetrahedrally oriented in the framework and carried a +4 charge, its incorporation into the zeolitic framework introduced no negative charges, and as such titanosilicates had limited to no applicability as

³ Atlas of Zeolite Framework Types by Baerlocher, CH.; McCusker, L.B.; Olson, D.H.; Sixth Revised Edition, 2007; with permission of Elsevier in the format Thesis/Dissertation via Copyright Clearance Center, Inc.

Brønsted acid catalysts. However, Ti can act as a Lewis acid and, when combined with the hydrophobic nature of silicates, makes these materials very useful for oxidation reactions of hydrocarbons that use hydrogen peroxide as an oxidizing agent [115,116]. While being quite revolutionary, TS-1 had a significant limitation: it had relatively small diameter pores at ~5.5 Å. This meant that larger organic molecules suffered from severe steric restrictions and TS-1 could not be used in processes that involved bulkier molecules [118]. For this reason, Ti was introduced into the framework of zeolite Beta, which has a larger 12-MR with 7.7 Å diameter [95,119]. The synthesized molecular sieve also had Al present, making it a titanoaluminosilicate polymorph of zeolite Beta. The Al had a negative effect on epoxidation reaction rates and a synthesis procedure was later developed for aluminum-free Ti-Beta [118]. Research continues in titanosilicates and, as these materials have weak to no Brønsted acidity, they will not be discussed in further detail here. Interested readers are directed to the review paper by Moliner and Corma [118].

The demand for larger pore size, ion-exchange capability, and different coordination environments of the Ti centres led to the discovery of ETS-10 and ETS-4 in 1989 – 1991 [120,121]. In these materials, Ti^{4+} is octahedrally oriented, meaning that the framework consists of negatively charged TiO_3^{2-} and neutral tetrahedrally oriented SiO_2 . The ETS frameworks thus have a substantial negative charge which must be balanced with extraframework cations [122]. ETS-4 is structurally related to the mineral zorite and, while possessing larger openings in its structure, structural disorder means that access is only through narrow 8-MRs. Besides being a relatively disordered structure, ETS-4 does not possess high thermal stability due to water that is contained in the framework structure of the channel system. Upon heating to temperatures of 200°C, this water is removed at which point the structure collapses. With proper ion-exchange (Sr, for example), this temperature may be increased to 300°C [123–125]. Due to the water loss upon heating, the pore size could be systematically decreased (called the "molecular gate" effect). This had many implications for the selective adsorption of smaller molecules over larger molecules [124]. ETS-10 has a three-dimensional 12-MR large pore system (the large micropores have dimensions \sim 14.3 Å x 7.6 Å) and is considerably more stable than ETS-4, maintaining its crystallinity even after calcination at 550°C [122,126]. Though ETS-10 has been investigated for use as a cracking catalyst, the acidity of ETS-10 is known to be modest, and it exhibits only low acidic catalytic activity [127]. ETS-10 has been shown to make an excellent base catalyst for reforming chemistry [128,129]. Aluminum may be added to the ETS-10 framework to introduce additional acidity.

One of the limiting factors of the materials presented thus far is that they are microporous. This limits the accessibility of catalytically active sites and, in some cases, may introduce additional mass transfer limitations. This spurred the development of ordered mesoporous silicate and aluminosilicate molecular sieves. The first member of this family, commonly called M41S materials, was MCM-41, successfully synthesized by Beck in 1991 [130,131] and shown in Figure 2.3. In order to develop a silicate with ordered mesoporous structure, a surfactant was used. The choice of the surfactant led to different pore sizes, and as such MCM-41 could be tailored to have pore openings between 16 Å and, potentially, greater than 100 Å [132]. The surfactant could be removed from the assynthesized product via calcination. The original MCM-41 possessed a hexagonal array, and shortly after the initial discovery, MCM-48 and MCM-50 were synthesized with a cubic and laminar array respectively. While the purely siliceous materials may be used as adsorbents and catalyst supports, they do not contain Al or any other metals, and therefore have limited acidity. MCM-41 containing Al has been synthesized and used as a cracking catalyst with some success [133,134]. The AI-MCM-41 has some advantages over US-Y but has been found to have comparatively very low activity. This is due to the larger number of Brønsted acid sites on US-Y and their much higher acid strength. To attempt to enhance the catalytic activity of the M41s materials, the isomorphous substitution of Ti, Zr, V, Fe, Co, B, Sn, and Pt has been conducted, with some promising results from Ti-MCM-41 for oxidation reactions. Incorporation of the other metals did not meet expectations [134]. For further information regarding these materials, the reader is referred to the reviews by Ciesla and Schüth (1999) and Corma (1997) [133,134].



Figure 2.3. Mesoporous siliceous MCM-41 with hexagonal array synthesized from silica and a surfactant species.⁴

⁴ Reprinted from Applied Surface Science, Vol. 282, F. Raji, M. Pakizeh, Study of Hg(II) species removal from aqueous solution using hybrid ZnCl₂-MCM-41 adsorbent, 415-424, Copyright 2013, with permission from Elsevier.

The past few sections were intended only to give a very brief overview of zeolites and should in no way be considered a comprehensive review of these materials. The intention of the author is that enough information is provided so that, if the reader encounters these materials in a paper, this background provides sufficient understanding about what that material is and its potential advantages and disadvantages in a very general sense. There are several thousands of publications available on these materials, and the reader is encouraged to find the referenced papers and books if further information is needed.

2.2 Zeolite acidity and use in catalysis

2.2.1 The nature of zeolite acid sites

Zeolites (and some zeotypes) are known for their Brønsted acidity (proton donor). In many scenarios, they may also possess limited Lewis acidity (electron pair acceptor) [108]. As stated earlier, Brønsted acid sites are generated in a zeolite with the isomorphous substitution of Al³⁺. This introduces negative framework charge which requires a compensating extraframework cation. During zeolite synthesis, the extraframework cation is typically Na⁺ [135]. It is very important to note that the extraframework cation does not bind to the Al atom itself. Rather, it binds to a bridging oxygen between the Si and AI [136]. These are also the points where ion-exchange occurs. From the synthesized material, the Na⁺ (or other compensating cation) may be ion-exchanged with NH_4^+ . After heating the zeolite, the ammonia desorbs, leaving the H^+ bound to the bridging O atom as shown in **2.3a** below. These are known as bridging hydroxyl groups, and in chemical notation are referred to as SiOHAI [137]. These types of acid sites are not exclusive to conventional zeolites and may also be present in SAPOs and Al-substituted M41S materials (in similar fashion to **2.3a**). They may also be present when different tetrahedrally coordinated metals aside from AI (as presented in earlier sections) are substituted into the zeolite framework [136]. However, it has to be remembered that the strength of the Brønsted acid site is dependent upon the local configuration, and substitution of Al with a different metal will have a significant influence on the acid strength and any associated catalytic activity [138]. Not only the composition, but the Si-O-T (where T is a tetrahedral oriented metal) angle will have an influence on the partial charge and acid strength of the hydroxyl group [136,137,139]. For mordenite, the Si-O-T angle may vary from 143° to 180° [140]. It is quite important, especially from a catalytic perspective, to realize that not all Brønsted acid sites on a particular zeolite have equal strength (acid site heterogeneity).



In addition to the immediate environment surrounding the framework Al atom, it has also been theorized that the distribution of framework AI may be the primary factor in determination of the Brønsted acid site strength [141]. Due to Löwenstein's rule, a framework AI will be connected to four Si atoms via bridging O atoms. These four Si atoms are the nearest neighbours. The Al or Si atoms connected to the nearest neighbours are called the next nearest neighbours (NNNs). It is theorized that the acid strength of SiOHAI groups in conventional zeolites is dependent on the number of framework Al atoms at these NNN positions. Based on electronegativity (Si has electronegativity of 1.9, Al has 1.61), it is assumed that the lower the number of Al atoms at these NNN positions, the higher the acid strength is of the site in question [136,142,143]. While this theory has considerable evidence, others have observed that, past the point where there is no Al in the NNN positions, the turnover numbers do not stay constant as would be expected [144]. Catalytic activity is therefore concluded to not just be a function of the acidity of the zeolite used. The hydrophilic or hydrophobic nature of zeolites mentioned earlier can also be suitably explained by the electrostatic differences between Si and Al. With purely siliceous frameworks, the electrons are balanced between the oxygen atoms and silicon atoms with electronegativity's of 3.44 and 1.9 respectively. With an even distribution of electrons, the oxygen atoms are not excessively polarized, meaning the polar water molecule is not attracted to the zeolite. However, with the introduction of AI, which has a comparatively low electronegativity of 1.61, the electrons are drawn much more strongly to the oxygen atoms. The zeolite framework thus becomes increasingly polarized with increasing Al content. The polar water molecules are then drawn to the framework by van der Waals forces.

Silanol groups, as shown in **2.4a**, terminate the zeolite crystal at the external surface and are also present at framework defects. These have a low acid strength. Defects in the structure can be introduced by a variety of means, but usually occur from calcination, steaming, or treatment with strong acids. At the higher temperatures of

calcination, protons are quite mobile and can be lost as water molecules. This typically results in the formation of Lewis acid sites, shown in **2.3b** [137]. Steaming or acid treatment results in dealumination, which can lead to the creation of a few other types of sites [136]. In some occasions, the framework may actually heal itself by migration of silicon. In the cases where the framework does not heal itself, silanol groups (**2.4a**) or hydroxyl groups at extraframework Al species (**2.4b**) may be created [145]. Lewis acid sites are also likely to form out of dealumination treatments.



As a final note, there might be some interaction between Lewis acid sites and Brønsted acid sites on zeolites in certain scenarios. This may result in the formation of what are referred to as superacidic Brønsted sites [146]. In the case of a mildly steamed ZSM-5, it was found that it had significantly improved catalytic activity for the cracking of n-hexane [147]. It was reasoned that framework Al could be partially hydrolyzed during the steaming treatment. These partially hydrolyzed Al might serve as strong electron-withdrawing centres for nearby SiOHAl groups, and consequently create very strong Brønsted acid sites.

2.2.2 The zeolitic catalytic cycle

Zeolites and zeotypes can be used in catalysis as either a support material for other catalytically active materials or directly for their Brønsted or Lewis acidity. In the context of this thesis, only the direct use of a zeolite for a reaction will be discussed.

Catalysis proceeds through several elementary reaction steps. Very generally, reactants must diffuse to the catalyst surface, chemisorb on a catalytically active site, react, desorb from the active site, and finally diffuse away from the catalyst surface. The catalytic cycle over a zeolite is not significantly different from this, though there are a few additional steps as shown in Figure 2.4. The reactants must first travel to the zeolite surface at which point they adsorb within the zeolite mouth and occupy a micropore. These adsorbed reactants must diffuse through the channels and pockets that make up the micropore volume and travel to a catalytically active site (whether it is a Brønsted or Lewis acid site). Here it can chemisorb to the site and react. This step can be very complex, dependent upon the reaction that is occurring. Regardless, once the reaction is complete the new product desorbs from the active site, diffuses away and occupies the micropore again. The product must then travel to the external surface of the zeolite crystal and desorb [94,135].



Figure 2.4. The catalytic cycle of a zeolite-catalyzed reaction.⁵

From the catalytic cycle, it can be seen that diffusion is a large aspect of practical zeolite catalysis, and can be a controlling factor in both the selectivity and activity for many reactions. If the zeolite micropore channels and cavities are substantially larger than the molecular dimensions of the reactants, diffusion will typically be of the Knudsen type [94]. However, especially with zeolites, this is not typically the case as the pore dimensions may be very similar to the dimensions of the molecule. In this case, configurational diffusion will be the primary means by which the reactants reach the active sites, though the size of the molecule has to be very near to the pore diameter for this type of diffusion to come into effect [148]. Configurational diffusion may also be referred to as intracrystalline diffusion or micropore diffusion [149–151]. There may also be single-file diffusion, which is a special case of configurational diffusion in a zeolite where the channels are one-dimensional. This type of diffusion occurs when molecules cannot pass one another in the channel due to the size-constraints [94]. Figure 2.5 shows the generally accepted transitions between

⁵ Handbook of Zeolite Science and Technology by Auerbach, Scott M.; Carrado, Kathleen A.; Dutta, Prabir, K; CRC Press, 2013. Reproduced with permission of Taylor and Francis in the format Thesis/Dissertation via Copyright Clearance Center.

molecular diffusion, Knudsen diffusion, and configurational diffusion as a function of pore diameter. It is shown that, below 10 Å, configurational diffusion dominates. This is the case for most zeolites.





This thesis is not intended as an in-depth review of the diffusion processes in zeolites. This very brief introduction was meant to simply introduce the various modes of diffusion in zeolites. When studying reaction kinetics, especially with zeolites, the researcher has to ensure that it is actually the reaction kinetics being studied and not the diffusion kinetics. It is important to realize that both are important for zeolite catalysis and need to be considered. For further information, the reader is directed to the referred textbooks and publications.

2.2.3 Shape selectivity of zeolites in catalysis

While the pore structure of the zeolite may impose diffusional constraints with regards to the reactants and products, these constraints may be an advantage. This invariably involves principles of configurational diffusion. While the pore and channel size

⁶ Reprinted from "Introduction to Zeolite Molecular Sieves" (J. Čejka, H. van Bekkum, A. Corma, F. Schüth, Eds.), Vol. 168 of Studies in Surface Science and Catalysis, D.M. Ruthven, *Chapter 21 Diffusion in Zeolite Molecular Sieves*, pp. 737-786, 2007, with permission from Elsevier.

(and dimensions) will impede the effective diffusion of reactants and products, they will also restrict what reactants can get into the zeolite, have access to active sites, and what products can leave the zeolite. This is commonly known as shape selectivity, and is an attribute that is quite attractive in zeolites, especially in adsorptive separations [152].

There are many shape-selective effects known today, the three main categories of which are displayed in Figure 2.6. All of the known effects today can usually be classified as one of the three categories.

- *Reactant shape selectivity*: This occurs when there are two reactants in the feed with different molecular dimensions. If there is a bulkier reactant, meaning that it has more branches or is perhaps a larger cyclic molecule, its diffusion into the pores will be hindered as compared to the smaller, less bulky molecules. The less bulky molecules, due to reduced diffusion constraints, will react preferentially. It may be the case where the bulkier molecule is completely excluded [93];
- ii. *Product selectivity*: This is again a selectivity rooted in diffusion constraints. This type of selectivity occurs when a product is formed within the pores of the zeolite that is simply too bulky to diffuse out and be observed as products. Two situations may occur in this scenario. The bulky product may continue to react and eventually leave the zeolite as smaller products. The other situation may be that it does not react or, when it does, it simply gets even more bulky, eventually blocking the pores and leading to deactivation of the catalyst [153]; and
- iii. Restricted transition-state selectivity: This type of selectivity is not grounded in diffusion constraints, but rather in the spatial configuration around the reaction. It occurs when the formation of transition states and/or reaction intermediates are sterically limited due to the shape and size of the rigid microporous framework of the pore/channel of the zeolite. Therefore, undesired side reactions that lead to coke formation may be suppressed [137,153]. Steric limitations may be necessary in order for a particular reaction to even occur. Energetically, a reaction may be less favourable as opposed to other reactions, but due simply to the steric limitations, it may be the only reaction that is allowed to occur.

REACTANT SELECTIVITY







Proper consideration of these three basic shape selective effects can give a good impression of the products that are likely to form in a particular situation. However, this is only a simple set of criteria that can aid in the selection of the proper zeolite for a reaction. There are many other aspects to consider. For example, this set of criteria does not necessarily address thermodynamics directly. Of all the possible transition states that may form, it must be remembered that those molecules with the lowest free energy of formation in their adsorbed phase will be favoured. Those molecules with the highest free energy of adsorption are more likely to desorb and leave the zeolite framework as the products. The same logic may be applied to the reactants. Those reactants with the lowest free energy of adsorption will preferentially adsorb and undergo reaction [154].

Aside from the three basic types of selectivity, there are many other effects which have been observed.

⁷ Reprinted from Zeolites, Vol. 4, July, S.M. Csicsery, Shape-selective catalysis in zeolites, 202-213, 1984, with permission from Elsevier.

- Inverse shape selectivity: In some situations with some molecular sieves, it seemed that preferential adsorption was given to the bulkier molecules rather than the less bulky molecules [155]. This behaviour is likely due to stabilizing interactions between the zeolite walls and the more highly branched hydrocarbons as opposed to linear hydrocarbons (not unrelated to the thermodynamics arguments presented earlier);
- ii. *Molecular traffic control*: This is another very specific type of reactant selectivity. It occurs when a molecular sieve with two or more pore systems with different sizes and shapes intersect [156]. In this scenario, the reactants can enter into one type of pore, react, and diffuse out through the other pore type. Product molecules may be able to exit the zeolite through the larger pore, while the reactant molecules enter through the smaller pore, enhancing overall diffusivity [157];
- iii. Pore mouth and key-lock selectivity: This is highly specific to the interactions of normal and branched paraffins in medium-pore molecular sieves with unidimensional pores [158]. It applies to the highly selective hydroisomerization of longer chain normal paraffins over certain molecular sieves;
- Window effect: Normally observed in chabazite and zeolite-T, the diffusivity of nparaffins seemed to increase and subsequently decrease with increasing carbon number [159];
- v. *Nest effect*: This type of selectivity specifically deals with the non-shape-selective active sites on the external surface of the zeolite crystals. It has been postulated that acid sites in the pores and channels of the zeolites have a different shape selectivity than those at the cavities on the external surface of the crystal [157].

Again, these types of selectivity typically only apply in highly specific scenarios and can usually be classified under the three more general types. It is these shape selective characteristics that make zeolites (and molecular sieves in general) attractive for catalysis, never mind their high acidity and thermal stability. While the images of zeolite frameworks and pore dimensions shown thus far have been quite circular and cylindrical in nature, this is not always the case. Ferrierite, for example (shown in Figure 2.7), has a 10-MR and 8-MR, both of which are more rectangular in shape. Many more examples are presented in the *Atlas of Zeolite Framework Types* [95]. While to some extent zeolites can be specifically selected for a reaction of interest based on the selectivity theories presented, it is usually necessary to test a large number of zeolites for one reaction. Not only are the size and shape of the channels important, but also the acidity and locations of the active sites.



Figure 2.7. The a) framework, b) 10-MR (viewed along (001)) and c) 8-MR (viewed along (010)) of ferrierite with the FER type framework (dimensions shown in Å).⁸

While on the discussion of shape selectivity, it is worthwhile to mention the size of the molecules of interest in this study. Frequently, a kinetic diameter is reported for molecules and used as a gauge of whether or not the molecules will enter the zeolite framework. Kinetic diameter is a measure of the likelihood that a molecule in a gas will collide with another molecule. It is similar to reporting the size of a target. This is not necessarily the most representative value for determination of whether or not a molecule is able to enter into the zeolite framework. The best example of this may be the kinetic diameter of a linear long-chain alkane with minimal branching. This molecule would be able to enter a zeolite end-on (like a piece of string being threaded through a needle) but not in any other orientation. A further example is a comparison of the kinetic diameter of carbon monoxide and dimethyl ether (DME). Carbon monoxide has a kinetic diameter of 3.8 Å [153] while dimethyl ether has kinetic diameter of 4.4 Å [160]. This is a relatively small difference despite dimethyl ether being a significantly larger molecule. For this reason, the dimensions of the molecules of interest in this study are shown by structures 2.5a for dimethyl ether, **2.5b** for carbon monoxide, and **2.5c** for methyl acetate. These dimensions were determined from density functional theory (DFT) optimized models using the 6-31G(2d) basis set implemented in the Gaussian 09 program (the methods used in the Gaussian 09 program are detailed in a later chapter). In these structures, gray atoms are carbon, white atoms are hydrogen, and red atoms are oxygen.

⁸ Atlas of Zeolite Framework Types by Baerlocher, CH.; McCusker, L.B.; Olson, D.H.; Sixth Revised Edition, 2007; with permission of Elsevier in the format Thesis/Dissertation via Copyright Clearance Center, Inc.









2.2.4 Ion-exchange in zeolites

The concept of ion-exchange has been very briefly mentioned in several of the earlier sections of this thesis. When referring to ion-exchange with zeolites, it simply means that the extraframework cations (typically Na⁺ in as-synthesized zeolites) that are required to balance the negative charge of the framework are not permanently affixed to the framework, and can be exchanged for other cations or cationic complexes [97,161,162]. As the amount of positive charge required to balance the negative charge of the framework, the negative charge of the framework is determined by the amount of Al in the framework, the cation exchange capacity (CEC) is a function of the amount of Al³⁺ substitution for Si⁴⁺ in the framework [161]. The CEC will vary with the structure of the zeolite and the exchange cation to be used [163].

Quite generally, there are five factors that will affect the ion-exchange behaviour of a zeolite [164]:

- 1. The framework topology, meaning the size and dimensions of the channels and their configuration,
- 2. The anionic charge density of the framework,

- 3. The ion size and shape (polarizability),
- 4. The ionic charge of the cation to be exchanged, and
- 5. The concentration of the ion to be exchanged in the electrolyte solution.

With regards to the framework topology impacting the effective ion-exchange, this is mostly explained by the shape selectivity inherent to zeolites already discussed in the previous section. Some cations are just too large to fit into some zeolites. This means that certain cations or cationic complexes cannot be ion-exchanged into a particular zeolite framework, no matter the conditions used [163].

A very simplified representation of aqueous, monovalent ion-exchange is shown in Scheme 2.1. In the simplest terms, ion-exchange is just the exchange of ions, and can be explained with the following equation:

$$M^+ + C^+ Z^- \leftrightarrow C^+ + M^+ Z^- \tag{2.1}$$

where C^+ can potentially be Na⁺, NH₄⁺, H⁺, or any other monovalent cation. The extraframework cations balancing the negative charge of the zeolite framework are simply swapped for the metal cations in the surrounding aqueous solution at proper stoichiometric ratios. A solid soluble salt-form of the metal to be exchanged is usually used and dissolved in the solution. The Na⁺ form of the zeolite, or potentially other forms of the zeolite such as its NH_4^+ or H^+ forms, is added to the liquid mixture and stirred [93,161,165]. Regardless of the form, when the zeolite powder is immersed in the aqueous metal-containing solution, the cations in the zeolite communicate with the external solution, and cations are exchanged between the solid zeolite phase and the solution [163]. The rate at which ionexchange occurs is influenced by only a few factors. It is primarily dependent upon the concentration of ions capable of entering the pores of the zeolite as well as the temperature at which the ion-exchange is conducted. Based on these factors, it can be considered that ion-exchange is an equilibrium limited process. The equilibrium obtained is unique for each zeolite and the cations used for ion-exchange [163,166]. While ion-exchange can be conducted at ambient temperature, performing it at an elevated temperature increases the rate at which it occurs. It does this by increasing the diffusion rate of the metal to be ionexchanged. At ambient temperature, the metal cations may also become hydrated complexes and, therefore, larger in size. At higher temperatures, the water is stripped from the ions, decreasing their size and increasing the rate at which they may enter the zeolite crystal [163].



Scheme 2.1. Schematic of monovalent ion-exchange of the extraframework cations in a zeolite (where Z is the zeolite, C is the current cation on the zeolite, and M is the metal to be ion-exchanged).

The concentration effect is not as straight-forward as the temperature effect on the equilibrium of the ion-exchange. As ion-exchange is still an equilibrium limited process, if the concentration of metal ions in solution is significantly higher than the number of metal ions in the zeolite, the maximum amount of ion-exchange will very likely occur, given enough time [161,163,166,167]. At lower concentrations of metal ions in solution, there are a couple of effects that may occur. Ion-exchange will follow several different types of isotherms, most of which will not be discussed here as it is beyond the scope of this thesis. An ion-exchange isotherm is a representation of how much ion-exchange occurs at differing concentrations of the metal in solution. It fully defines the equilibrium that is achieved at a certain temperature and solution normality [161]. For the following arguments, the metal to be ion-exchanged is denoted as M, while the current metal on the zeolite is specified as C. Specific zeolites may be more selective towards the metal to be exchanged (the metal in the solution), and even at very low M/C, ion-exchange will readily occur. Other zeolites may be unselective towards M, and it will take high M/C for ion-exchange to occur. Some zeolites may exhibit no selectivity, and in such a case the amount of ion-exchange will vary linearly with the concentration of M [161,167]. In other cases, the selectivity may vary. This means that selectivity towards M may be initially high, but then a selectivity-reversal occurs at higher concentrations and selectivity becomes lower, or vice-versa. Interestingly, there is also what is called a concentration-valency effect. This effect applies specifically to when the valency of C is not equal to the valency of M. In the case of M being divalent and C being monovalent, the selectivity towards M may actually be higher at lower M

concentrations [161]. This rule generally applies at lower concentrations where the amount of metal ions in solution does not exceed the number of possible ion-exchange sites on the zeolite. To reiterate, if the concentration of M is suitably high, the maximum amount of ionexchange will occur. In this thesis, the thermodynamics of ion-exchange was not studied, and very high concentrations of metal in solution were used for ion-exchange in order to achieve the maximum amount of ion-exchange possible. For more information on the thermodynamics of ion-exchange, and discussions on the kinetics of ion-exchange, the reader is referred to the following references [161,163,164,166,167].

To some extent the pH also affects the amount of ion-exchange that occurs, though this is not as well understood as the other effects. In some cases, it has been found that increasing the pH of the electrolyte solution (to ~9-10) increases the amount of cation exchange that can take place [168]. However, in many cases the pH cannot be increased without precipitation of the metal ions in the electrolyte as hydroxides, as would be the case with Cu [169]. In these cases, it was found that decreasing the pH was actually beneficial. In other cases, still with Cu, it was found that pH had nearly no effect at all [170,171]. It is likely that there is no universal rule that may be applicable with regards to the effect of pH on the effective ion-exchange levels. No conclusions will be made here as to the effect of pH, and rather it is intended here that the reader be aware that pH may have some influence on the ion-exchange behaviour that is observed.

It is important to realize that achieving 100% of the theoretical CEC is not always possible, especially in the case of ion-exchange with divalent cations, shown in Equation 2.2 below [161,167,170–172]:

$$M^{2+} + 2C^{+}Z^{-} \leftrightarrow 2C^{+} + M^{2+}Z^{-}$$
(2.2)

where *C*⁺ can potentially be Na⁺, NH₄⁺, H⁺, or any other monovalent cation. The amount of possible ion-exchange is again dependent on the zeolite used as well as the cations to be used for ion-exchange. While this may have to do with the size of the cation to be exchanged, it may also have to do with the orientation of Al in the framework. It has been theorized that in an ion-exchange solution (and mentioned earlier) that transition metals in solution may form hydroxides [170]. These large transition metal hydroxide complexes may not be able to access every part of the zeolite due to steric restrictions, and therefore only a certain level of ion-exchange is possible. This limitation may not be observed for the alkaline earth metals, which can participate in higher levels of ion-exchange as they are less inclined to form these large hydroxyl complexes [172]. In the opinion of this author, while

steric limitations may be likely if hydroxyl complexes are formed, the amount of ionexchange possible with divalent (and, for that matter, trivalent and beyond) metals and complexes may depend strongly on the distribution of Al in the framework [167]. A divalent cation will require two Al's in close proximity to facilitate a proper ion-exchange, shown in Scheme 2.2. If the framework Al's are not close enough, which could especially occur at higher Si/Al ratios, ion-exchange would be unlikely, shown in Scheme 2.3a. If the framework Al's are not in the proper orientation, ion-exchange may also be quite difficult (Scheme 2.3b). If ion-exchange does occur with two Al's, another Al may be left in a position where it cannot be used for ion-exchange. In this case, the maximum ionexchange amount that could occur is ~67% (assuming every 2 out of 3 Al's is involved in ion-exchange). Regardless, complete divalent ion-exchange may be impossible over a zeolite for certain metals. For mordenite, this has been known for many decades [161,170– 172].



Scheme 2.2. Successful ion-exchange of a divalent metal onto a zeolite, displacing two monovalent cations.



Scheme 2.3. Unsuccessful ion-exchange of a divalent metal onto a zeolite, where a) framework Al are too far apart, and b) Al are not in the proper orientation.

Ion-exchange may also be conducted in the solid-state with little to no aqueous medium involved. The two solids involved in the ion-exchange could be a zeolite and a metal salt, or two zeolite samples. Solid state ion-exchange may be conducted for several reasons. It could be that the cation with its hydrate shell is too large to enter the pores of the zeolite, or the cation salt with the desired valence state may be unstable or insoluble in water [93]. Solid-state ion-exchange is quite simple, though energy intensive. The zeolite is usually physically mixed with the solid metal salt containing the ion. It is very important to ensure that the two are thoroughly mixed. This can be done either by milling or by suspending both the solids in a volatile solvent, mixing thoroughly, and then allowing the solvent to evaporate [167]. This is followed by a thermal treatment, performed usually in a vacuum or under a flow of inert gas, at temperatures of 300 to 400°C. The solid-state ion-exchange typically requires a few hours at these conditions for maximum exchange. The starting form of the zeolite is usually the NH_4^+ or H^+ forms [173].

In terms of when ion-exchange may be useful, there are a few applications where it may be used directly. Zeolites are very often used in detergents, where they are used to remove Ca²⁺ and Mg²⁺, thereby softening the water [93,167]. Zeolites, specifically clinoptilolite and chabazite, may also be used to remove radio-nuclei from low- and medium-level nuclear waste. Zeolites also find use in the treatment of agricultural and municipal wastewater, where they are used to remove ammonia and ammonium ions [167]. Ion-exchange is also used to create many zeolite catalysts in use today, where a transition metal (or any other metals, for that matter) is exchanged onto the zeolite and used directly for catalysis. The applications are too numerous to mention here. Typically, there are two ways in which an ion-exchanged metal may be used for catalysis. A metal may be left at its ion-exchanged position, in which case it will act as a metal oxide catalyst. The zeolite may serve to enhance the metal stability and help to prevent sintering of the metal. In other cases the metals may be reduced and form nanoparticles, the size of which would be constrained by the pores and channels of the zeolite. In this case, the zeolite is used mostly as a support for the creation of metal nanoparticles with constrained size [174].

2.2.5 Mesoporosity in a microporous framework – the hierarchical zeolites

One of the advantages which can simultaneously be a disadvantage of conventional zeolites is their microporous channels and pores. The microporous nature of zeolites presents many opportunities for shape selectivity for catalysts, and, along with their acidity and thermal stability, is the chief reason they are finding increasing usage in catalysis. One of the reasons for wanting mesoporosity in these materials has already been discussed.

Many larger molecules cannot access the acid sites of the zeolite, which spurred the creation of the M41S family with large mesopores. Indeed, Al-MCM-41 has seen increasing interest for many applications. Unfortunately these materials do not have as strong acidity when compared to conventional zeolites, which may be due in part to the rather amorphous nature of the walls of the mesopores [133,134]. Research continues into resolving this issue. The second reason mesopores are desired in a zeolite is due to the diffusional limitations imposed by the microporous framework. As previously shown, below ~ 10 Å configurational diffusion takes over (if diffusion into the zeolite can occur at all) [175]. In some cases, the low diffusivity in the micropores limits the reaction rate, and, due to the longer time that reactants and products spend in the framework, may give more opportunity for secondary reactions that lead to coke formation or cracking [176,177]. Therefore, to have the best of both worlds, it would seem that introducing mesoporosity into the microporous zeolite frameworks may be the solution. This should increase site accessibility, allowing larger molecules to react. It should remove diffusion limitations as well, and reduce the likelihood of product cracking or other secondary reactions that may lead to catalyst deactivation. The zeolites with added mesoporosity, whether synthesized that way or via post-synthesis treatment, have been given the term "hierarchical zeolites" [178].

One of the more well-known methods of dealumination of zeolites (increases the Si/Al ratio) is by steaming the zeolite at high temperature. Typically, either the ammonium or hydrogen form of the zeolite is steamed at temperatures in excess of 450-500°C. The mechanism of steaming and dealumination is quite simple. The AI-O-Si bonds are hydrolyzed, with the aluminum eventually being removed from the framework. This leaves a vacancy or creates a partial amorphization of the framework [176]. If amorphization does take place, the Si species contained in the amorphous material may be mobile, and some of the vacancies created by the aluminum removal may be repaired. Those vacancies that are not repaired are allowed to grow to form mesopores [163]. Mesoporous channels may be formed in regions of the zeolite crystal where there is a higher concentration of defects, though this may require a significant amount of dealumination [179]. During steaming, the removed AI may be deposited onto other parts of the framework, and any mesopores that are formed may be filled with this extraframework Al or other debris. This extraframework material is typically removed by a mild acid leaching procedure after the steaming [180,181]. If no acid leaching is performed, the bulk Si/Al ratio remains the same but the framework Si/Al increases. The zeolite ultra-stable Y, used in fluid catalytic cracking, is typically created through the steaming and mild acid leaching of zeolite Y, and is shown in

Figure 2.8. Large mesopores are typically only created with significant dealumination of a low Si/Al ratio zeolite, as only in this occasion are the vacancies close enough in the framework to combine and grow to form them. While mesopore creation is useful, steaming does result in partial framework amorphization and subsequent crystallinity loss. Combined with the Al removal, the number and the strength of the acid sites are changed, which can have a significant effect on the use of the zeolite as a catalyst [163,176]. However, the higher Si/Al ratio also means the zeolite is more stable and acid sites might be created that have higher strength [182].



Figure 2.8. TEM image of severely steamed and acid-leached zeolite Y (on left). On right is a 3D-TEM reconstruction of the same crystal.⁹

Acid leaching can be used to clean up the extraframework Al on a zeolite that are created either by steaming or as a result of a thermal treatment. Acid leaching can also be used directly to remove framework Al. Typically, strong inorganic acids are used for dealumination (as opposed to the milder, diluted acids used for washing) and the effectiveness of acid leaching is dependent on the zeolite, with mordenite being one of the more successful cases of mesoporosity being induced directly by acid leaching [176,183–185]. A great variety of acids have been used for acid leaching, such as acetic, oxalic, nitric, sulfuric, and hydrochloric acids, with different concentrations leading to differing amounts of dealumination [182]. The disadvantage to acid leaching is that removal of framework Al (and increase of Si/Al ratio, changing the acidity) and introduction of mesopores happens simultaneously, meaning the impact to catalytic activity is a summation

⁹ Reprinted from Catalysis Reviews, Vol. 45, No. 2, Generation, Characterization, and Impact of Mesopores in Zeolite Catalysts, S. van Donk, A.H. Janssen, J.H. Bitter, K.P. de Jong, pp. 297-319, 2003, with permission of Taylor & Francis.

of both effects. It is usually desired to study each effect separately. Crystallinity can also be significantly decreased by acid leaching, which could again result in changes to acidity (most likely decreases) [182,184].

Desilication has recently attracted significant attention as a means to introducing mesoporosity in zeolites. The mesopores that are formed from dealumination, both by steaming or acid treatment, may not extend through the entirety of the zeolite crystal and may exist only as cavities inside the crystals. While some mesoporosity may be created, it may not be extensive and it may not be particularly effective at removing diffusion limitations [186]. Given that the minimum for Si/Al ratio is 1, and there is almost always substantially more Si than Al in a zeolite (mordenite, for example, has a minimum Si/Al ratio of 5 [140]), the creation of mesopores that extend throughout the entire crystal may be more readily accomplished by desilication. Whereas acids are used to remove Al, treating the zeolites in an alkaline media (using a base) removes Si, though not necessarily selectively [187,188]. Desilication usually involves a one-step treatment with approximately 0.2 M NaOH at elevated temperature (25 – 80°C) for a minimum of 30 minutes [182]. A more intense treatment conducted over a longer period will result in increased mesopore creation. However, early studies of desilication showed that the extraction of silica in this manner was limited to Si/Al ratios of 25 to 50 [177,182,184,187]. Below Si/Al of 25, the negatively charged Al tetrahedra in the framework prevented Si extraction. Above Si/Al of 50, excessive extraction of Si gave wide pore size distributions and, in some cases, nearly complete dissolution of the zeolite, resulting in low yields of material [182]. As was the case with dealumination, each zeolite is unique and requires optimization of the treatment to maximize the benefit. Otherwise, base leaching of Si decreases the micropore volume and may destroy a significant amount of the zeolite.

Significant recent research has been conducted into controlling desilication. This has resulted in several procedures that have allowed for expansion of the relevant Si/Al range, as well as maintenance of the crystallinity. Alternatives to NaOH have been found, such as sodium aluminate. Sodium aluminate appears to form a protective aluminum hydroxide layer on the zeolite surface that helps to control the dissolution of Si. This amorphous layer can later be removed by acid washing. This treatment resulted in a material that had a high level of mesoporosity, although the formed mesopores were smaller. This procedure can be used for both low and high Si/Al zeolites [182,189]. Using other metal hydroxides, which have come to be known as "pore-directing agents", the effective Si/Al range for desilication was extended to ~12-1000. However, with these procedures a substantial loss in

crystallinity was still observed. To solve the crystallinity issue, it has been shown that desilication is much more difficult when the template used to help synthesize the zeolite was left inside and not calcined out. After desilication with the template still there, the resulting desilicated material had much more of its crystallinity preserved [190]. The template may also be added back to the post-calcined zeolite and provide the same stabilizing effect in desilication [191]. In addition to these templating methods, some success has been shown using surfactants that are normally used for the creation of mesoporous materials (M41S family). These surfactants, when combined with a mildly basic solution such as NH₄OH, can induce a reassembly of dissolved Si and Al species from the zeolite leaching. Specifically, cetyltrimethylammonium cations (CTA⁺) have been used for this purpose. This has resulted in the formation of mesoporous materials or composites of zeolites and mesoporous materials with high crystallinity [182,191–194]. The various routes used for desilication are summarized in Figure 2.9.



Figure 2.9. Summary of desilication procedures grouped by applicable Si/Al ranges. (a) At low Si/Al ratio, dislodged alumina forms at the mesopore surfaces and prevents dissolution.
Blockage must be removed by acid washing. (b) At medium Si/Al ratios, the one-step desilication by NaOH can be effectively done. (c) At high Si/Al ratio, the use of pore-directing agents (PDA) and surfactants is required to prevent dissolution of the zeolite.¹⁰

So far, the methods for creating mesoporosity in zeolites have been what are called "top-down" methods. In "bottom-up" methods, the synthesis procedure of the zeolite is changed so that either nanosized zeolite crystals, zeolites with a secondary mesopore

¹⁰ Reproduced from K. Möller and T. Bein, Chem. Soc. Rev., 42 (2013), 3689 with permission of The Royal Society of Chemistry.

system, or zeolite composites, are synthesized. While these procedures work, they are often not easily scaled up to industrial levels. The additives and templates required for the synthesis mixtures may also be quite costly [187]. Bottom-up procedures will not be discussed in further detail here.

2.2.6 Summary of zeolites in catalysis

The previous sections have been a short introduction into what a zeolite is and how it may be used for catalysis. What should be obvious from this brief introduction is the sheer number of degrees of freedom that work in zeolites presents. Firstly, there are several different types of zeolites to choose from for a particular application, all varying in acid strength and framework structure. Secondly, the acid strength can be further tuned by adjusting the amount of Al in the framework. This can be done by either synthesizing it directly or by changing it post-synthesis with dealumination. The Al content will also have an impact on the pore size, as AI – O bonds are longer than Si – O bonds. Also, it doesn't even have to be AI. There are several other metals which are known to be able to be integrated into the framework of the zeolite. Each will have its own unique influence on the pore size and on the acid strength. Thirdly, if a particular zeolite works for an application but has high diffusion limitations or the pore size is otherwise too small, large mesoporous channels can be created in it to remove the limitation, either through dealumination/ desilication or by changing the synthesis procedure of the zeolite. Further still, metals can be ion-exchanged onto the zeolite to change their catalytic behaviour, or the zeolite can be used as a support for the creation of small, size-controlled nanoparticles.

Unfortunately, the impact of a lot of changes cannot necessarily be predicted from theory. They must be tried and tested under controlled circumstances and compared. One application of interest could potentially be catalyzed by several different zeolites, each with a different Si/Al ratio. Even if the Si/Al ratio is not changed, a partial ion-exchange could influence the overall acidity as well. There are not a large number of zeolites available commercially either, meaning that many have to be synthesized. Such is the case with many SAPOs. Any MeAPO or zeolite containing a metal other than Al would have to be synthesized directly as well. There are simply too many possibilities with zeolites for them all to be available for purchase. Typically, only the conventional zeolites, or the aluminosilicates, are available and can be purchased, and even then only the common ones. These include (but are not limited to) ferrierite, faujasite, mordenite, ZSM-5, zeolite Y, zeolite Beta, zeolite A, and SAPO-34. Even among these, the zeolites coming from different suppliers, even if they are both the same type of zeolite, may be different. Every mordenite

synthesis, for example, could potentially produce a slightly different mordenite. As such, any research conducted into zeolites must be simple and be able to be applied broadly for it to be considered at an industrial scale.

2.3 DME carbonylation over zeolites

2.3.1 Early work

The possibility of DME carbonylation being performed over a zeolite was first theorized by Fujimoto et al. [82] in 1984 in a short letter. Fujimoto et al. [82] had been working on an alternative to the Monsanto process for methanol carbonylation (the BP Cativa[™] process had not been developed at the time [63,68]), and had found that the carbonylation of methanol could be performed over a strong solid acid without methyl iodide promotion. Specifically, zeolite Y, ZSM-5, and mordenite were investigated. For all these catalysts, the main product was DME and not acetic acid as in the Monsanto process. The partial pressure of CO in the feed was found to have no impact on the formation of DME, and the authors figured it was formed by the acid catalyzed dehydration of methanol. Aside from the produced DME, zeolite Y also produced methyl acetate at 200°C, but an increase to 300°C shifted the selectivity to favour other hydrocarbons. Over ZSM-5 and mordenite, some acetic acid was formed along with some methyl acetate and methyl formate. Also as part of this study, Fujimoto et al. [82] also ion-exchanged Cu²⁺ onto mordenite and ZSM-5, and found that it accelerated carbonylation rates but did not change the product distribution. By this period in time, Ono et al. [83] had already hypothesized about the creation of methyl carbonium ions (CH_3^+) over acidic zeolites and them serving as the active species for these types of reactions. Fujimoto et al. [82] figured the products aside from DME were formed by the carbonylation of this methyl active group, similar to a Koch type reaction shown in Figure 2.10. The CO would react with this methyl group to form an acetyl carbonium ion (CH_3CO^+) . This acetyl carbonium ion would either lead to the formation of acetic acid via hydrolysis, or methyl acetate via methanolysis. It was noted that catalytic activity of the zeolites was quite low, and was attributed to poisoning of the acid sites by water. Fujimoto et al. [82] thus figured that DME carbonylation, which should not produce water, may be more effectively catalyzed by a zeolite.



Figure 2.10. Carbonylation of methanol catalyzed by a strong acid zeolite (from Fujimoto et al. [82]).¹¹

It was not until ~2006 that DME carbonylation over zeolites began to attract attention again. Iglesia's group out of Berkeley [89], in collaboration with BP Chemicals Ltd., tested mordenite (with Si/Al ratios of 10 and 45), ferrierite (Si/Al of 33.5), ZSM-5 (Si/Al of 12.5), ultra-stable Y (Si/Al of 3), zeolite beta (Si/Al of 12.5), and an amorphous aluminosilicate (Si/Al of 3) in DME carbonylation with a gas comprised of 93% CO, 2% DME, and balance inert at 1 MPa total pressure and temperatures of 420-513 K. The mordenite with Si/Al ratio of 10 showed the highest activity for DME carbonylation, giving high peak selectivity (>99%) to methyl acetate. Cheung et al. [89] also determined that the reaction seemed to depend on CO pressure but not DME pressure. At the time, Cheung et al. [89] did not observe deactivation of the mordenite, but reaction tests did not proceed for a long enough time to accurately assess the stability of the mordenite catalyst (longest time shown was 2 hours of reaction time).

Cheung et al. [90] performed further research on DME carbonylation and observed some interesting behaviours. Reactions were performed at 438 K using the same mixture and pressure as in their original study. This time, reactions were run until 7 hours, at which point it could be observed that some deactivation of the mordenite was beginning to take place. Water was also found to have a strong inhibitory effect on the synthesis rate of methyl acetate. Instead, with increased water content more methanol was formed. In both

¹¹ Reproduced from K. Fujimoto, T. Shikada, K. Omata, H.-o. Tominaga, Vapor Phase Carbonylation of Methanol with Solid Acid Catalysts, *Chem. Lett.*, 13 (12), 1984, 2047-2050, with permission from The Chemical Society of Japan.

of their studies, Cheung et al. [89,90] observed that the catalyst had an induction period – an approximate 4 hour time from first exposure to the reactant mixture before a steady state synthesis rate of methyl acetate was achieved. It was also determined at this point that the reaction seemed to have a first-order dependence on CO and zero order dependence on DME. Using what they observed, Cheung et al. [90] proposed a reaction scheme. This is shown visually in Scheme 2.4. Firstly, they assumed that CO and H₂O would competitively bind to the same sites on mordenite:

$$CO + S_a \leftrightarrow CO * S_a \tag{2.3}$$

$$H_2 0 + S_a \leftrightarrow H_2 0 * S_a \tag{2.4}$$

On the acidic sites of the zeolite, it was hypothesized that DME would react with the proton to form methanol and a chemisorbed methyl group. The formed methanol would go on to react with another acidic site to form another chemisorbed methyl group and water.

$$CH_3OCH_3 + H * S_b \leftrightarrow CH_3OH + CH_3 * S_b$$
(2.5)

$$CH_3OH + H * S_b \leftrightarrow H_2O + CH_3 * S_b$$
(2.6)

Adsorbed CO would react with the chemisorbed methyl group to form an acetyl group. The acetyl group was then hypothesized to react with free dimethyl ether to form methyl acetate and regenerate the methyl group active site.

$$CO * S_a + CH_3 * S_b \to COCH_3 * S_b + S_a$$
(2.7)

$$CH_3OCH_3 + COCH_3 * S_b \to CH_3COOCH_3 + CH_3 * S_b$$
(2.8)

It was also assumed that DME would freely exchange methyl groups with the acid sites, shown in Scheme 2.4 as "DME scrambling".



Scheme 2.4. DME carbonylation elementary steps as proposed by Cheung et al. [89,90] (scheme from Cheung et al. [90]).

By this proposed reaction mechanism, the observed induction period was attributed to the slow replacement of the acid sites (or protons) with the active methyl groups. Isotopic evidence was presented as proof of this reaction mechanism [90].

Cheung et al. [90] further attempted to study the performance of H-MOR with different concentrations of Brønsted acid sites. They accomplished this by ion-exchange with Na⁺ or by chemically dealuminating the MOR. If the reaction were to proceed on all Brønsted acid sites, then the reaction rate should vary linearly with the number of acid sites. This was not found to be the case. In fact, methyl acetate synthesis rates did not seem to increase or decrease with increasing H⁺ concentration. At the time, Cheung et al. [90] figured that the reactivity of methyl groups must depend on the number and identity of sites within the vicinity of each other, or that it could depend on the location of the acid sites in the channels or side pockets. The foregone conclusion made in this paper was that Brønsted acid sites were required for the reaction to proceed.

2.3.2 The mordenite framework

Mordenites are natural and synthetic zeolites. Natural mordenites tend to have Si/Al ratios of 4.3-6.0, while synthetic mordenites have Si/Al ratios of 5.0 to 12.0 [195,196]. The structure of MOR can be described as being composed of edge-sharing 5-MR of tetrahedra that form along the *l* axis. This creates the larger 12-MR channels with dimensions 6.5 x 7.0 Å, and the smaller 8-MR channels with dimensions 2.6 x 5.7 Å, shown in Figure 2.11. These two larger channels are interconnected by 8-MR side pockets (along the *k* axis). Mordenite has an orthorhombic topography with space group *Cmcm* [140]. In the MOR unit cell, there are four symmetrically independent tetrahedral sites, usually called T1, T2, T3, and T4, which are shown in Figure 2.12. T3 is located in the 8-MR, while T2 and T4 are accessible from the 12-MR. T1 is shared between the 8-MR and 12-MR, but is more accessible from the 12-MR. Synthesized MOR is typically not perfect, and usually contains framework defects that make determination of the real symmetry difficult [140].



Figure 2.11. The a) framework, b) 12-MR (viewed along (001)) and c) 8-MR (viewed along (001)) of mordenite with the MOR type framework (dimensions shown in Å).¹²

¹² Atlas of Zeolite Framework Types by Baerlocher, CH.; McCusker, L.B.; Olson, D.H.; Sixth Revised Edition, 2007; with permission of Elsevier in the format Thesis/Dissertation via Copyright Clearance Center, Inc.



Figure 2.12. The four unique tetrahedral atom locations in mordenite, labelled as T1, T2, T3, and T4. 13

The smaller 4-MRs of MOR are typically the richest in Al, meaning that the distribution of Al in the framework follows the order T3 > T4 > T1 > T2 [197–199]. More quantitatively, the acid site distribution could be assumed to follow T1:T2:T3:T4 of 36:20:43:29 [200].

2.3.3 The active methyl group (methoxy site)

Cheung et al. [90] proposed a reaction mechanism that seemed to fit what they observed during reactions and their isotopic studies, but the idea of a methyl cation acting as an active group on a zeolite was not a new concept. It had been proposed by Ono et al. [83] a couple of decades prior. While the reaction mechanism appears to fit the data and most research groups working in the area assume it to be the most likely process by which methyl acetate is formed, the formation of a methyl group has been evaluated by other groups, albeit for different reactions (usually methanol to olefins or fluid catalytic cracking), but the theory is nonetheless applicable.

It is accepted as true that, under the influence of a Brønsted acid site, a hydrocarbon reactant can transform into a carbocation species [137,201]. The stability of these carbocations is shown in Figure 2.13. With increased branching, these carbocation species are increasingly stabilized. In terms of the reaction rate to form these carbocation species,

¹³ Reprinted with permission from M. Boronat, C. Martínez-Sánchez, D. Law, A. Corma, Enzyme-like Specificity in Zeolites: A Unique Site Position in Mordenite for Selective Carbonylation of Methanol and Dimethyl Ether with CO, *J. Am. Chem. Soc.*, 130 (2008), 16316-16323. Copyright 2008, American Chemical Society.

it decreases from tertiary to primary, and the activation energy increases with the increasing energy level of the final state [137]. The primary alkylcarbenium ions have very high energy content, and they are usually avoided when proposing reaction mechanisms. The formation of methyl and ethyl cations is particularly unfavourable, and is often used as an explanation for why there is hardly any methane and C₂ hydrocarbons formed in acid-catalyzed processes [136,202].



Figure 2.13. The relative stability of alkyl carbonium ions where R is an alkyl group.¹⁴

Among the mechanisms proposed for methanol-to-olefins processes, many involve the formation of an oxonium cation. An oxonium cation contains a tri-coordinated oxygen, and NMR studies have shown that a trimethyloxonium cation can form via disproportionation of DME on acidic ZSM-5 [203]. In this case, methanol is produced, and this methanol interacts with another zeolite acid site to produce a methoxonium species using the oxygen in the framework (this would be identical to the methyl group mentioned above and shown in Equation 2.6). It is acknowledged that these methoxonium species are not easily formed, and usually the use of a methyl halide is required [204,205]. Equation 2.9 below shows the formation of the trimethyloxonium cation from two DME molecules.

$$H-Z + 2CH_{3}OCH_{3} \iff \bigvee_{H_{3}C} CH_{3}^{+} + Z^{-} + CH_{3}OH$$
(2.9)

There is considerable evidence indicating that methanol will react over an acidic zeolite to form the methoxy species shown in Equation 2.6 (the terms "methyl group", "methoxonium species", and "methoxy species" are used interchangeably) [206–208].

¹⁴ This article was published in J. Čejka, H. van Bekkum, A. Corma, F. Schüth (Eds.), "Introduction to Zeolite Science and Practice", *Studies in Surface Science and Catalysis*, Vol. 168, "Chapter 22 Acid and Base Catalysis on Zeolites" (J. Weitkamp, M. Hunger), pp. 787-835, Copyright Elsevier B.V., Amsterdam, 2007.

These methoxy species have also been shown to be highly reactive. At room temperature, they may react with water to produce methanol again. From those same experiments, it was shown that the conversion of methanol to methoxy species was a reversible process, and potentially was equilibrium limited [206]. These methoxy species may also react with ammonia at room temperature to form methylamines and methylammonium cations [209]. At temperatures less than 160°C, the surface methoxy species were able to methylate toluene. While temperatures for methanol-to-olefins processes are normally in excess of 300°C, these methoxy species can likely react with aromatic compounds at much lower temperatures, leading to methylation reactions. At temperatures in excess of 220°C, the methoxy species likely act as precursors of carbene or ylide intermediates [206,210]. While the methoxy species were shown to be relatively stable at temperatures around 200°C, at 250°C the methoxy species were found to decompose and lead to the formation of hydrocarbons.

It is to be remembered that reaction mechanisms, despite however much proof may be available, are always just a theory. There is considerable evidence provided by different research groups to support the formation of a methyl group on a zeolite [206,208–211]. It is to be understood that the formation of a methyl group is a difficult process without the use of a promoter, such as a halide, although the formation of methoxy groups from methanol has been reported at temperatures less than 200°C [206]. This is possibly why the induction period before peak production of methyl acetate is nearly 4 hours on mordenite (or other zeolites). In this scenario, the zeolite itself is acting as a promoter, eliminating the need for a halide. Likely the induction period would vary dependent upon the zeolite used.

The information presented in this section was meant to provide more background information on the formation of these methoxy species and how reactive they may be. While the activation of DME on a zeolite is open to interpretation, it has been shown that DME alone can lead to formation of methoxy species on a zeolite [208].

2.3.4 A unique site on mordenite for producing methyl acetate

The inaugural work of Cheung et al. [89,90] had unveiled some interesting reaction behaviour with regards to methyl acetate formation rate as a function of the number of acidic sites. It seemed that Brønsted acid sites either needed to be within reasonable proximity of each other for the reaction to occur, or that there was a specific acid site that was more selective towards the formation of methyl acetate than the others. Regardless,
the behaviour merited further research.

Bhan et al. [212] sought to understand how the reaction may occur over mordenite and ferrierite by using partial ion-exchange of Na⁺ and coupling the results with IR spectroscopic measurements. This was a continuation of the work of Cheung et al. [90] and was performed by the same research group. Bhan et al. [212] determined that the H⁺ cations in the 8-MR of MOR were preferentially replaced with Na⁺ in ion-exchange, and only after increasing amounts of ion-exchange did Na⁺ begin to populate the sites in the 12-MR. This preferential ion-exchange had been determined by other groups as well [213,214]. With only partial ion-exchange, the DME carbonylation rates sharply decreased, which indicated that the methoxy groups in the 8-MR seemed to have more of an affinity for producing methyl acetate than those methoxy groups located in the 12-MR. This was not the first time a reaction had seemed to preferentially occur in the 8-MR of MOR. Veefkind et al. [214] had reacted ethanol with NH₃ over MOR, and found the reaction rate was ~ 1.5 times higher in the 8-MR pockets compared to the 12-MR channels. This discovery also explained why the reaction did not proceed over H-MFI, H-BEA, H-USY, and amorphous silica-alumina samples. These did not contain a crystalline 8-MR. This study did not resolve the issue of site proximity being required for the reaction to occur, but did narrow it down to the reaction occurring preferentially in the 8-MR.

Boronat et al. [215] approached this issue from a modeling perspective. Cheung et al. [89,90] and other groups [209,212] had determined that the rate limiting step was likely the insertion of CO into the surface methoxy group and the formation of the acetoxy group. This is the stage of the reaction that Boronat et al. [215] decided to simulate. They built cluster models of each of the four unique tetrahedral locations of MOR (shown previously in Figure 2.12) and placed a methoxy active site on each of them. By means of density functional theory (DFT), they measured the interaction of this methoxy group with CO, H_2O , CH₃OH, and DME in the transition states shown in Figure 2.14. It was found from the models that CO attack on the methoxy group always involved the highest activation barrier, typically between 20 and 28 kcal/mol. By comparison, the activation barriers for DME, CH₃OH and H₂O were 11-14 kcal/mol lower when the methoxy group was located in the 12-MR. However, in the 8-MR, the activation barriers for CH_3OH and DME were higher than that of CO, while the barrier for H_2O was comparable to the energies calculated in the 12-MR. It was determined that this had to do with the geometry around the 8-MR limiting the transition state that could potentially form, and steric limitations that prevented DME and CH₃OH from effectively accessing the methoxy sites in the 8-MR [215]. Since the 8-MR

would sterically limit the formation of hydrocarbons, the activation barrier for the carbonylation reaction was substantially lower comparatively. In the 12-MR, the interaction of DME and CH₃OH with the methoxy sites would form the oxonium cations shown in Figure 2.14c,d, and subsequently lead to formation of other hydrocarbons. The interaction of water with the methoxy groups likely would lead to competitive adsorption with CO, explaining the observed inhibitory effect of water in other studies [89,90]. It was therefore determined from this study that only the T3-O33 (otherwise known as T3-O9 in other studies) position in the 8-MR was selective towards the formation of methyl acetate from methoxy groups. The other sites, especially those in the 12-MR, favoured the formation of other hydrocarbons.



Figure 2.14. The transition states used for the attack of a) CO, b) H_2O , c) CH_3OH , and d) DME on a surface methoxy group.¹⁵

In Boronat et al.'s [215] initial study, the activation energy for the reaction of CO with the surface methoxy groups was similar in both the 8-MR and 12-MR, indicating that there should be a similar activity for all sites. This is not observed experimentally [90] and Boronat et al. [216] decided that pure DFT methods were insufficient for determination of the activation energies, and that additional dispersion interactions had to be included. The study proceeded analogously to their first one. Their results confirmed that dispersion interactions were more important inside the 8-MR pockets than in the 12-MR main channel, and also confirmed the activation energy for CO attack of the methoxy group in the 8-MR to be significantly less as compared to in the 12-MR (12.9 kcal mol⁻¹ vs. 19.2 kcal mol⁻¹). It was confirmed that in the 12-MR, interaction of the surface methoxy groups with methanol would likely form DME and an acid site, while interaction with DME would lead to the formation of the trimethyloxonium cation that could further react to yield other

¹⁵ Reprinted with permission from M. Boronat, C. Martínez-Sánchez, D. Law, A. Corma, Enzyme-like Specificity in Zeolites: A Unique Site Position in Mordenite for Selective Carbonylation of Methanol and Dimethyl Ether with CO, *J. Am. Chem. Soc.*, 130 (2008), 16316-16323. Copyright 2008 American Chemical Society.

hydrocarbons. The formation of the trimethyloxonium cation was figured to be the source of deactivation of the catalyst [216]. What was hinted at in their first study but determined more strongly in their second study was that, due to steric restrictions, DME could not react with the acetyl intermediate formed in the 8-MR. Only MeOH or H_2O could access the acetyl intermediate here, resulting in the formation of methyl acetate or acetic acid and an acid site on the zeolite, shown in Equations 2.10 and 2.11 [216].

$$CH_3OH + COCH_3 * S_b \to H * S_b + CH_3COOCH_3$$
(2.10)

$$H_2O + COCH_3 * S_b \to H * S_b + CH_3COOH$$

$$(2.11)$$

DME could interact with acetyl groups in the 12-MR, which would lead to the formation of methyl acetate and a methoxy group. Thus, the reaction from Equation 2.8 likely only proceeds in the 12-MR, and is not as favourable as the reactions that lead to hydrocarbons. From Equations 2.10 and 2.11, the surface methoxy groups would have to be reformed from DME or MeOH for the next catalytic cycle. It could be interpreted then that feeding MeOH as part of the reaction mixture could give enhanced reaction rates, and it may for a short while. However, MeOH interaction with a Brønsted acid site would form H₂O molecules, which tend to form clusters that will block the 8-MR pockets and inhibit carbonylation. The interaction of MeOH with a Brønsted acid site to form the methoxy group and water (as shown in Equation 2.6) is energetically more favourable than the interaction of DME with the same acid site. Excess produced water would deactivate the catalyst even more quickly. Based on this work by Boronat et al. [216], it would seem that no matter what happens, catalyst deactivation will happen, whether it be by produced hydrocarbons that are too strongly adsorbed to the framework or excess water produced by the reaction of MeOH with surface acetyl groups.

As an experimental proof of what Boronat et al. [215,216] and Cheung et al. [90], among others, had proposed, Li et al. [217] conducted DME carbonylation with MOR with acid sites localized to the 8-MR and 12-MR while performing in situ solid state NMR spectroscopy. Partial ion-exchange with NaNO₃ was used to produce H-MOR with acid sites located only in the 12-MR as others had done [212–214]. To synthesize mordenite with acid sites located only in the 8-MR, pyridine was used to block the 12-MR channels. It is known previously that pyridine cannot access the 8-MR directly, and as a probe molecule, is indicative only of the acid sites in the 12-MR and in the 8-MR pockets [169,218,219]. From NMR, Li et al. [217] were able to observe the formation of the methoxy and acetoxy groups in the 8-MR, and their subsequent reaction with DME to yield methyl acetate. It was

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observed that methyl acetate could be produced in the 12-MR as well, but formation of acetoxy groups were not observed there. The formation of hydrocarbons was more strongly favoured in the 12-MR than the formation of methyl acetate, though some small amount of methyl acetate was still produced. Some acetaldehyde was detected in the experiments that led to the formation of methyl acetate, and it was theorized that it may act as an intermediate in the reaction. Some MeOH was detected during the exposure of DME to acetyl groups over all experiments with H-MOR, though no conclusions were made as to whether or not this MeOH would directly react with acetyl groups to form methyl acetate as Boronat et al. [216] had theorized from modeling. The rest of the observations from Li et al. [217] appeared to be in line with Boronat et al.'s [215,216] theoretical studies.

While on the topic of the reaction mechanism, it is worthwhile to mention another study with regards to another possible reaction intermediate. Rasmussen et al. [220], through DFT modeling, showed that the interaction of CO with a methyl group would react to produce an acetyl carbocation, CH_3CO^+ , while the negatively charged O atom of the zeolite framework would remain free. This carbocation would physisorb onto the zeolite framework by giving up one of its hydrogens, forming a ketene intermediate and a Brønsted acid site. The ketene on the Brønsted acid site would then restructure itself into the acetyl. This sequence of steps is shown in Equations 2.12 and 2.13 [220].

$$CH_3CO^+ - [SiOAl]^- \rightarrow CH_2CO - [SiO(H)Al]$$
(2.12)

$$CH_2CO - [SiO(H)Al] \rightarrow [SiO(COCH_3)Al]$$
(2.13)

There is a very low energy barrier associated with this sequence of steps, and the carbocation would likely have a very short lifetime. Rasmussen et al. [220] used deuterium oxide, D_2O , to show experimentally that the ketene was present. Ketenes are highly reactive over a zeolite, and can undergo polymerization into polyketones at low temperature [221,222]. These intermediate ketenes were therefore predicted to be a potential source for the build-up of strongly adsorbed carbonaceous species that would lead to deactivation of the catalyst [220].

2.3.5 BP Chemicals Ltd. goes on a patent spree

The work of Cheung et al. [89,90], Bhan et al. [212], and Boronat et al. [215] was performed in collaboration with BP Chemicals Ltd. BP Chemicals Ltd. continued the research and filed several patents covering the development of the DME carbonylation to methyl acetate process using mordenite as a catalyst.

One of the first patents reported on the use of mordenite as a catalyst for the carbonylation of dimethyl ether, dimethyl carbonate, or methanol with carbon monoxide and hydrogen. This was reported to produce acetic acid and methyl acetate. The in situ regeneration of mordenite using an oxygen-containing gas was also included in the same patent [223]. In the patent, it was acknowledged that mordenite was a highly effective carbonylation catalyst but was prone to deactivation, likely by formation of carbonaceous deposits, or coke. This coke would block access to active sites. The regeneration could take place in a total pressure range of 1 to 100 bar and in a temperature range of 225 to 325°C. The mordenite used could have a Si/Al molar ratio between 3 and 45, but more preferably 5 to 20. The patent was also not exclusive to Al being included in the framework, also including boron, iron, and gallium. The mordenite used was preferably in its acid form, but could also be ion-exchanged with Cu, Ag, Au, Ni, Ir, Rh, Pt, Pd, or Co, with preference given to Cu and Ag. The concentration of O_2 in the regenerating gas could be between 0.1 and 25 mol%. By in situ regeneration, it was meant that the carbonylation reaction would be stopped, the catalyst regenerated, and the carbonylation reaction started again all without removal of the catalyst from the reactor. Regeneration could be carried out up to 5 times. In the presented examples, reactions proceeded using 0.625 g of catalyst and a reaction pressure of 70 bar. The catalyst was first treated with a 4:1 CO/H_2 mixture at a flow rate of 4 I/h for 3 hours at 220°C. Temperature was then ramped to 300°C where it was again held for a period of 3 hours. The gas feed was then switched to a $CO/H_2/DME$ mixture with ratio 72/18/10, again fed at 4 l/h (GHSV of 4000 h^{-1}). The catalyst used was either H-MOR or Cu/H-MOR (with 55 mol% Cu loading relative to Al, Si/Al = 10). The catalysts were allowed to run for approximately 97 hours before the first regeneration was required. After the first regeneration, H-MOR was shown to achieve the same activity. The regenerated Cu/H-MOR did not achieve the same activity as the fresh Cu/H-MOR. In further examples, the reaction gas mixture was changed to $CO/H_2/DME$ with ratios 76/19/5. With this mixture, the regenerated Cu/H-MOR catalyst did achieve the same activity as the fresh catalyst. The selectivity to MeOAc decreased with increasing regeneration of H-MOR, but was maintained at >95% with the use of Cu/H-MOR. Ag/H-MOR (with loading 55 mol%) with respect to AI) was also tested but did not show the same high activity with regeneration as Cu/H-MOR did.

BP Chemicals Ltd. refined their regeneration process and submitted another patent specifically for the process of regeneration of zeolite catalysts used in carbonylation [224].

As opposed to regeneration using an oxygen-containing gas [223], this regeneration process used hydrogen or a mixture of hydrogen and carbon monoxide at temperatures in the range of 250 to 600°C for regeneration of the zeolite. The pressure during regeneration could be in the range of 1 to 100 bar. The zeolite could be either of mordenite, ferrierite, or offretite. DME carbonylation reactions were carried out as previously described in their earlier patent with CO/H₂/DME ratio of 72/18/10 [223] and were again performed with H-MOR, Cu/H-MOR, and Aq/H-MOR (with the same metal loadings as previously described, Si/Al = 10). In the first examples presented, the gas used for regeneration was pure H_2 at a pressure of 70 bar and temperature of 400°C. The catalyst, in this case, Cu/H-MOR, was allowed to regenerate for 10 hours. The selectivity to MeOAc was restored with this regeneration but the initial peak activity of the fresh catalyst was not. As shown in the patent, the initial yield of the Cu/H-MOR catalyst was ~920 g kg⁻¹ h⁻¹. After the first regeneration (with pure H₂), the peak yield was \sim 700 g kg⁻¹ h⁻¹. After the second regeneration (again with pure H₂), the peak yield was \sim 580 g kg⁻¹ h⁻¹. In further examples, a gas mixture of CO/H₂ with ratio 4:1 was used for regeneration at the same conditions as the earlier example. As before, regeneration restored the selectivity to MeOAc, which was \sim 90%. Unlike before, the initial peak activity was largely restored. The peak activity of Cu/H-MOR was 1017 g kg⁻¹ h⁻¹, and after regeneration, activity was restored to 964 g kg⁻¹ h^{-1} . For a Ag/MOR catalyst, the original activity was 940 g kg⁻¹ h^{-1} , and after regeneration was 905 g kg⁻¹ h⁻¹ [224]. This patent showed the feasibility of using a syngas mixture for regeneration of the catalyst, which meant an oxidizing gas, such as oxygen, did not have to be introduced into the process for catalyst regeneration.

Many of the later patents BP filed were mainly refinements to the process and ways to enhance the stability or selectivity. Such was the case with Armitage et al. [225], who refined the metal-loaded catalysts. Prior to this, Cu or Ag was ion-exchanged onto MOR (Si/Al = 10) at 55 mol% loading relative to Al (meaning 55% of the negative framework charge created by Al was compensated for by the ion-exchanged metal). In this patent, it was found considerably less metal could be used. In the case of Ag/MOR, the Ag loading was decreased to 39 mol% relative to Al. The Cu loading was decreased to 15 mol% relative to Al. Several metal-loaded mordenites were also prepared by impregnation. For Ag/MOR by impregnation, the Ag loading was 57 mol% relative to Al. For Cu/MOR by impregnation, the Cu loading was 59 mol% relative to Al. DME carbonylation reactions were again carried out as described in BP's earlier patent with CO/H₂/DME ratio of 72/18/10 [223]. The metal-loaded catalysts prepared by ion-exchange had higher activity (slightly) and better selectivity to MeOAc as compared to the catalysts prepared by impregnation. In

these original examples, the difference in catalyst behaviour could have been due to the different metal loadings. In the final example presented in this patent, Cu/MOR was prepared by ion-exchange and impregnation with identical metal loading. Again, the catalyst prepared by ion-exchange showed better activity (~15% higher activity). Approximately the same peak selectivity to MeOAc was achieved, but on the deactivated ion-exchanged catalyst the selectivity to MeOAc was 90%, while for the deactivated impregnated catalyst it was 85% [225].

Further changes were made to the catalyst in the next patent by Ditzel et al. [226]. This time the examples provided used catalysts containing Pt. Specifically, bimetallic Cu-Pt/MOR or Ag-Pt/MOR catalysts were shown to have significantly higher catalytic activity as opposed to their monometallic counterparts or acidic MOR. High loadings of Cu and Ag were again used for the catalysts in this study (55 mol%), though the patent claimed the loading could be anywhere from 1 - 200 mol% relative to Al. Pt loading was comparatively low, being from 1 - 10 mol% with catalysts in the examples having only 1 mol% relative to Al. One example was presented where the Pt loading was increased to 10 mol%. The catalysts in this particular patent were prepared by impregnation. In the case of the bimetallic catalysts, the two metals were added simultaneously, though the patent did claim sequential metal addition would also work. DME carbonylation reactions were again carried out largely using the same method as in earlier patents, however the reaction pressure was decreased to 45 bar and the $CO/H_2/DME$ ratio was varied during the reaction. In this case, the ratio of $CO/H_2/DME$ was 76.6/19.2/4.2 for the first 28 hours of reaction followed by alteration to 73/18.2/8.8 for 28 to 54 hours and finally 69.3/17.3/13.4 for 54 hours to catalyst deactivation at 95 hours. The bimetallic 10% Pt 55% Cu on MOR catalyst gave a peak MeOAc production level of 700 g L^{-1} h^{-1} , while the 1% Pt 55% Cu on MOR catalyst managed 600 g L⁻¹ h⁻¹. Specifically, the bimetallics performed very well with the increase of DME concentration at 28 hours where they achieved their peak productivity. 55% Cu/MOR by comparison had its peak MeOAc production at the start of reaction, reaching ~550 g L^{-1} h⁻¹ ¹. The Cu/MOR deactivated during the entirety of reaction and did not show much enhancement with increased DME concentration. It is to be noted that the bimetallic catalysts containing Pt, while having higher activity, did still show signs of deactivation [226].

Another patent for BP Chemicals Ltd. by Hazel et al. [227] introduced the idea of adding methyl acetate or acetic acid to the reaction gas as a means of providing a more stable reaction and decreasing the rate of deactivation. In the earlier patents by BP Chemicals Ltd., the undesired by-products of the reaction were usually methane or C_{2+} hydrocarbons (ethane, ethylene, propane or propylene). The possibility also exists for the formation of aromatic hydrocarbons. By adding methyl acetate or acetic acid to the gaseous reaction mixture, the formation of these by-products could be considerably suppressed. It was shown that typically less than 5 mol% of methyl acetate or less than 1 mol% acetic acid is needed to accomplish this. For the examples presented in the patent, a Cu/MOR catalyst with 55 mol% Cu relative to Al was used. The reaction conditions used were somewhat different compared to the prior patents. In these examples, 1.948 g of catalyst was used. The catalyst was pretreated using a $2:1 \text{ CO/H}_2$ mixture at 70 bar and 220°C for 3 hours. After this, temperature was increased to 300°C and the gas mixture was switched to a CO/H₂/DME/Ar/MeOAc/N₂ with ratios 54/29/2.5/5/1/8.5 at a flow rate of 12 I/h (giving a GHSV of 4000 h^{-1}). A second experiment was performed with no MeOAc in the feed. The results showed that the addition of MeOAc significantly hindered the formation of methane and C_{2+} hydrocarbons, decreasing methane production from ~2 g L⁻¹ h^{-1} to ~0.75 g L⁻¹ h^{-1} . The selectivity towards MeOAc in this scenario was increased from 80% with no MeOAc co-fed to 90% with MeOAc co-fed. Production of C_{2+} hydrocarbons decreased by approximately 50%, and after 100 hours of reaction no C₂₊ hydrocarbons were detected with MeOAc co-feeding. Acetic acid was tested as well, and exhibited the same inhibitory behaviour as MeOAc on the formation of methane and hydrocarbons during reaction.

Returning to modification of the catalyst to enhance its behaviour, Armitage et al. [228] patented the use of a desilicated mordenite catalyst for the carbonylation of methanol, methyl acetate, or dimethyl ether to produce acetic acid or methyl acetate. In this case, the mordenite had to have a Si/Al ratio in the range of 6 to 125, with preference given to the range of 12.5 to 30. In this patent, the mordenite was desilicated by means of a basic aqueous solution, created by using either alkali metal hydroxides or alkaline earth metal hydroxides. Typically, 0.2 M NaOH was mixed with the mordenite at a temperature in the range of 60 - 70°C for 10 to 45 minutes. It was acknowledged that the desilicated mordenite catalyst may have had to be prepared from a dealuminated mordenite. In the patent, the dealumination was conducted by both steam and acid treatment. The mordenite that was steamed was not fully acidic, containing some partially ion-exchanged univalent metal from Group 1 or Group 11 of the periodic table. In one of the examples provided, ammonium mordenite was first partially ion-exchanged with NaNO₃, then vacuum filtered, dried and calcined. This material was then steamed at 500°C. The steamed mordenite was treated with a 1 M solution of HCl at 80°C for a period of 1 hour. The material was then

dried and shown to have a Si/Al ratio of 17.5. Desilication of this material was conducted using a 0.2 M NaOH solution at 65°C for 0.5 hours. The solution was filtered, and the resulting material was ion-exchanged with NH₄NO₃ and finally calcined to give the acidic form. This material had a Si/Al ratio of 14.5. The performance of this catalyst was compared against a sample of H-MOR from Zeolyst with Si/Al ratio of 10, a dealuminated H-MOR (taken from the previous sample before desilication), and a desilicated H-MOR. The desilicated H-MOR was prepared from a mordenite with Si/Al ratio of 10 and was prepared as described above. Reactions were conducted at 20 bar and 300°C using a CO/H₂/DME mixture with ratios 76/19/5. The GHSV used was 5000 h^{-1} . The desilicated dealuminated catalyst gave an acetyls production rate at 10 hours of reaction of 403 g L⁻¹ h⁻¹, compared to 130 and 144 g L^{-1} h⁻¹ for the dealuminated and desilicated catalysts respectively. The H-MOR with Si/Al ratio of 10 gave an acetyls production rate of 111 g L^{-1} h⁻¹ at the same time. The desilicated dealuminated catalyst did deactivate quite quickly, losing ~75% of its acetyl production rate by 30 hours. The dealumination procedure as described above (with partial ion-exchange) was later patented separately as a means to selectively dealuminating the 12-MR of MOR, leaving the Al in the 8-MR alone [229].

In a recent patent application, Ditzel et al. [230] were attempting optimization of the reaction conditions so as to prolong catalyst lifetime. They found that if the DME carbonylation process was carried out with an equimolar or molar excess of CO relative to H_2 which was then changed to have a molar excess of H_2 relative to CO, the catalyst lifetime could be extended significantly and coke formation was reduced. It was even hypothesized that the coke generated may be beneficial to the catalyst selectivity. The other reaction conditions, such as temperature and pressure, were kept the same as in the original patents [223]. In an example with an acidic mordenite catalyst (Si/Al ratio of 10), in the first 3-5 hours of reaction the mixture consisted of 6.0 mol% DME, 75.2 mol% CO, and 18.8 mol% H₂. For times on stream of 5-215 hours, the mixture was changed to 10.0 mol% DME, 72.0 mol%, and 18.0 mol% H_2 . For times on stream of 215 – 379 hours, the mixture was changed to 10.0 mol% DME, 30 mol% CO, and 60 mol% H₂. Very high selectivity to MeOAc was reported in the first 215 hours of reaction (>97%), which decreased to ~92% with the increase in H_2 at 215 hours. Prior to this change, the catalyst was producing 300 g L⁻¹ h⁻¹ of acetyls (acetyls are defined as the production of methyl acetate multiplied by 0.81 to give an idea of how much acetic acid could be produced). This decreased with additional H_2 but was still ~250 g L^{-1} h⁻¹. The other examples were simply variations of this one, finding the optimum feed compositions for different times of reaction.

Moving on from the use of mordenite, Daniel et al. [231] sought to produce acetic acid more directly over ferrierite. It is reported in this patent that methanol and methyl acetate could be contacted with a zeolite catalyst that has at least one channel with a 10-MR (like ferrierite) to produce acetic acid and dimethyl ether. This reaction could be performed at low temperatures in the range of 140 to 250°C. As detailed in the patent, a mixture of dimethyl ether and acetic acid is produced by the simultaneous dehydration and hydrolysis of a feed containing methanol and methyl acetate. Though ferrierite was used, other zeolites that were suggested included ZSM-35, clinoptilolite, ZSM-57, and stilbite. All these zeolites would preferably have Si/Al ratios in the range of 7.5 to 30. In the example provided, the reaction was carried out at 170°C and 50 bar with a liquid hourly space velocity of 4 h⁻¹. The feed consisted of 50 mol% MeOH and 50 mol% MeOAc. Mostly DME was produced from the reaction, with selectivity to acetic acid not exceeding ~33% [231]. This patent is not directly relevant to the reaction being carried out in this thesis and will not be discussed in any more detail.

From the patents, it appears BP Chemicals Ltd. has developed a process by which they can carry out the carbonylation of DME to MeOAc over mordenite in quite a stable fashion, though some deactivation still occurs. It must be noted, however, that BP Chemicals Ltd. is operating at more intense conditions. Most examples presented seem to be conducted at 300°C and 70 bar. There is also a considerable amount of H₂, which would not be used directly for DME carbonylation. Rather, it appears BP Chemicals Ltd. is operating at conditions where by-product hydrocarbons may more readily leave the mordenite framework, preventing catalyst deactivation by coke formation that eventually blocks the active sites. The substantial amount of H₂ may also be actively cleaning the mordenite and aiding in the removal of by-products, indicated by one of the primary byproducts being methane. Cheung et al. [89,90] showed that this reaction can proceed at much milder conditions and without the use of excess H₂. While the conditions selected by BP Chemicals Ltd. do enhance catalyst stability, the development of a catalyst that can be more stable at lower temperature, lower pressure, and without so much H₂ in the feed, could substantially reduce operating costs.

2.3.6 Other studies on DME carbonylation over zeolites

Many other groups went in the same direction as BP Chemicals Ltd. with regards to the stabilization of MOR by ion-exchange and dealumination. Zhang et al. [92] performed DME carbonylation over Cu/H-MOR prepared by several different methods with the objective of improving the activity. The original H-MOR had Si/Al ratio of 10. Cu/H-MOR was

prepared by conventional ion-exchange (1.80 wt% Cu loading), ammonia evaporation (4.76 wt% Cu loading), urea hydrolysis (6.92 wt% Cu loading), and incipient wetness impregnation (5.00 wt% Cu loading), and then tested in a packed-bed reactor. DME carbonylation was carried out at 1.5 MPa and 210°C with CO/DME ratio of 47. Catalysts were calcined at 500°C and activated in situ using a 20% $H_2/80\%$ N_2 mixture at 270°C. With each of the Cu/H-MOR catalysts, Zhang et al. [92] noted that the BET surface area decreased by nearly 13% compared to the original H-MOR. Pore area was shown to decrease by $\sim 18\%$. Pore volume decreased by a similar level, and pore size was shown to decrease by $\sim 30\%$. The Cu/H-MOR prepared by ion-exchange showed the smallest decrease in surface and pore area, which was assumed to be an indication of high Cu dispersion. A decrease in MOR crystallinity with Cu loading was also observed by XRD. For all Cu/H-MOR samples, Zhang et al. [92] showed a very large increase in the conversion of DME compared to H-MOR alone. DME conversion on H-MOR at the conditions tested was below 42%, while for all Cu/H-MOR catalysts a conversion was achieved of >90% after 2 hours of reaction. All catalysts showed >90% peak selectivity to MeOAc. The Cu/H-MOR prepared by ion-exchange showed the best activity and stability. All catalysts showed rapid deactivation after only 3 hours in reaction with selectivity to MeOAc decreasing to <70% after 10 hours of reaction time. Cu/H-MOR prepared by ion-exchange was studied in more detail with different Cu loading amounts. Higher Cu loading gave higher DME conversion and better selectivity to MeOAc, though all catalysts prepared by ion-exchange had substantially deactivated by 10 hours of reaction time.

With ion-exchange determined to be the best method of getting Cu onto H-MOR for use in DME carbonylation, Zhang et al. [232] attempted to find the best calcination temperature for Cu/H-MOR. This was conducted again using the same MOR with Si/Al ratio of 10. The Cu loading amount was not reported in the paper. Catalysts were calcined in batches at 270, 350, 430, 500, and 600°C for a period of 4 hours before being granulated. The Cu/H-MOR calcined at 430°C gave the highest surface area, micropore volume, and micropore area. CuO was detected in all cases from XRD. Gas phase carbonylation was carried out as described in Zhang et al.'s [92] earlier paper. Catalysts were first activated using a 20% H₂/80% N₂ mixture at 270°C. The catalyst calcined at 270°C gave a DME conversion of only 18.6% and peak MeOAc selectivity of 75.4%. The catalyst calcined at 430°C gave the best performance, with 97.2% peak DME conversion and 98.8% peak selectivity to MeOAc. The catalyst calcined at 600°C gave a DME conversion of only 38.8%, though the peak MeOAc selectivity was still high at 92.9% (data taken at 145 minutes of reaction)

Keeping with ion-exchange, Wang et al. [233] ion-exchanged Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Ag⁺ onto H-MOR (Si/Al of 9) and compared each of their performances in DME carbonylation. It was suggested that, due to the different diameters of the ions of these metals, they would coordinate in different H-MOR channels and lead to differences in the catalytic performance. In each case, the catalysts were prepared in the same manner. A 0.02 mol/L solution of the metal salt was prepared and H-MOR added to it. It was stirred so that H-MOR was suspended and left for 24 hours. The catalyst was dried overnight and then calcined in air at 500°C. The final exchanged metal amounts varied, with 1.74% Cu, 1.30% Ni, 1.36% Co, 1.67% Zn, and 1.64% Ag. DME carbonylation was carried out using 0.5 g of catalyst. The temperature and pressure used were 210°C and 1.8 MPa respectively, with a CO/DME/N₂ mixture with a CO/DME ratio of 19. For most of the catalysts, metal ion-exchange decreased surface area only slightly ($\sim 6\%$). This was not the case with ion-exchanged Co²⁺, which decreased surface area by 16% compared to original H-MOR. Micropore volume decreased only slightly as well. Metal ion-exchange did not change the XRD pattern significantly with no shift in peak position and no diffraction lines attributable to a new phase. From TEM, it appeared that Ag⁺ did not necessarily follow conventional ion-exchange, and highly dispersed nanoparticles were observed on the surface of MOR instead. All six catalysts (H-MOR and the 5 ion-exchanged H-MORs) showed >90% selectivity to MeOAc with the main by-products being methanol and methane. Cu-, Co-, and Ni-modified H-MORs gave higher conversion of DME compared to H-MOR, while the Zn- and Ag- modified H-MORs gave lower conversion than H-MOR. Cu/H-MOR was observed to give the best conversion and highest selectivity to MeOAc. After only 4 hours on stream, both Cu/H-MOR and H-MOR showed signs of deactivation. However, on deactivation, Cu/H-MOR was shown to maintain high selectivity to MeOAc. As for a conclusion regarding where the metals would preferentially ion-exchange, it was suggested that Zn^{2+} ion-exchanges preferably in the 12-MR. Given the smaller radii of Cu^{2+} , Co^{2+} , and Ni²⁺, it was hypothesized that these species ion-exchanged in the 8-MR. The authors also suggested that Ag₂O just covered some active sites and was responsible for that particular catalysts poor performance in DME carbonylation [233]. This is shown in Figure 2.15. No supporting evidence was provided for the hypothesized metal ion-exchange locations.



Figure 2.15. Hypothesized position of ion-exchanged Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, and Ag⁺.¹⁶

It was previously mentioned that zeolites may have substantial diffusion limitations due to their small pore sizes. Xue et al. [91] attempted to remove these diffusion limitations from DME carbonylation by synthesized nanosized mordenite crystals. Nanosized zeolites are also suspected to aid in the suppression of coke deposition as species that may lead to coke formation can leave the zeolite crystal much more quickly and easily [234]. Normally synthesized zeolite crystals are typically at the micrometer scale. In order to synthesize nanosized crystals of mordenite, Xue et al. [91] added Et_6 -diquat-5 and Al(NO₃)₃·3H₂O to a 1.0 M NaOH solution, followed by addition of silica sol. This mixture was stirred for 24 hours at ambient temperature and crystallized for 7 days in an autoclave while being stirred. This produced MOR crystals with a diameter of approximately 50 to 100 nm and Si/Al ratio of 22. The nanosized MOR crystals were also ion-exchanged with Cu. Contrary to what was suggested by Wang et al. [233], Xue et al. [91] observed via infrared spectroscopy that Cu²⁺ likely ion-exchanged in the 12-MR of MOR. DME carbonylation was conducted using 0.1 g of catalyst at 300°C and 1.0 MPa. Catalysts were initially calcined at 500°C in air and pretreated in a 20% H_2/CO mixture. The reaction mixture consisted of DME, CO, H₂, and He with a constant ratio of CO/DME of 15.2 (totaling 81% of the gaseous mixture) and varying amounts of H_2 and He. The total flow rate used was 8.34 mL/min. In reaction, the nanosized H-MOR crystals and nanosized Cu/H-MOR gave very high initial conversion of DME (\sim 90%) compared to micrometer-sized H-MOR (Si/AI = 9), which gave an initial peak conversion of 70% before deactivating quickly. By 10 hours, the micrometer-sized H-MOR had deactivated completely while the nanosized H-MOR was at a conversion of ~70%. The nanosized H-MOR and Cu/H-MOR were still active at 40 hours of

¹⁶ Reprinted from S. Wang, W. Guo, L. Zhu, H. Wang, K. Qiu, K. Cen, Methyl Acetate Synthesis from Dimethyl Ether Carbonylation over Mordenite Modified by Cation Exchange, *J. Phys. Chem. C*, 119 (2015), 524-533, in accordance with ACS AuthorChoice Usage Agreement 2015.

reaction but had decreased to less than half their initial activity. The nanosized MOR catalysts showed better selectivity to MeOAc during reaction compared to micrometer-sized H-MOR. Addition of H₂ to the reaction gas mixture was shown to decrease coke formation but not substantially. At 40 hours on H-MOR, 138.0 mg of C/g had been deposited with no H₂ present, while with 19 vol% of H₂ present in the reaction gas mixture, 102.0 mg of C/g had been deposited [91]. While the use of nanosized MOR and having a large amount of H₂ in the feed may decrease the deactivation rate of the catalyst, it does not prevent the eventual complete deactivation.

From the same research group, Xue et al. [235] sought to selectively dealuminate the 12-MR of MOR and increase the stability of the catalyst by complete removal of the coke-creating acid sites. The dealumination procedure was slightly different as compared to the procedure patented by BP Chemicals Ltd. [229], but was based on the same idea. An H-MOR sample (Si/Al of 7.4) was initially purged with a 2.0% pyridine/ N_2 mixture. It was assumed that after this treatment the 12-MR of MOR was blocked with pyridine. Xue et al. [235] then treated these samples with 0.05 M NaOH to replace the protons in the 8-MR with Na⁺. This sample was then calcined at 500°C in air to remove the pyridine in the 12-MR. After this, the sample was steamed at 750°C for 5 hours in a gas stream containing 30% H_2O in N_2 . The now dealuminated sample was ion-exchanged with 1 M NH₄NO₃ and calcined to form the H-MOR with dealuminated 12-MR channels. The steamed sample was shown to still have high crystallinity (~92%) compared to the original H-MOR. The steam treatment also seemed to have no effect on the surface area, though micropore surface area and volume were both reduced. Total pore volume of the steamed H-MOR had increased due to the creation of inner mesoporous cavities. DME carbonylation was performed using 0.6 g of catalyst at 200°C with 1.0 MPa pressure and a gas mixture of 5% DME/50% CO/2.5% $N_2/42.5\%$ He. The GHSV was 1250 ml/(g·h). The dealuminated H-MOR showed much higher stability compared to the original material. By 15 hours, the original H-MOR had decreased to 12.5% conversion of DME while the dealuminated H-MOR was at 40% conversion. The peak conversion for both samples was $\sim 60\%$. The dealuminated sample showed nearly 100% selectivity to MeOAc during the 15 hours of reaction, while on deactivation the original H-MOR had decreased to ~55% selectivity to MeOAc. It is to be noted that the dealuminated sample was deactivating quickly at 15 hours, which was attributed mostly to the acid sites that had not been removed by dealumination [235].

As the belief surrounding the idea that the 12-MR was the source of the deactivation of the MOR catalyst spread, Liu et al. [236] figured one of the best options to deal with that

channel was to simply block it completely. To do this, the H-MOR (Si/Al of 6.4) had pyridine adsorbed prior to using it in reaction. After calcining the catalyst at 500°C, pyridine was adsorbed at 300°C using a 1.3% pyridine/98.7% N₂ mixture. A slightly dealuminated catalyst prepared by acid leaching was prepared as well with Si/Al ratio of 9.6. DME carbonylation was conducted using 0.6 g of catalyst at 200°C and 1.0 MPa and a 5% DME/50% CO/2.5% N₂/42.5% He mixture with GHSV of 1250 ml/(g·h). The H-MOR catalysts with Si/Al ratios of 6.4 and 9.6 gave similar results in reaction, but the sample with pyridine pre-adsorbed showed almost no sign of deactivation after 50 hours of reaction, maintaining a ~33% conversion of DME with nearly 100% selectivity to MeOAc and no detected hydrocarbons. It was reported that the conversion of DME had decreased from 33% to 20% after 250 hours on stream though these results were not shown.

Liu et al. [237] also attempted DME carbonylation over H-ZSM-35 as opposed to the use of H-MOR, again citing that the 12-MR of MOR was responsible for the deactivation of the catalyst. ZSM-35 has a 10-MR with an intersecting 8-MR. The H-ZSM-35 was prepared via hydrothermal process with a Si/Al ratio of 8.1. The Si/Al ratio of the H-MOR used for comparison was 11.6. DME carbonylation was conducted using 0.6 g of catalyst at 200°C and 1.0 MPa with a 5% DME/50% CO/2.5% N₂/42.5% He mixture at a flow rate of 12.5 ml/min. DME conversion over both catalysts was low, with peak conversion not exceeding 10%. By 20 hours, H-MOR had substantially deactivated while H-ZSM-35 was still at a conversion level of 10%. H-MOR showed its characteristic high peak selectivity to MeOAc and lower selectivity (~60%) with deactivation. However, H-ZSM-35 showed nearly 100% selectivity to MeOAc over the entirety of the 35 hours of reaction. The H-ZSM-35 was slowly deactivating during the entirety of reaction, but the rate of deactivation was very low. The only by-product detected on H-ZSM-35 was MeOH.

The substantial research into the use of MOR for DME carbonylation has repeatedly shown that it is unstable and subject to deactivation. Most groups seem to accept that this is by coking, though it has been suggested that excess water produced through the reaction mechanism could also be a source of deactivation [216]. While it would seem, especially based on the patents from BP Chemicals Ltd., that the process conditions can be altered so that acidic MORs with the common Si/Al ratio of 10 can be used in reaction for times in excess of 200 hours, this does not come without its own costs. The conditions of reaction are notably more intense compared to most studies and substantial amounts of H_2 are required in the feed [230]. The H_2 acts to continually clean the surface of the MOR and terminate any hydrocarbons that begin to form large carbonaceous deposits. Many differing alternatives have been discussed in this section for stabilization of MOR, but many of these methods have drawbacks. The synthesis of nanosized MORs, for example, is difficult and involves the use of expensive template molecules. Dealumination via steaming could be scaled up to an industrial level, but not if the acid sites in the 8-MR are to be protected. Armitage and Sunley [229] likely developed the most easily scaled technique, but this dealuminated MOR was not shown to be that much more stable than the initial material. The use of pyridine to block the 12-MR and enhance MOR stability would also be unfavourable at an industrial level, as pyridine is highly flammable and also poses certain health risks (causes severe eye and skin irritation, burns, possible respiratory tract irritation, liver and kidney damage). Ion-exchange of metals onto MOR would very likely be one of the safest and simplest ways to help stabilize MOR.

2.3.7 Alternatives to zeolites

There have only been a few alternatives to zeolites proposed for carbonylation of DME to MeOAc. MeOH and DME had been reported to react with CO in the presence of BF₃ or BF₃-H₂O to give AcOH or MeOAc [238,239]. However, these reactions required pressures of 800-900 atm and temperatures in the range 150-325°C. Bagno et al. [240] sought to do the same reaction at milder conditions using HF-BF₃ and trifluoromethanesulfonic (triflic) acid. Over HF-BF₃, MeOH did react to produce MeOAc and AcOH, with temperatures around 200°C favouring MeOAc and temperatures >260°C favouring AcOH. However, this still required a pressure of 150 atm. Carbonylation of DME over HF-BF₃ gave a 66% selectivity to MeOAc with the remaining product being AcOH, but again required temperatures >190°C and a pressure of 160 atm. Higher temperatures (>260°C) again favoured formation of AcOH. Triflic acid did not work as well as HF-BF₃. These processes did not offer any advantages over the Monsanto process for producing acetic acid, as they were conducted at substantially higher pressure. These also involved the use of very strong acids and still used halides.

Shortly after the work by Bagno et al. [240], Wegman [81] reported the use of metal-ion exchanged heteropoly acid catalysts for carbonylation of MeOH or DME. With heteropoly acids alone, MeOH was converted mostly to DME and some other hydrocarbons. With Rh or Ir exchange onto tungstophosphoric acid, the carbonylation of MeOH could be conducted at 225°C and 1 atm CO. The use of RhW₁₂PO₄₀ deposited on SiO₂ in MeOH carbonylation gave selectivities of 49% to DME and 34% to MeOAc. When used for the reaction of DME with CO (1:3 molar ratio) at the same conditions, the only product detected was MeOAc. This was quite the discovery at the time, since these reactions were performed

at only 1 atm of pressure while the Monsanto and BP CativaTM processes were still operated at 30 - 60 atm. The use of heteropoly acids also did not require the use of a halide co-catalyst.

Later, Volkova et al. [241] expanded on the earlier work of Wegman [81] and used cesium salts of 12-tungstophosphoric acid promoted with Rh for DME carbonylation. At conditions of 10 bar total pressure (CO/DME ratio of 10) and 200°C, the selectivity to MeOAc was very high (>90%) and increased with Cs content. A ratio of Cs/P of 1.5 and Rh loading of 0.5-1 wt% was found to be optimal for activity and selectivity. Reactions were only conducted for a period of 120 minutes. As before with the work of Wegman [81], these catalysts did not require the use of a halide co-catalyst.

At the same time as Volkova et al. [241], Sardesai et al. [242] used metalsubstituted 12-tungstophosphoric acid as well, specifically using metals from group VIII of the periodic table (Rh, Ru, Ir). DME carbonylation was conducted at 225°C and atmospheric pressure with a CO/DME ratio of 3. SiO₂ was used as a catalyst support. In all cases, the catalysts did not show strong activity, with less than 10% conversion of DME (similar to Wegman [81]). Rh was found to give the highest peak selectivity to MeOAc at nearly 90%, but this was only at about 1 hour of reaction. By 5 hours of reaction, the selectivity had decreased to less than 40%. Ir provided more stable selectivity, around 70% for 7 hours of reaction, but was decreasing with increasing reaction time. Ru gave very low selectivity to MeOAc and very low activity, and was considered not suitable for use as a catalyst in this scenario.

As these few studies show, there is very little research outside of zeolites for use in vapour phase DME carbonylation. A more in depth study of the use of heteropoly acids for this reaction is required at higher pressures and longer reaction times, as the work of Volkova et al. [241] did show some promise.

2.4 Similar uses of ion-exchanged Cu on MOR

Cu-loaded MOR has received some attention by BP Chemicals Ltd. as well as other research groups [92,223,232], but this is certainly not the first use of a Cu-loaded MOR. Cu on MOR has, in the past, attracted attention as a deNO_x catalyst [243–248], though this is a somewhat different application from the topics discussed in the present thesis. More applicable is the use of a Cu-loaded MOR catalyst for the selective partial oxidation of methane to methanol. One of the first reports of using Cu/MOR for this application was by

Groothaert et al. [249]. In this first report, methane was adsorbed at 175°C and, using a water/acetonitrile mixture, methanol was desorbed. When pure He was used for desorption at higher temperature, only CO_2 was detected. It was theorized based on UV-vis spectra that a bis(μ -oxo)dicopper core was responsible for the primary activation of CH₄. It was also found that the best activity occurred in a select range of Cu loadings (0.2 < Cu/Al < 0.3). At the time, Groothaert et al. [249] also tested Cu-exchanged zeolite Y, ZSM-5, and amorphous silica. Cu-loaded MOR and ZSM-5 were, by a wide margin, the best. Groothaert et al. [249] also tested the interaction with ethane of Cu-ZSM-5 with the water/acetonitrile extraction, yielding both ethanol and acetaldehyde.

Methane-to-methanol over Cu-mordenite attracted attention again seven years after the initial report by Groothaert et al. [249]. Alayon et al. [250] synthesized Cu/MOR by ionexchange and again found evidence for the characteristic dicopper active site that Groothaert et al. [249] had reported on. The Cu/MOR was reacted with methane at 200°C followed by extraction of methanol by stirring the CH₄-adsorbed Cu/MOR catalyst with water at room temperature. The formed methanol could not be desorbed by heating in He, indicating that the intermediate that is formed on the dicopper species is very strongly bound. Alayon et al. [251] later did more work on determining the intermediate species formed between CH₄ and the Cu species. This time they did not remove the Cu/MOR catalyst with CH₄ adsorbed from the packed bed reactor, and instead exposed it to wet helium at room temperature to form the methanol. It was observed during the reaction that >60% of Cu^{2+} on the MOR does reduce to Cu^{+} with methane chemisorption at 200°C, but upon interaction with the wet He only some of the Cu⁺ sites were re-oxidized. The XANES spectrum remained quite similar between methane interaction and interaction with water, which was used as evidence that most of the intermediates formed were not desorbed. This was used as an explanation for the 3-5 hours it took for 0.7 g of Cu/MOR to desorb the entirety of the methanol formed. In further publications, Alayon et al. [252,253] identified that, in addition to the bis(μ -oxo) dicopper species, mono(μ -oxo) dicopper species and other Cu²⁺ species could also activate methane.

Still with methane-to-methanol, it was proposed that there was another Cu-state that was responsible for the reaction. Again using a plug flow reactor, Grundner et al. [169,254] exposed Cu/MOR to methane at 200°C, followed by a decrease in temperature to 135°C at which point steam was passed over the catalyst to produce methanol. Grundner et al. [169,254] observed that the amount of methanol produced seemed to be directly related to a Cu active centre consisting of 3 Cu atoms, or an active site with the formula $[Cu_3(\mu-O)_3]^{2+}$, which they supported with DFT calculations of possible Cu states. It was also found that the catalyst could be regenerated in O₂ at 500°C and used again with no decrease in activity. This was shown to be true even after regenerating the catalyst eight times. The active site is still open to interpretation, though. In a recent publication, Tomkins et al. [255] found that activation of Cu/MOR at high temperature (calcination) was not necessary if higher pressures of CH₄ were used in the adsorption stage. Adsorption of CH₄ and exposure to steam to produce methanol were both conducted at 200°C. At these conditions, no spectroscopic signal was observed for a dicopper site. Instead, small Cu clusters were assumed to be the active species.

It would appear that at this point in time, the methane-to-methanol process using Cu/MOR is not yet ready for industrial implementation, nor has there been much work on development of a continuous process by which it could be done using this catalyst.

In a similar application, Zhang et al. [256] tested Cu-exchanged mordenite for use in the oxidative carbonylation of methanol to dimethyl carbonate. While CO does preferentially adsorb on Cu⁺, it was found that CH₃OH could adsorb in competition with it, especially when using Cu on zeolite Y. When CH₃OH and CO were adsorbed on Cu/MOR or Cu/ZSM-5, it seemed that CO and CH₃OH were co-adsorbed on Cu⁺ cations. The reaction was performed at 130°C using a mixture of CO/O₂/CH₃OH. Cu/MOR was not found to be highly selective to formation of dimethyl carbonate, reaching only about 35% selectivity. The reaction over Cu/MOR also produced dimethoxymethane and methyl formate. Cu on zeolite Y was found to give much better selectivity to dimethyl carbonate. It is to be noted that these catalysts were not made by liquid-based ion-exchange, instead being made by solid-state ion-exchange.

In a hybrid catalyst configuration, Cu/MOR can be used together with a Pd/CeO₂ catalyst to produce acetic acid directly from methanol in the vapour phase with no additional halide [257]. In this application, the Pd/CeO₂ catalyst is responsible for the decomposition of methanol while the Cu/MOR is used for carbonylation. The CO necessary for carbonylation is generated in situ by the incomplete decomposition of methanol. Reactions were performed at 300°C using only MeOH in inert Ar as feed. When the Pd/CeO₂ catalyst was placed before the Cu/MOR catalyst (in a stacked reactor bed configuration), acetic acid was produced with >90% selectivity with the only other product being methyl acetate. When physically mixed, the amount of acetic acid and methyl acetate produced was substantially less.

2.5 Prevention of coking on zeolites

While it has been explained that zeolites can be very useful in catalysis, the main disadvantage is their quick deactivation. In most of the processes zeolites are used in, the deactivation is due, for the most part, to the trapping of heavier organic compounds (coke) in the micropores. These are usually a result of secondary reactions or feed impurities [258]. The coke either poisons the active sites directly or can just block access to them by clogging the pores and channels of the zeolite. Coke removal typically involves oxidative treatment at high temperatures, and even though zeolites are typically very thermally stable, there's usually a negative effect of the coke removal. The negative effects may take the form of dealumination or degradation of the zeolite, but may also involve sintering of any supported metals that are present [234]. In the present discussion, the main deactivation mechanism by which acidic MOR is rendered inactive in DME carbonylation is considered to be coking. The various means by which coke may form on zeolites are shown in Figure 2.16.





Characterization of the coke that forms on zeolites is considered fundamental to fully understanding how to prevent its formation. There has been considerable research by some groups in the world on the best procedures to follow for fully characterizing the coke that forms. This is considered to be out of scope of the current project. Interested readers who want more details are referred to the work of Guisnet et al. [234]. It is to be understood

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that successful characterization of the coke that forms is a difficult task. Soluble coke, or coke that dissolves in HF or CH_2Cl_2 , can be characterized using GC or MS relatively simply. The coke that is left behind after these treatments is called the insoluble coke, and is thought to consist mostly of highly polyaromatic species. It is acknowledged by Guisnet et al. [234] that successful characterization of the insoluble coke is typically impossible. The best that can be hoped for in this situation is incomplete information on the elemental composition.

More applicable to the present work, there are a few different parameters that will influence the rate of coke formation on zeolites in catalysis. Coke is formed from species that do not easily desorb from the zeolite, and a fundamental step in coke formation is their retention within the pores of the zeolite or on the crystal surface. Coke molecules may be unable to leave the zeolite due to steric restrictions, chemisorption on active sites, or their low volatility (for gas phase reactions) [234]. The rate of coke formation is determined by three factors:

- 1. General reaction features, which includes the reactant characteristics (size and shape) and the type of reactor used,
- 2. Operating conditions, such as pressure and temperature, and
- 3. The catalyst used, which includes such characteristics as the strength, number, and location of active sites and the size and shape of the pores, channels, and other openings.

Thus, there may not be one simple solution for limiting the rate of coke formation. To properly inhibit the rate of coke formation, these three factors all need to be optimized.

As indicated in Figure 2.16, alkenes, dienes, and polyaromatics are typical coke maker hydrocarbons on zeolite catalysts. These molecules undergo quick condensation reactions and form heavy and polar products. Polyaromatics are not as reactive, but due to their size and polarity they are often strongly retained on acid zeolites. To limit coke formation, it is best to simply run the reaction at conditions that will favour desorption of coke precursors and prevent them from forming into larger coke molecules [259]. Another way to limit coke formation is to operate with a substantial amount of hydrogen in the feed. Coke formation can occur from non-substituted monoaromatics, alkanes, and naphthenes, which may transform into alkenes and polyaromatics. Hydrogen can prevent these species from being transformed and allows them to be desorbed [234]. This is the primary method employed by BP Chemicals Ltd. to limit coke formation on MOR in DME carbonylation [230]. Temperature will have a large effect on the rate of coke formation. It is not necessarily true that lower temperatures will prevent coke formation. Lower temperatures will mean that adsorbed species may not desorb as quickly (or at all). This gives these species a longer period of time in which they may react (or over react) and form coke. Temperature must be optimized for each situation. It is widely accepted that the reaction temperature strongly influences the composition of the coke, and as a result coke may be classified into low temperature (≤200°C) and high temperature (>350°C) cokes [260]. Low temperature coke typically consists of olefins and alkanes, formed by alkylation and cracking reactions. High temperature coke usually consists of polyaromatic species. Low temperature coke simply does not have enough energy to desorb, while the high temperature coke is usually trapped in the microporous framework of the zeolite [261].

Several characteristics of the zeolite used for catalysis will influence the rate of coke formation and the type of coke formed. The concentration, strength, and proximity of acid sites and the size and shape of channels and intersections all have an influence on coke formation. While each situation is different and acidity varies among zeolites, there are some general guidelines. The stronger the acid sites of the zeolite, the more guickly the reactions occur, and the coke is formed faster and is chemisorbed more strongly. If acid sites are highly dense and the distance between them is small, successive reactions can occur by reactant molecules along the channels and coke is more likely to form more quickly [234]. This is summarized in Figure 2.17. The effect of pore structure is a little more difficult to develop a general rule for regarding coke formation. It may be simplest to approach this issue from a diffusion perspective. If reactants are placed in a scenario where they are trapped or they diffuse slowly, this increases the residence time within the zeolite framework and increases the opportunities for other chemical reactions and subsequent coke formation. However, this does not necessarily mean that a small pore size is bad. Smaller pore sizes will restrict the intermediate species that can form, and may limit the number of species formed that will lead to the development of coke.



Figure 2.17. The effect of zeolite acidity on the formation of coke.¹⁸

Thus, a general set of rules can be put together for the selection of a zeolite for a reaction that will have the lowest rate of coke formation possible, shown in Figure 2.18. Unfortunately this is a highly experimental process, and it could potentially take years to find the best combination of zeolite attributes and reaction conditions for a certain reaction.



Figure 2.18. General guidelines for reducing coke formation on zeolites.¹⁹

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In the context of the current work, diffusion of reactants in mordenite is unidirectional in a reaction. Deactivation of MOR is nearly always due to pore blockage by coke molecules, and as diffusion is unidirectional, it may be possible that one coke molecule in a large channel of MOR may be enough to block the active sites of that entire channel. While the active sites themselves may still be available for reaction, there is no way for the reactants to get to them and then leave the crystal, and thus the catalyst appears to be deactivated [234]. The heterogeneous distribution of acid sites on MOR doesn't help things either. This was mentioned above in the work of Bhan et al. [212] and Boronat et al. [215,216], where it was suggested that the active sites in the 12-MR behaved completely differently from the active sites in the 8-MR. To enhance the stability of MOR for DME carbonylation is therefore a very tricky process. Something must be done to the acid sites in the 12-MR without compromising the ability of the active sites in the 8-MR to catalyze the reaction. Given that there is considerable evidence showing that the next nearest neighbours of an Al site have an influence on the acidity of the Al site [141–143], a highly experimental approach is required that, unfortunately, consists of trial and error to find a way to stabilize MOR in an effective yet simple way.

2.6 Summary

Ever since zeolites began to be synthesized by man, they have had a strong presence in catalysis. For example, zeolites X and Y, some of the first zeolites to be synthesized, have completely changed how fluid catalytic cracking is conducted [93]. Since that time, zeolites have slowly spread into several other applications and the number of "zeotypes", materials with a zeolitic framework but do not fall into the aluminosilicate category, have increased. Recently zeolites have found considerable use in the upgrading of syngas and its substituents. The zeolite mordenite, which is available commercially, has been identified as highly active and selective for the carbonylation of dimethyl ether to methyl acetate. However, acidic mordenite (or mordenite in its protonic form) typically lasts between 10 and 20 hours for DME carbonylation when performed only in the presence of DME and CO. The deactivation mechanism is attributed to excessive formation of heavier organic compounds, or coke, in the pores and channels of mordenite, blocking access for the reactants to the active sites.

Since the original discovery of the use of mordenite for this reaction, considerable work has been conducted around understanding and stabilizing it. It was identified that only those acid sites in the 8-MR of mordenite were selective for DME carbonylation to MeOAc. Acid sites in the 12-MR have been hypothesized to only lead to formation of coke

or other by-products. As the 12-MR of mordenite provides less steric restrictions to the diffusion of reactants to the active sites (through the 8-MR side pockets), coking in the 12-MR will block most of the access to the acid sites in the 8-MR.

Armed with this knowledge, several groups have attempted to poison, block, or otherwise remove those acid sites in the 12-MR and leave the 8-MR intact. Some of these attempts have failed to substantially enhance the stability of mordenite. Selective dealumination of the 12-MR, by both BP Chemicals Ltd. and Xue et al. [235], did not significantly enhance the stability [229,235]. Blocking the acid sites in the 12-MR seemed to enhance stability, but the activity was significantly (and understandably) lower with the blockage [236]. Ion-exchange of Cu onto MOR showed some stability enhancement and stabilization of the selectivity, but catalyst deactivation was still rapid [92]. BP Chemicals Ltd. has found greater success with adding substantial amounts of H₂ to the feed and operating at higher temperatures [230]. However, the purpose of the H₂ is strictly to clean the mordenite and prevent excessive formation of coke, and is not necessary for DME carbonylation. Many of the methods which did show some enhancement to the stability of mordenite were simply too complicated (or too expensive) to scale up to an industrial scale.

Unfortunately stabilizing a zeolite for use in a reaction is a challenging task, due quite simply to the many degrees of freedom that are available. Alternatives to mordenite could be used, but unfortunately even members in the same family of zeolites may behave very differently with changes in their Si/Al ratios. To that end, the Si/Al ratio of mordenite itself could be optimized by synthesizing several mordenites with different Al contents and testing each in reaction. However, usually the intent is to use what is commercially available and simply find a way to make it better (post-synthesis enhancement). For example, ion-exchange of nearly any transition metal could be conducted. The metal Cu was originally selected for its ability to activate CO in its monovalent state, and under the right conditions it did show an enhancement to the activity of mordenite. It did not help with maintaining stability though, and from that regard many other metals could be ion-exchanged and tested. Dealumination procedures have been limited to steaming. Dealumination via acid leaching has not been explored yet with regards to DME carbonylation over mordenite.

While many publications will be singing praises about zeolite catalysts, they are not the solution to every problem and there are incredibly few scenarios where the acidic zeolite with no alteration will be inherently stable and do what the researcher wants it to do. While many advanced techniques exist to enhance zeolites, the focus of this thesis is on those techniques which may be applied simply and are easy to scale up for industrial production of MeOAc from DME and CO. The main objective of this work was to enhance the stability, but this is not the only aspect of the catalysts that should be considered. Zeolite deactivation has been known since they were first used in catalysis, and it is already known how to deal with it. Regeneration of zeolite catalysts is dealt with periodically by thermal techniques with hydrogen or oxidative gases. While one catalyst bed is regenerated, usually another is used so that production does not stop. The lifetime extension of catalysts is important for making these regeneration treatments less frequent and having greater overall production, but from the viewpoint of green chemistry and avoiding expensive separations, it may be more important to maintain high selectivity during the catalyst's entire lifetime rather than just at peak activity. The process then does not need to be run differently at different times, and makes its operation easier and far more flexible.

Chapter 3

Catalyst Characterization Procedures

It is a capital mistake to theorize before one has data. Insensibly one begins to twist facts to suit theories rather than theories to suit facts.

--Sherlock Holmes

3.1 Introduction to catalyst characterization

In catalysis research, finding a catalyst that performs well for a particular reaction is only the first step. In early catalyst research (prior to approximately 1950s and 60s) this may have been the only step [262]. Even today, this is sometimes the only step. So long as the catalyst worked and could be suitably applied at an industrial level, it did not necessarily matter how it worked. It wasn't that early researchers did not want to understand how the catalysts worked; it was more because the tools either did not exist for gathering data or they were inaccessible and otherwise expensive. Since the 1950s and 60s, catalyst characterization techniques have seen remarkable development. Several factors are responsible for this growth [262,263]:

- While initial catalysts performed adequately and could be implemented in early industrial processes, they were not optimized. To optimize already operating processes properly, decrease costs and minimize waste, it became necessary to better understand the catalyst;
- The rise of new materials that were not so simple to understand and apply, such as zeolites or other highly porous materials; and

 The advancement of technology and computers that allowed for more powerful and user-friendly versions of known techniques and the development of new characterization techniques.

Nowadays, catalyst engineers have a great many characterizations they can choose from in order to better understand the material they are working with. In many instances now, the bulk of the work is not in finding a catalyst and testing it in the actual reaction. Especially with zeolites, a great deal of time must be spent characterizing the catalyst so as to develop a reasonable theory on how the catalyst works. It is important to note that the way in which a catalyst works is always a theory and should not be accepted as fact. Data from characterizations, even those done *in situ* at reaction conditions, is always open to interpretation.

3.2 Types of characterizations

There are a few different general areas of science in which the different characterizations fall. These will be introduced only briefly. All catalyst characterization techniques can be derived from a handful of sources, shown in Figure 3.1.



Figure 3.1. Sources of nearly all catalyst characterization techniques used today. Inward arrows show the excitation processes while the outward arrows show how the information should be gathered.²⁰

²⁰ I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, p. 130, 2003, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Adsorption of probe molecules is a technique used quite often on any kind of catalyst. As the first step of a reaction occurring over a catalyst is adsorption, it is important to understand how a molecule adsorbs onto the catalyst surface and its subsequent desorption. At a purely macroscopic level, probe molecules may be adsorbed onto the catalyst (at a variety of temperatures) and then desorbed using elevated temperature. For simplicity, the temperature is usually increased at a fixed rate but may also be increased stepwise. This is collectively referred to as temperature programmed desorption (TPD) and can give a variety of information. More strongly bound species will require more energy to desorb from the catalyst surface. Therefore, the required temperature for desorption is usually used as a gage of the acid strength of the catalyst. The higher the desorption temperature, the stronger the acidity [264]. With proper instrument calibration, it is also possible to determine the number of probe molecules adsorbed and determine the number of sites available for reaction. In the case of nanoparticles, this can also be used as an estimation of the nanoparticle size. TPD must typically be performed in the presence of an inert gas so as to ensure there is no interaction between the gas and the adsorbed probe molecules. However, the limitation of this technique is differentiating between the probe molecules that are physisorbed and those that are chemisorbed [262,265,266]. Only those molecules that are chemisorbed should be used when determining nanoparticle size and acid strength. To ensure only chemisorption occurs, pulsing the adsorbent in at small, controlled amounts and observing the amounts of adsorption with each pulse is sometimes used. Even when using pulse chemisorption, differentiation between physisorption and chemisorption can be difficult for some materials.

The increase of temperature (whether a steady or stepwise increase) in the presence of a reducing gas is called temperature programmed reduction, or TPR. In this instance, freshly synthesized catalyst (possibly calcined) is heated in the presence of a reducing agent, often H_2 . Based on the H_2 that is consumed, it is possible to determine at what temperature the metals present will reduce to a lower oxidation state. This is important as certain oxidation states of metals may be more active for the reaction of interest [267].

Another temperature programmed technique is temperature programmed oxidation, or TPO. This involves the heating of a catalyst (typically used) to high temperature in the presence of an oxidizing gas, usually O_2 . This technique is often used in determining the types of coke that have formed on a catalyst [262,268].

Physisorption is still a quite useful technique, and can be used as a means to determining the catalyst morphology. When used with N_2 or Ar and conducted at their

respective boiling points, it gives information on the total surface area, as well as pore size and volume. With the proper data, it can differentiate between the micropores, mesopores, and macropores. As for when to use N_2 or Ar for physisorption, it is better to use Ar when studying micropores as it is less interactive than N_2 [262,269]. The difficulty in processing the data here lies in differentiating between monolayer and multilayer adsorption. The BET surface area assumes multilayer adsorption while the calculation of Langmuir surface area assumes monolayer adsorption.

Adsorption/desorption and their substituents by themselves may be described as macroscopic techniques, meaning that they do not yield much information regarding the state of the metals present or how they are bound together. To obtain this information, one often has to turn to spectroscopic techniques. There is a great variety of spectroscopic techniques available. Quite generally, spectroscopic techniques allow for the determination of local and structural characteristics. Local characteristics include such information as oxidation state, ligands nature and number, and symmetry. Structural characteristics include the type of framework, degree of crystallinity and the crystal size [262]. While no single spectroscopic technique can give all this information, when using several together a picture of the catalyst structure can be painted.

One of the simplest spectroscopic techniques is x-ray diffraction (XRD), which gives information about the framework. In XRD, crystalline atoms cause an incident beam of X-ray photons to scatter. The scattered X-rays that are in phase give constructive interference which produces a measurable diffraction line. By measuring both the angle and intensity of this constructive interference, the position of atoms in the crystal structure can be ascertained and consequently the crystalline phases and size. To some extent, the chemical bonds can also be determined. Using the Bragg relation, the lattice spacing can be determined [262,267]. XRD is a very common technique (especially in zeolites) as it is relatively cheap and easy to do. XRD is limited in that it cannot detect particles that are too small nor can it give any information about the amorphous phases.

Another very common technique is infrared (IR) spectroscopy. This uses IR light in the frequency range 400 to 4000 cm⁻¹ to obtain information about the chemical bonds in a catalyst. IR spectroscopy is based on the phenomenon that molecules in the catalyst will absorb specific frequencies that are characteristic of their structure, known as resonant frequencies. However, to be viewable by IR the mode of vibration or rotation of the molecule has to produce a variation in the dipole moment. The IR radiation when at the correct energy is capable of altering the speed of vibration or rotation of the molecule and is absorbed [267,270]. The absorbance of light can be measured, and from calibration using appropriate molecules and measured frequencies the bonding structure can be determined. For heterogeneous catalysis, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is typically used. While IR spectroscopy is usually qualitative, it is possible in some scenarios to quantify the data. IR spectroscopy is usually not performed on the material by itself. A probe molecule, such as CO, NO, NH₃, or pyridine, can be adsorbed. IR spectroscopy can then be used to determine how the probe molecule is adsorbed, can differentiate between different types of acid sites, and can yield information about how molecules may interact with the catalyst in a reaction environment [262,268]. For this reason, *in situ* IR spectroscopy is becoming increasingly common as the reaction environment can be more accurately reproduced. IR spectroscopy of samples with pyridine chemisorbed is particularly useful, as pyridine chemisorbs differently to the different kinds of acid sites. On a Brønsted acid centre, pyridine chemisorbs as a pyridinium ion through a hydrogen bond, shown in Equation 3.1 [271], and produces a distinct IR signal at ~1540 cm⁻¹.

$$\begin{array}{ccc} OH & O^{-} \cdots H^{+} NC_{5}H_{5} \\ \downarrow \\ AI + py & \longrightarrow & AI \end{array}$$
(3.1)

On a Lewis acid centre, the pyridine chemisorbs by a coordinative acid-base interaction and produces a unique IR signal at ~1465 cm⁻¹. This is shown in Equation 3.2 [271]. In an ideal case, with proper calibration the ratio between the number of Lewis and Brønsted acid centres can be determined from the IR signal peak areas.

$$AI^{3+} + py \longrightarrow AI^{3+} - NC_5H_5$$
(3.2)

X-ray photoelectron spectroscopy (XPS) is typically used to measure the elemental composition, chemical state, and electronic state of the elements of a catalyst, though it must be recalled that it is a surface-sensitive technique and can only measure to about 10 nm below the surface of the material. In XPS, the sample is bombarded with a beam of X-rays (photons). The incident X-rays transfer energy to the elements in the sample, and cause the elements in the catalyst to emit electrons. These are called photoelectrons. The intensities of the photoelectrons are measured which are a function of their kinetic energy.

From the incident X-ray energy and kinetic energy, along with the work function of the spectrometer, the binding energy of the photoelectron can be measured. Binding energies are unique in that they are specific to each element and its oxidation state and electronegativity [267,272]. Since the mean free path of electrons in metals is on the level of nanometers, XPS must be performed in a vacuum. XPS can be both a qualitative and quantitative technique. If performed properly, it can give an accurate picture of the surface of a catalyst. As catalysis occurs at the surface, this is highly valuable information.

Ultraviolet-visible (UV-Vis) spectroscopy is much like IR spectroscopy but is performed using ultraviolet light. The spectral range is usually 10000 – 50000 cm⁻¹, which is the range required to possibly investigate d-d transitions. This can be especially useful for the study of the transition elements. Using UV-Vis spectroscopy, information about the electronic structure and the first coordination sphere of the examined ions can be directly determined, specifically the oxidation state, types of ligands and coordination. The disadvantage to this technique is that it is often difficult to interpret the spectra, and broad bands are often yielded that cover a large spectra region. It is possible to get quantitative data from UV-Vis spectroscopy, though this requires considerable time and effort [262].

Another perhaps less commonly used spectroscopic technique is nuclear magnetic resonance (NMR). As its name implies, NMR spectroscopy uses the magnetic properties of nuclei to determine such information as structure, dynamics, reaction state, and chemical environment of molecules. NMR exploits the spin state of atomic nuclei to gain information. When a nucleus with a spin (some nuclei do not have spin) is placed in a magnetic field, it can either align itself with the field in a lower energy state or align itself against the field in a higher energy state. In NMR that uses radio waves, nuclei in the low energy state can absorb energy from the radio waves and jump to the higher energy state. The absorption of energy or the release of energy as the nucleus falls back to its lower energy state can be observed and measured in NMR. In a molecule, the magnetic field felt by a specific nucleus includes the applied field and also the effect of nearby nuclei and electrons. The signal from the radio waves therefore absorbs at a slightly different frequency and depends on the environment around the atom. With proper calibration, the environment and bonding of the element of interest can be determined [273]. For NMR with solid powders, the magic-angle spinning (MAS) technique is often employed. The sample is spun at a certain angle relative to the direction of the magnetic field, which allows for much higher resolution and better identification and analysis of the spectrum [274,275].

In addition to adsorption/desorption and spectroscopic techniques, microscopy techniques are also available. This is another macroscopic technique in that it does not necessarily give information about chemical bonding. Instead, these techniques give morphological information, such as particle size and shape. The discussion on microscopy here will be limited to electron microscopy, specifically transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In electron microscopy, a primary electron beam is focused on the sample. The electrons that make it through the sample, or the transmitted electrons, produce an image on the detector (TEM). SEM is based on measuring the secondary and/or backscattered electrons. Secondary electrons have lost energy due to consecutive inelastic collisions. Backscattered electrons are electrons that have collided with atoms in the sample and simply scattered back [267]. These different types of electrons produced upon interaction with the sample are shown in Figure 3.2. TEM can yield usually around 0.5 nm resolution while SEM can give a resolution of 5 nm. The biggest difference between TEM and SEM is that SEM can see contrast due to the topology and composition of the surface. TEM can only produce a 2-dimensional image [267].





Also shown in Figure 3.2 was that the primary electron beam may also produce xrays upon contact with the sample. The primary electron beam causes electrons to be ejected from the atoms. The resultant vacancy is filled by electrons from a higher state,

²¹ I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, p. 144, 2003, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

which causes an x-ray to be emitted as a means of balancing the energy difference between the two states. This x-ray is characteristic of the element from which it came. By measuring these x-rays, the composition of the sample can be determined. This is called energy dispersive x-ray spectroscopy (EDX) [267,272]. SEM and TEM instruments may be equipped with an EDX spectrometer with the proper x-ray detector.

There are many other characterizations that may be used in heterogeneous catalysis. What has been so far discussed is most relevant to the results yet to be presented in this thesis and is only intended to provide a very brief background on the science behind the techniques. The quality of characterization data is strongly dependent on the equipment used, not to mention the abilities of the user of the equipment. It is also not always possible to perform all characterizations. NMR, for example, requires very expensive equipment and is a very expensive characterization to perform. Other examples include extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) which require a synchrotron. In other cases, so long as the equipment is available, the characterizations are relatively cheap to run. Such characterizations include XRD, adsorption/desorption, physisorption, and DRIFTS. Often times it may be the case that if enough other, more cost-effective, characterizations are performed, it is not required to use the more advanced and expensive techniques. Regardless, one characterization by itself is not enough to explain how the catalyst does what it does. A variety of techniques with results combined is the only means by which a proper theory of how the catalyst works can be developed. And so, in modern catalysis research, finding a catalyst that works for the reaction is only the beginning.

3.3 Catalyst testing procedures

In this section, the procedures used for testing the catalyst in the carbonylation reaction as well as the characterization procedures will be discussed in detail. Catalyst synthesis procedures is discussed in the appropriate chapters of this thesis. Any deviation from the described procedures is also mentioned in the appropriate chapter.

3.3.1 DME carbonylation conditions

The carbonylation of DME to MeOAc was carried out using a Micromeritics Autochem 2950 HP equipped with a Pfeiffer Vacuum Thermostar GSD 320 mass spectrometer for analysis of the effluent gas. Prior to being placed in the Autochem, the synthesized catalysts were stored in an oven maintained at a temperature of 60°C for a period of time

no less than 12 hours. The catalyst was only removed from the oven immediately before being placed into the reactor. Usually 0.3 g of catalyst was loaded into a stainless steel Utube reactor with quartz wool placed on both sides of the catalyst, forming the bed. When packed, the 0.3 g of catalyst formed a layer covering the entirety of the inside tube diameter. The selection of 0.3 g of catalyst was specifically to avoid by passing of the reaction gas around the catalyst bed. After the catalyst was loaded into the U-tube reactor, the reactor was mounted into the Autochem. The tube was flushed with helium (He, 99.999% purity, Praxair) to remove any air present. The entire system was then tested for leaks using high pressure He (>200 psi) by blocking the effluent gas line. The system was determined to be leak proof when gas flow as measured by the mass flowmeter decreased to 0 mL/min. The system was then depressurized and the calcination procedure started. The gas flow was switched to $10\% O_2/He$ (Praxair) and the sample heated to $110^{\circ}C$ at a rate of 10°C/min. The catalyst was maintained at this temperature for a period of 3 hours before being heated to 350°C at the same heating rate. The catalyst was held at this temperature for 1.5 hours. Finally, the catalyst was heated to 550°C at the same heating rate where it was maintained for a period of 3 hours. This stepwise calcination procedure was used so as to avoid damage to MOR from adsorbed water and excessive heating rates.

The catalyst preparation procedure could now proceed in one of two ways. If the sample had ion-exchanged metals present, specifically Cu^{2+} and/or Zn^{2+} , the catalyst was reduced using a 10% H₂/Ar (Praxair) mixture. After spending 3 hours at 550°C in 10% O₂/He, the temperature of the catalyst bed was decreased to 300°C. When this temperature was reached, the active flow through the sample was switched to pure He for 15 minutes. This was done in order to flush out remaining O₂ that was present in the system from the calcination. After this time, a flow of 10% H₂/Ar was directed through the sample and the temperature increased to 325°C. The temperature selected was based on the results of TPR, which will be presented in Chapter 4. The catalyst was maintained at these conditions for a period of 2 hours. After the reduction, the active flow through the sample was switched to He and the temperature decreased to ambient conditions. The catalyst was kept under a low flow of He until the time of reaction.

If the sample had no ion-exchanged metal present, the catalyst temperature was decreased from 550°C to 300°C at which point the active gas flow through the sample was switched to pure He. The temperature was then further reduced to ambient conditions. The catalyst was maintained under a low He flow until the time of reaction.

The mass spectrometer was calibrated daily for DME, CO, H₂, and He. Helium was used as an internal standard and was not intended for any other purpose. It is acknowledged here that, as the DME carbonylation reaction is exothermic, the He may have served to remove excess heat from the catalyst bed (heat transfer medium). Calibration for MeOAc and MeOH was typically performed once a month or after the mass spectrometer had been switched off. The MeOAc mixture used for calibration consisted of 2.5% MeOAc/53% Ar/44.5% He (certified standard, Praxair). The MeOH mixture used for calibration consisted of 1% MeOH/54.5% Ar/44.5% He (certified standard, Praxair). Only masses in the mass spectrometer that were unique to each species were used for conversion of the raw ion signal to molar fractions. For MeOAc and MeOH, peaks 74 and 32 were used respectively. For DME, CO, H₂ and He, calibration was performed using the reaction gas mixture itself and peaks 46, 12, 2, and 4 respectively.

Carbonylation reactions were performed using a gas mixture of 50.0% CO/2.4% DME/2.9% H₂/44.7% He (certified standard, Praxair). The presence of H₂ in the mixture was only intended to more accurately replicate the industrial conditions present in a plant that produces syngas from biomass gasification. It is often not practical to completely separate the CO and H₂ in the syngas. It is to be noted here that, due to equipment limitations, no higher than 2.5% DME could be used in the reaction gas mixture. In the event of complete conversion of DME to MeOAc, there would be ~2.5% MeOAc in the effluent gas stream. While most of the lines in the Autochem 2950 HP are heated and insulated, there is one line present before the backpressure controller that is not heated and not insulated and decreases to ambient temperature before the pressure is released. The possibility existed that, at the higher pressure used for reaction, some MeOAc could condense in the lines, affecting the performance of the Autochem and potentially damaging the backpressure controller. As Cheung et al. [90] had theorized that the reaction was first order to CO, a higher amount of CO was desired in the reaction gas. Thus, a CO:DME ratio of ~20 was selected.

Before reaction, the reaction gas mixture was directed to bypass the sample and go directly to the mass spectrometer. A stair scan was started on the mass spectrometer and the signals were allowed to stabilize for a period of one hour before starting the reaction. While the mass spectrometer signals were stabilizing, the catalyst was heated to the reaction temperature of 210°C at 10°C/min under a low flow of He and allowed to stabilize. After the mass spectrometer and temperature of the sample had stabilized, the reaction gas mixture was directed to flow through the sample. After switching the active gas flow the
reactor was immediately pressurized to a total reaction pressure of 20 bar using a 100 mL/min flow rate of the reaction gas mixture. After the pressure was met, the flow rate was immediately decreased to 15 mL/min STP and stabilized. The reactions were run until conversion of DME was <15% at which point the catalyst was assumed to be deactivated and the reaction was terminated by releasing the pressure, decreasing temperature, and stopping flow of reaction gas. The sample tube and system was further flushed using pure He to remove the excess CO, H₂, and DME.

External mass transfer limitations were tested for at these conditions and it was determined that there were none (a further reaction was performed using 0.4 g and 20 mL/min). Internal mass transfer limitations were also tested for. The size of the received MOR crystals was ~5 μ m. A sample of MOR was ground over a period of 72 hours in a planetary mill after which the crystal size was ~1 μ m (determined by SEM). This ground sample was then used at identical reaction conditions (0.3 g). The results were identical with that of the received size, indicating that at the reaction conditions there were no internal mass transfer limitations.

The flow rate of 15 mL/min STP was quite low, and the gas flow was in the laminar flow regime. Given the estimated catalyst particle size d(p) of 5 µm, typical bed length L(b) of 0.38 cm and reactor inner diameter d(t) of 0.7 cm, ideal plug flow can be assumed with d(t)/d(p) = 1400 (wall effects on flow pattern can be neglected) and L(b)/d(p) = 735 (negligible axial dispersion). Ideal plug flow is achieved when d(t)/d(p) > 10 and L(b)/d(p) > 50 [276]. The used inert-exclusive gas hourly space velocity (GHSV) was 3500 h⁻¹. The inert-exclusive weight hourly space velocity (WHSV) was 2.1 h⁻¹. The GHSV was selected to be similar to the reported values by BP Chemicals Ltd. [223,228,230] (~4000 h⁻¹), so that the obtained research results may be compared. Other groups used either higher (~25000 h⁻¹) [212] or lower GHSVs [233].

Due to safety concerns, the reactor exhaust was combusted to CO_2 using ultra-dry air (Praxair) over a pelletized 1 wt.% Pt/Al₂O₃ catalyst (Sigma-Aldrich) in a packed bed reactor heated to 250°C before being vented. The flow rate of ultra-dry air was typically 200 mL/min and mixed with the reaction gas effluent before the Pt/Al₂O₃ catalyst. At these conditions, <2 ppm CO was detected after CO combustion and the exhaust was vented into the fumehood. The conversion of DME was calculated based on the molar fraction of total DME reacted, or:

$$X_{DME} = \frac{F_{DME}^{Inlet} - F_{DME}^{Effluent}}{F_{DME}^{Inlet}}$$
(3.3)

Selectivity to MeOAc and MeOH was calculated based on their molar flow rates in the effluent gas and total DME converted, as well as the assumption that one mole of DME can create two moles of MeOH:

$$S_{MeOAc} = \frac{F_{MeOAc}^{Effluent}}{F_{DME}^{Inlet} - F_{DME}^{Effluent}}$$
(3.4)

$$S_{MeOH} = \frac{F_{MeOH}^{Effluent}}{2(F_{DME}^{Inlet} - F_{DME}^{Effluent})}$$
(3.5)

To account for DME that was not converted to either MeOAc or MeOH, a selectivity to others value was calculated assuming 1:1 molar stoichiometry of DME to the unidentified products. Raw ion profiles from the mass spectrometer were also considered when determining the plausible selectivity to others value.

$$S_{Others} = \frac{F_{DME}^{Inlet} - F_{DME}^{Effluent} - F_{MeOAc}^{Effluent} - 0.5F_{MeOH}^{Effluent}}{F_{DME}^{Inlet} - F_{DME}^{Effluent}}$$
(3.6)

The selectivity to others as defined includes unidentified hydrocarbons, oxygenates, and any formation of heavier carbonaceous compounds that may occur from DME. The mass balance for the reaction was closed to an error of <5% using mass spectrometer data and CHNS analysis of a used catalyst.

During the reaction, the mass spectrometer was set to measure all m/z between 0 and 75 amu. Beyond a mass of 46 amu (due to DME), the only other masses typically detected were 59 and 74 amu, which are both attributable to MeOAc. A mass of 56 amu was sometimes detected at very high conversion and can also be considered to be due to the presence of MeOAc. There was nothing between a mass of 46 and 75 amu to indicate any other product was being formed aside from MeOAc.

It is important to note that a mass peak at 44 amu was present in nearly every reaction, and was also detected in the calibration and reaction gases. Mass peaks at 18 and 17 amu were also detected during reaction and were present in the calibration and reaction gases at well. It is acknowledged here that there may be a water-gas shift occurring as well as some impurities present in the gas mixtures. Typically a reaction gas may be passed over a bed of desiccant prior to reaction, but in the present case this was not done as the effect on DME was unknown.

3.3.1.1 Further justification of CO:DME ratio

To justify further the choice of CO:DME ratio, some simple thermodynamic modeling was carried out using VMGSim v8.0. This modeling was based on the use of equilibrium constants at different temperatures. The five reactions modeled were the primary carbonylation of DME to MeOAc shown in Equation 1.1 and the following reactions:

$$CH_3OCH_3 \leftrightarrow CH_3OH + 0.5C_2H_4 \tag{3.7}$$

$$CH_3OCH_3 \leftrightarrow C_2H_4 + H_2O \tag{3.8}$$

$$CH_3OCH_3 \leftrightarrow 0.5CH_4 + CH_3OH + 0.5C \tag{3.9}$$

$$CH_3OH + CO \leftrightarrow CH_3COOH$$
 (3.10)

The equilibrium constants were calculated based on the equation relating Gibb's energy to equilibrium constant K and the shortcut of van't Hoff equation, shown in Equations 3.11 and 3.12 respectively [277].

$$\Delta G^{\circ} = -RTln(K) \tag{3.11}$$

$$ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^{\circ}_R}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
(3.12)

The reactor was simulated as isothermal at 200°C and 1 MPa total pressure. Only CO and DME were considered in the feed – no H_2 was included. The results for the conversion of DME and CO (defined as the fraction converted compared to what was in the original feed) and the predicted molar fractions of products (only compared to the other products that were formed, does not include reactant CO or DME in the reactor effluent) are shown in Figures 3.3 and 3.4 respectively. DME was fully converted to products at all CO:DME ratios while CO conversion was commensurate with the amount of CO in the feed and DME conversion. As shown in Figure 3.4, at nearly all CO:DME molar ratios simulated

the only product detected was MeOAc. Only when the CO:DME molar ratio was lower (~1) did acetic acid become the more favoured product, along with some ethylene and water. This served as sufficient evidence that the molar CO:DME ratio had to be >1 to prevent other side reactions from occurring. Given the theory that the order of reaction with respect to CO is 1 and is effectively 0 for DME [90], having substantially more CO compared to DME is desirable anyways.



Figure 3.3. Predicted conversion of CO and DME from simulation of Equations 3.7–3.10 at 200°C and 1 MPa pressure at different CO:DME ratios.

Figure 3.4. Molar fraction of products from the simulation of Equations 3.7–3.10 at 200°C and 1 MPa pressure at different CO:DME ratios.

In addition to these preliminary models, the effect of temperature was tested with a different reaction feed composition and additional reactions. The feed was changed to 50% CO/2.5% DME/3% H₂/44.5% He (similar to the reaction gas mixture used in experiments) and temperature was varied from 180°C to 300°C. The reactor was again considered to be isothermal and 1 MPa total pressure was used. The primary reaction of DME carbonylation shown in Equation 1.1 was again simulated along with those reactions shown in Equations 3.8 and 3.9. The other reactions added to the simulation were:

$$CH_3OCH_3 + H_2 \leftrightarrow CH_3OH + CH_4$$
(3.13)

$$CH_{3}OH + H_{2} \leftrightarrow CH_{4} + H_{2}O \tag{3.14}$$

$$CH_{3}OCH_{3} + CO + H_{2} \leftrightarrow CH_{3}COOH + CH_{4}$$
(3.15)

Results for calculated selectivities (based on total amount of DME converted) from the simulation results are shown in Figure 3.5 at the different temperatures tested. As shown, only at very high temperature does selectivity towards MeOAc begin to decrease, and even in this case the decrease is very low. The only other product in the reactor effluent is methane, formed at the higher temperatures tested (\geq 240°C).



Figure 3.5. Results from simulation of the reactions shown in Equations 1.1, 3.8, 3.9, 3.13-3.15 at 1 MPa pressure with 50% CO/2.5% DME/3% $H_2/44.5\%$ He feed assuming an isothermal equilibrium reactor operating at different temperatures.

While these were very limited and only initial simulations, the impression from them is that as low a temperature as possible should be used for reaction and the molar amount of CO should be in excess of DME in the reaction feed. These simulations were only based on thermodynamics and equilibrium constants and did not consider reaction kinetics.

3.3.2 Hydrogen TPR

TPR of calcined catalysts was performed using a Micromeritics Autochem II 2920. In a typical TPR characterization, 0.15 g of catalyst was loaded into a quartz tube with quartz wool placed on both sides, forming the catalyst bed. The tube was mounted into the Autochem II and calcined at the conditions given in section 3.3.1. The temperature of the catalyst was decreased to 100°C at which point the gas flow through the catalyst was switched to pure Ar. After flushing the tube with Ar (99.999%, Praxair) for a period of 15 minutes (intended to remove any lingering O_2 from the calcination), gas flow was switched to 10% H₂/Ar at a flow rate of 15 mL/min. The catalyst was maintained under these conditions until a stable TCD signal was established. The catalyst was then heated to 750°C at a rate of 10°C/min with the TCD signal being recorded each second.

3.3.3 Oxygen TPO

TPO of used catalysts was occasionally performed immediately following the reaction. After the catalyst had sufficiently deactivated, the system pressure was decreased to ambient, the active gas flow through the catalyst was changed to pure He, and the temperature was allowed to decrease. When the temperature of the catalyst had reached \sim 80°C, the gas flow through the sample was switched to 20 mL/min of 10% O₂/He. The TCD signal was then allowed to stabilize. At the same time, the mass spectrometer was being purged with a separate flow of 10% O₂/He so as to establish a clean mass spectrometer profile. Once the mass spectrometer was showing a clean gas spectrum and the TCD signal had stabilized, the catalyst was heated to 750°C at a rate of 10°C/min with the TCD signal being recorded each second and the mass spectrometer doing a stair scan of the effluent gas from 0 to 75 amu.

3.3.4 DME adsorption and TPD

To gain a better understanding of how the catalysts interact with one of the reactants, the levels of DME adsorption and desorption were measured using the Autochem HP 2950 and mass spectrometer detailed in Section 3.3.1. The catalyst was loaded into the stainless steel U-tube with quartz wool placed on both sides. In the study detailed in Chapter 4 concerning Cu-Zn ion-exchanged mordenites, 0.2 g of catalyst was used for each test. In the study detailed in Chapter 5 concerning acid-leached dealuminated mordenites, 0.15 g of catalyst was used in each test. This change is due to refinement of the technique between the two studies. In both cases, the MOR catalysts were loaded into the Autochem in their NH₄- form. The catalysts were calcined in situ following the calcination procedure described in Section 3.3.1. In the case of the bimetallic Cu-Zn/H-MOR study detailed in Chapter 4, the catalysts were also reduced. All calcined and/or reduced catalysts were stored under a low flow of pure He prior to the characterization.

DME adsorption was evaluated using a gas mixture of 2.0% DME/4.9% He/93.1% Ar (certified standard, Praxair). Prior to characterization, the DME gas mixture was directed to bypass the catalyst bed and flow to the mass spectrometer so as to establish a stable baseline. For these experiments, both masses 45 and 46 were specifically tracked for DME, masses 31 and 32 for MeOH, masses 17 and 18 for water, and 4 for He. The mass

spectrometer was calibrated for DME prior to each reaction with He acting as internal standard. The monthly calibration for MeOH was used. The mass spectrometer was not calibrated for water.

While the stable baseline was being established in the mass spectrometer for DME content, the catalyst bed was heated under a low Ar flow to a temperature of 210°C. The reaction temperature was used as it was desired to understand how DME interacted with the catalyst at that temperature. The catalyst was heated under Ar flow as opposed to He flow because the use of He would have caused an initial spike in He concentration in the mass spectrometer when the DME gas mixture was switched to flow through the sample. This would have created anomalous results and introduced errors.

After the mass spectrometer had stabilized and the temperature of the catalyst had steadied at 210°C, the DME gas mixture was diverted to flow through the sample at a rate of 20 mL/min (STP). To avoid issues with varying flow rate, the flowmeter was calibrated immediately prior to the characterization being performed. By tracking the raw ion signal of DME in the mass spectrometer, it was possible to determine when the sample had been saturated with DME. It typically took a period of 20 minutes to an hour to saturate the sample with DME. To terminate the adsorption stage of the characterization, the DME gas mixture flow was stopped and the mass flow meter was allowed to evacuate the remains of the DME gas mixture out of the lines in the Autochem. During this time, the sample temperature was also allowed to begin to return to ambient. As soon as the flow of the DME mixture had reached 0 mL/min, the active flow through the tube was switched to Ar and set to 20 mL/min. The furnace was also opened at the same time and the tube quickly cooled using pressurized air. To leave as much DME adsorbed on the sample as possible, the Ar was only flowed for approximately 2 minutes, or until the sample temperature had decreased to below 100°C. The intent of this step was simply to remove any DME remaining in the gas phase in the tube and not to remove any adsorbed DME. With all flow shut off to the catalyst sample, the mass spectrometer was purged using He.

Once the mass spectrometer was showing a clean gas profile with only He present, a 20 mL/min flow of He (calibrated daily) was directed through the catalyst and the catalyst was heated to 100°C where it was maintained until a stable TCD signal had been established. Under these conditions, the mass spectrometer did not show any DME being desorbed from the sample. Once the TCD signal had stabilized in the Autochem (typically taking 15 – 30 minutes), TPD of the catalyst was begun. The TPD was conducted in one of two ways. With the catalysts in the bimetallic Cu-Zn/H-MOR study (detailed in Chapter 4),

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the sample was heated stepwise to 160°C, 210°C, 250°C, 300°C, and finally 400°C. A temperature ramping rate of 10°C/min was used to reach each temperature. The catalyst was maintained at each temperature for a period of 30 minutes. This was usually enough time to allow for nearly all of the DME that could be desorbed at that temperature to be desorbed. In the dealuminated MOR study detailed in Chapter 5, the sample was heated to 400°C at a rate of 3°C/min. During desorption, the ion signals for DME, MeOH, and H₂O were tracked in the mass spectrometer. Both the TCD signal of the Autochem and the mass spectrometer were recording data each second so as to not miss any changes.

Using the results, it was possible to calculate the number of active sites that convert DME to methyl groups as theorized by Cheung et al. [89,90] and others [83,206–208]. In each experiment, there was a difference between the amount of DME that was adsorbed and the amount desorbed. This value was also corrected for the tube volume (filled with DME at the start of the experiment). This unaccounted for DME could be assumed to have reacted with the protonic sites on MOR to form methoxy active sites (or methyl groups). Stoichiometrically, one DME molecule could form two methyl groups on protonated MOR.

3.3.5 CO adsorption and TPD

CO adsorption and TPD of catalysts that had been calcined and reduced were conducted using a Micromeritics Autochem II 2920. Typically, 0.15 g of catalyst was loaded into a quartz tube with quartz wool on both sides and calcined and reduced in situ (as described in Section 3.3.1) before being returned to ambient temperature under a 10 mL/min flow of He. The intent of the reduction step was to reduce Cu²⁺ to Cu⁺ based on the results of TPR characterization. It is well-known that Cu⁺ is highly selective towards the adsorption of CO while Cu²⁺ and Cu are not as selective [278–281]. The low flow rate of He was switched to a 15 mL/min flow of 3% CO/He (certified standard, Praxair) for a period of 30 minutes while the sample was sustained at ambient temperature. After this CO adsorption stage, the sample was purged using a 15 mL/min flow of He and heated to 100°C at a rate of 10°C/min where it was maintained for a period of one hour. This was intended to remove any weakly physisorbed CO and to establish a stable TCD signal prior to TPD. TPD was conducted using a 15 mL/min flow of He while the sample was heated from 100°C to 750°C at a ramping rate of 10°C/min with the TCD signal being recorded each second. Based on the calibration of the TCD signal for CO, the amount of CO desorbed from the catalyst was calculated. As this value likely included both physisorbed and chemisorbed CO, it was not possible to determine the Cu dispersion.

3.3.6 CO isotherms

In order to determine a value for Cu dispersion on MOR, CO isotherms were measuring using a Micromeritics ASAP 2020. In a typical experiment, 0.3 g of catalyst was loaded into a guartz sample tube and calcined following the procedure outlined in Section 3.3.1. The catalyst was further reduced in situ at 325°C using a 5% H_2/He (certified standard, Praxair) gas mixture. The sample tube with the catalyst was then evacuated and incrementally dosed with CO (99.5% purity, Praxair) at a rate of 0.5 cm³/g STP with a 15 second equilibration interval at a temperature of 30°C until saturation. After this initial adsorption experiment, physisorbed CO was removed by evacuation and dosing with CO was repeated in order to more accurately differentiate the chemisorbed CO from physisorbed CO. Adsorbed CO was then removed completely by heating under evacuation and another adsorption isotherm was produced at a temperature of 200°C following the same dosing procedure as before. The intent of using the higher temperature was to more accurately differentiate between physisorbed and chemisorbed CO, as these can be competing processes over Cu⁺ (indicated by failed pulsed CO chemisorption experiments). Dispersion of Cu on MOR was calculated based on the data obtained at the temperature of 200°C and the assumption that one mole of CO adsorbs on one mole of Cu⁺.

3.3.7 Ammonia TPD

In a normal NH₃-TPD test, 0.15 g of catalyst was loaded into a quartz tube with quartz wool to make a packed bed. The sample was loaded into the Autochem II and calcined and/or reduced in situ as described in Section 3.3.1. Once the sample had returned to ambient temperature after pretreatment, the active gas flow through the sample was switched to a 20 mL/min flow of 5.2% NH₃/He (certified standard, Praxair) for a period of one hour. After this NH₃ adsorption period, the flow through the sample was switched to 15 mL/min He and the sample was heated to 100°C to remove any weakly physisorbed NH₃. The sample was maintained at this temperature for a period of one hour at which time it was assumed the TCD signal was steady. The sample was then heated to 800°C at a rate of 5°C/min with the TCD signal being recorded each second. Temperatures in excess of 800°C (even in excess of 700°C) may be damaging to the MOR framework and data past that temperature may be unreliable [282–284].

3.3.8 Pyridine TPD

Catalysts to be used for Py-TPD were calcined in the Autochem II as described in Section 3.3.1. After calcination, samples were removed from the quartz tube, put into glass vials and placed in a desiccator. On the morning of the day the TPD was to be run, the sample was removed from the desiccator. A stainless steel $\frac{1}{2}$ " reactor was first filled halfway with glass beads onto which a bed of quartz wool was placed. Approximately 0.3 g of catalyst was then placed onto this bed. The reactor was then mounted into a Thermo Scientific Lindberg Blue M tube furnace. The sample was first heated to 550°C under a 50 mL/min Ar flow to remove any water that may have adsorbed onto the sample during its handling after calcination. The sample was kept for 1 hour at this temperature before being cooled. For the bimetallic Cu-Zn/H-MOR study detailed in Chapter 4, the sample was then reduced at 325°C using a 5% H₂/He mixture with flow rate 50 mL/min for a period of one hour. The sample was then cooled to \sim 80°C. In the case of the dealuminated MOR study detailed in Chapter 5, the sample was simply cooled to ~80°C immediately after the high temperature treatment to remove water. To expose the catalyst to pyridine, a 50 mL/min flow of Ar was directed to flow through a gas bubbler containing pyridine (anhydrous, 99.8%, Sigma-Aldrich). The sample was then exposed to this Py-saturated Ar gas mixture for a period of one hour at which point it was assumed the sample would be saturated with Py. The gas flow was then switched to bypass the Py bubbler and the sample (and reactor) was purged for a short while with pure Ar. The reactor was then removed from the furnace and the sample reclaimed from the tube. Approximately 0.15 g of the Py-adsorbed catalyst was immediately loaded into a quartz reactor with quartz wool placed on each side and mounted in the Autochem II. The rest of the Py-adsorbed catalyst was set aside for another characterization. The sample in the Autochem II was put under a 15 mL/min flow of He and heated to a temperature of 100°C so as to remove any weakly physisorbed Py. The sample was maintained at this temperature for a period of 30 minutes at which point the TCD had achieved a steady baseline. The sample was then heated to 800°C at a rate of 5°C/min with the TCD signal being recorded each second.

3.3.9 DRIFTS

DRIFTS spectra were recorded in a NEXUS 670 FT-IR equipped with a smart diffuse reflectance accessory. DRIFTS analysis was performed on calcined catalysts, as well as catalysts that had CO and Py adsorbed on them. Samples for CO-DRIFTS were prepared in the Autochem II. The catalysts were calcined and reduced as described in Section 3.3.1 (CO-DRIFTS was not performed on dealuminated MOR catalysts). After calcination and

reduction, the approximately 0.15 g of sample was kept under a 15 mL/min flow of 3% CO/He mixture for a period of one hour at ambient conditions after which the quartz reactor containing the sample was purged with He. The catalyst with adsorbed CO was then retrieved and stored in the desiccator until the time at which DRIFTS would be performed. Samples for CO-DRIFTS were prepared the same day as they were tested. Samples for Py-DRIFTS were prepared as described in Section 3.3.8.

DRIFTS samples were mixed with an equal amount by weight of KBr and placed in the solids sample holder. The DRIFTS spectra were recorded against a KBr standard with 128 scans and a resolution of 2 cm⁻¹. The data was processed using the OMNIC software and relevant peaks were deconvoluted using the software Origin.

3.3.10 UV-Vis spectroscopy

UV-Vis spectroscopy was performed in a Perkin-Elmer Lambda 1050 UV-Vis-Nir spectrophotometer equipped with a 150 mm integrating sphere. Calcined H-MOR catalysts containing Cu and/or Zn (calcination performed as described in Section 3.3.1 and in the Autochem II) were mixed with an equal amount of KBr by mass and pressed under a pressure of 7 tons for a period of 3 minutes to form a pellet. The pellet made by this process was hung in the middle of the integrating sphere. Reflectance spectra of the sample were collected between 300 and 800 nm with an interval of 1 nm and integration time of 1 second. The H-MOR catalysts containing Cu and/or Zn were not initially reduced as, upon exposure to air, the half-reduced Cu⁺ would likely re-oxidize to Cu²⁺. UV-Vis spectroscopy was only performed on the Cu and/or Zn containing H-MOR catalysts as the technique would not have yielded much useful information on the dealuminated MORs.

3.3.11 XPS

XPS measurements were performed on calcined catalysts using a Kratos Analytical AXIS-165 spectrophotometer. A monochromatic Al K α (hv = 1486.6 eV) was used at a power of 168 W. Initial survey scans were collected for a binding energy span of 1100 to 0 eV at steps of 0.4 eV with an analyzer pass-energy of 160 eV. For the higher resolution spectra, the pass-energy was decreased to 20 eV and the step size decreased to 0.1 eV. To compensate for any sample charging that may have occurred an electron flood neutralizer was applied. Compositions (when applicable) were calculated based on the high resolution spectra using instrument software with RSF of Scofield and Shirley background. Peak

deconvolution and identification was conducted using CasaXPS software. Binding energies were referenced to carbon 1s (284.7 eV).

3.3.12 ²⁷AI MAS NMR

²⁷AI MAS NMR was used to evaluate the approximate ratio of framework AI (tetrahedrally coordinated, occurs at 60 ppm) to extraframework AI (octahedrally coordinated, occurs at 0 ppm) in dealuminated MOR catalysts [285–289]. In a typical solidstate NMR characterization, 0.5 g of calcined material was used. It must be mentioned here that if a zeolite, especially mordenite, is not properly hydrated, an issue arises where the NMR spectrum shows no Al. This issue is described in detail elsewhere [285–287]. To avoid this issue, calcined catalysts were left on a bench in a crucible in the laboratory and exposed to atmosphere overnight. Samples were then packed into 4.0 mm zirconia rotors and mounted into a Bruker Avance 500 spectrometer and run at 130.4 MHz for Al-27. Spectra were acquired with magic angle spinning at 12 kHz. All spectra were referenced to the Al-27 NMR peak of solid NH₄AlSO₄ \cdot 12H₂O which was set to 0.0 ppm. A Bloch decay pulse, with H-1 decoupling, was used in the acquisition of all spectra. The Al-27 90° pulse was 3.0 microseconds with a relaxation delay of 1.0 seconds. The number of transients recorded per spectrum ranged from 924 to 12000. From the results, it was assumed that 1000 transients were already more than sufficient to obtain reasonable spectra. To properly compare the results, every spectrum was scaled so that the 60 ppm peak was of the same intensity. The peak ratios were compared by both area and intensity.

3.3.13 XRD

XRD patterns were taken of calcined catalysts using a Rigaku Ultima IV unit equipped with a Co tube (38 kV, 38 mA) with an average K wavelength of 1.79 Å and a D/Tex detector with Fe filter. Samples were run using a Si sample holder with scans taken at a speed of 2.0° 20/min with a step size of 0.02°. XRD patterns were recorded between 5 and 90° 20. Data was baseline corrected and interpreted using the software JADE 9.5. Two samples were given of each catalyst: one with the catalyst mixed with an equal amount of quartz powder by mass and the second the catalyst by itself. This was intended to track and correct any shifts in the XRD pattern due to the presence of ion-exchanged metal or removed Al as well as to recover from any differences in how the catalyst was placed on the XRD sample holder.

3.3.14 Surface area and pore volume measurements

The surface area and pore volume of calcined samples were measuring using a Micromeritics ASAP 2020. Typically, 0.2 g of catalyst was used for each characterization. Samples were degassed overnight at 350°C under vacuum prior to the tests. Wet and dry weights were taken with the sample tube backfilled with He. While experiments were performed with both liquid N₂ and liquid Ar, Ar was found to deliver much better results and was chosen to be used as adsorbent. Prior to the physisorption test, the sample was pumped/purged with Ar several times to ensure as much He was removed from the zeolite sample as possible. After achieving a consistent vacuum pressure of the sample, it was further left for another 3 hours under vacuum prior to Ar dosing. Dosing was conducted at a rate of 1-4 cm³/g with lower dosing rates used for low P/P₀ and higher dosing rates used at higher P/P₀. Physisorption data was taken until P/P₀ of ~0.3 in the case of the Cu and/or Zn containing H-MOR catalysts detailed in Chapter 4. For that study, it was only desired to understand the impact on the micropores of ion-exchange. For the dealuminated MOR study detailed in Chapter 5, physisorption data was taken until P/P₀ of 0.995, followed by desorption data measured from 0.95 to 0.2 P/P₀ in decrements of 0.05.

All data analysis was performed using the software Microactive. Langmuir surface areas were taken between absolute pressures of 0.005 kPa and 0.030 kPa as this is the point where the initial very strong adsorption ends. BET surface area was taken between 0.001 and 0.1 P/P₀. The micropore behaviour was measured using the t-plot method with the data between 3.0 Å and 10.0 Å used and the Harkins and Jura thickness curve model selected. Desorption data, when applicable, was analyzed using BJH analysis and the Harkins and Jura thickness curve model with Faas BJH correction. Differentials were not smoothed as there was not enough desorption data. Pore volume was also evaluated using the Horvath-Kawazoe (HK) model. Cylindrical pore geometry (Saito-Foley) was used with the computed interaction parameter. Differentials were smoothed in this case and the Carbon-Graphite (Ross/Olivier) adsorption model was selected as this gave a prediction for the pore size distribution that seemed to be in better agreement with what is known about MOR compared to what the zeolite models were predicting.

3.3.15 Microscopy techniques

High-resolution TEM (HR-TEM) images were taken on a JEOL 2100 transmission electron microscope using a 200 kV acceleration voltage. SEM-EDX compositions were taken on a Tescan VEGA3 SEM-EDX at a 20 kV acceleration voltage. Samples were first pressed into a thin disk with 16 metric tons of force before being mounted on the SEM sample stub with conductive tape. A large area at low resolution was used in order to obtain a composition more representative of the entire sample. EDX analysis was conducted using the INCA software. Due to the consistent results obtained by this method, only 2-3 spots were taken for composition measurement and the results were averaged to obtain the final composition.

Compositions from other characterization techniques (XRF, NAA) were not as accurate when predicting the amount of Si in the samples. ICP-OES was investigated as another means to determining the composition as it is sometimes used in papers on zeolite research. With the equipment available at the university, it was reported that this technique also did not predict the Si content accurately.

3.4 Quantum-chemical modeling

3.4.1 Introduction to computational chemistry

Computational chemistry has been used extensively to determine probable molecular structures as well as possible reaction mechanisms. There can be considered to be two broad areas within computational chemistry, though both serve the same purposes. These are molecular mechanics and electronic structure methods. Both can be used to compute the energy of a structure, optimize it, and compute vibrational frequencies. Molecular mechanics simulations are based on the laws of classical physics and utilize a force field. A force field consists of a set of equations that define the energy of a molecule, a series of atom types, and a parameter set with force constants. Molecular mechanics methods do not treat electrons explicitly and instead focus on the interactions of nuclei. With this in mind, the correct force field for a system must be used to obtain good results. Also, as the electrons are not treated directly, molecular mechanics methods cannot be used for problems where electronic effects are dominant [290,291].

Electronic structure methods are rooted in the laws of quantum mechanics and the various methods are based on mathematical approximations of the Schrödinger equation, shown below (the Schrödinger equation can only be solved exactly for systems with a single electron, like a hydrogen atom).

$$H\Psi = E\Psi \tag{3.16}$$

In the above equation, Ψ is the wavefunction. When multiplied with its complex conjugate, it is related to the probability distribution of a particle. The wavefunction is a function of all coordinates of all particles for a particular system and time. E is the energy of the particle and H is the Hamiltonian operator. The Hamiltonian consists of both kinetic and potential energy terms. The potential energy is defined as the repulsion between each pair of charged entities, and includes electron-nuclear attraction, electron-electron repulsion, and nuclear-nuclear repulsion. Kinetic energy is simply the motion of all particles in the system. To help simplify the analysis of the Hamiltonian, the Born-Oppenheimer Approximation is applied. It allows for the separation of nuclear and electronic motions so that they can be solved separately. In this approximation the nuclei are considered to be fixed while the electrons are mobile. When the problem is solved, two separate Hamiltonians are calculated. One is used for the determination of the potential energy surface, and the other is used for determination of the vibrational, rotational, and translational states of the nuclei [290,292]. The various methods available in electronic structure methods differ in how they treat the wavefunction and the positions of the electrons and their interaction. As the purpose of this thesis is not to describe how the Schrödinger equation is approximately solved in these methods, it will not be further discussed. For further information, the reader is referred to the excellent introductory book by Foresman and Frisch [290].

Two subclasses exist within electronic structure methods: semi-empirical and ab initio. Semi-empirical methods utilize experimentally-derived parameters to simplify calculations and solve an approximate form of the Schrödinger equation. Much like molecular mechanics methods, semi-empirical methods rely on having good parameter sets. Ab initio methods, by comparison, use no experimental parameters. The computation in these methods is based entirely on the laws of quantum mechanics and on a few physical constants, such as the speed of light, masses and charges of electrons and nuclei, and Planck's constant. Ab initio methods can be quite computationally expensive dependent on the size of the system but can provide highly accurate predictions for many systems [290].

Also included within electronic structure methods is density functional theory (DFT), which has found increasing use in recent years. DFT is similar to ab initio methods but also include the effects of electron correlation. Electron correlation means that the electrons in a molecular system will react to one another's motion and will attempt to stay away from one another. Hartree-Fock (HF) methods (an inexpensive ab initio method) consider this behaviour only in an average sense. HF is therefore less accurate for some types of

systems than DFT methods. DFT is used specifically when a computation for energy must be highly accurate, such as when computing probable reaction mechanisms [290].

In the present work, DFT methods were not attempted. Some initial models with semi-empirical methods were attempted but proved to be ineffective as will be discussed later in Chapter 4. The bulk of the modeling work was conducted using HF methods. HF is particularly useful for providing initial predictions for many systems and for computing structures of stable molecules. It should not be used for accurate modeling of the energetics of reactions or bond dissociations [290]. In the present work, this was not going to be attempted and determination of only the stable ion-exchange locations was desired for which HF methods were considered to be sufficient.

3.4.2 Hartree-Fock modeling

As part of the bimetallic Cu²⁺ and/or Zn²⁺ ion-exchange onto MOR study with results detailed in Chapter 4, it was desired to know from a theoretical perspective what the probable ion-exchange locations were. To accomplish this, HF theory was utilized in the Gaussian 09 modeling software. The original MOR structure was built in Gaussview V5.0 according to available information about its structure [140]. The purely siliceous MOR structure was optimized using HF with basis set 6-31G(d) as this basis set provided the optimum balance between computational requirements and reasonable agreement with known bond lengths and angles for MOR (detailed in Chapter 4). Models were run using Compute Canada resources, specifically the computing facilities managed by Westgrid.

Keeping in mind Löwenstein's rule [98,99], Al atoms were placed in the optimized siliceous MOR structure in as close of proximity as possible and either Cu^{2+} or Zn^{2+} was bonded to the different O atoms around those sites and in different geometric configurations (2 – 4 bonds). Using the ONIOM scheme, the majority of the zeolite structure was frozen in place with only the area around the theoretical ion-exchange location being allowed to be optimized. In terms of determining the size of the area to be optimized, it typically included the Al and its next nearest neighbours (previously defined in Section 2.2.1). This usually meant 15-20 atoms were free to be optimized. To increase the efficiency of the optimization, the frozen part of the structure was evaluated using the STO-3g basis set and the flexible atoms evaluated using the 6-31G(d) basis set. Models that did not successfully optimize in this manner had their constraints loosened and the number of atoms for optimization increased (typically to 40 atoms). These changes often did not help the failed model to optimize successfully. The most probable Al site positions were also considered

when evaluating ion-exchange locations [197–200]. While the T2 site may not be the most probable location to have AI in the mordenite framework, it was still evaluated as a potential ion-exchange location.

Once models had been optimized, the energy of the entire structure was reevaluated at full HF 6-31G(d) theory. This was meant to avoid any errors associated with using lower levels of theory to evaluate the majority of the structure as would have been present while utilizing the ONIOM scheme. To determine the most probable locations and orientations of the ion-exchanged Cu^{2+} and Zn^{2+} , the energies of all of the models had to be normalized for effective comparison. To accomplish this, the zeolite structures were reoptimized with Al atoms in place and no compensating cations. For these models, the charge of the entire structure was set to -2 prior to the optimization. The energy of Cu and Zn atoms were also evaluated individually. The energy associated with the ion-exchange location was then evaluated as the difference between the energy of the ion-exchanged metal on the zeolite and the sum of the separate atom energy and zeolite energy. While the energies that would be gained from using HF were known to be inaccurate, it was assumed that, so long as the technique was kept the same among all the models, that the relative energy amounts would give some indication as to the most likely ion-exchange locations. However, after initial data processing it was apparent this assumption was incorrect. The energies obtained often differed by an order of magnitude rather than by an expected <20%. To obtain proper energies, one would likely have to use DFT theory [290]. The problem with using DFT for the models was that they were simply too large. The use of DFT would have required additional computational resources which exceeded those that were available. As such, the probability of ion-exchange locations was evaluated based on deformation to the framework caused by the ion-exchange.

3.5 Chapter summary

In this chapter the fundamental principles behind some of the characterization techniques used along with the procedures utilized to characterize the catalysts are presented. Advances in catalyst characterization techniques are still rapidly occurring with the further advancement of technology and the need to better understand how catalysts work. It will again be mentioned here that, despite however much data is gathered, how a specific catalyst works for a specific reaction will always be a theory and cannot be conclusively stated. The advancement of in situ techniques has allowed for great advances in the understanding of catalysis, but these techniques are often plagued with data interpretation difficulties. Equipment for in situ techniques is also sometimes rare and can be quite expensive. The characterizations used for the work presented in this thesis have allowed for the development of a theory regarding how DME carbonylation proceeds over both ion-exchanged and dealuminated MOR catalysts. Only by the combination of all of the data obtained from the characterizations and the Hartree-Fock modeling has a reasonable theoretical picture of how the catalyst behaves during reaction been painted. These data and these theories will be presented in the following chapters.

Chapter 4

Stabilization of mordenite via bimetallic ion-exchange of Cu²⁺ and Zn²⁺

I know that you believe you understand what you think I said, but I'm not sure you realize that what you heard is not what I meant.

--Robert McCloskey

4.1 Introduction

As discussed in Section 2.2.4, ion-exchange is one of the simplest means by which a synthesized zeolite can be modified and is the basis of a zeolite's ability to be used in many separation processes [93,97,161–166]. Playing on a zeolite's remarkable ability for ion-exchange, metals that are catalytically active can be placed onto the zeolite framework in extraframework positions. The metals can then serve as a catalyst directly in their metal oxide form (the oxygen being "borrowed" from the zeolite framework) or can be reduced into tiny metal nanoparticles whose shape and size may be partially controlled by the confinements of the zeolite framework. This is the basis of using Cu-exchanged MOR for the conversion of methane to methanol or as a deNOx catalyst [243–247,249–255].

Ion-exchanged Cu on MOR has already seen some use in DME carbonylation by BP Chemicals Ltd. and other groups [92,223,232,233]. However, it does not appear that Cu/H-MOR has much added stability. In recent patents, BP Chemicals Ltd. has shown that H-MOR, given varying amounts of H_2 in the feed and optimization of other reaction conditions,

can have its lifetime extended considerably [230]. The investigation of selectively dealuminated or desilicated MOR has also been conducted in an effort to make MOR more stable in other reaction conditions [228,229]. Indeed, if the MOR could be made inherently stable without the use of an ion-exchanged metal, it may be more cost-effective (dependent on the metal that would be used for ion-exchange). In-situ regeneration of the Cu/H-MOR catalyst also showed that the original activity was not fully restored, which implies that either all of the coke was not burned off with the regeneration or that the catalyst was damaged or otherwise changed in some way [223]. The possibility exists that the ion-exchanged Cu simply sintered during the reaction and/or during the regeneration treatment and has blocked pores and channels that, on the fresh catalyst, were accessible and contained active sites [234]. Despite the work that has been directed at Cu/H-MOR in DME carbonylation, this deactivation behaviour has not been well studied.

While the use of H₂ in the reactant mixture to enhance the stability of MOR is not necessarily a bad idea, especially in a facility where gasification is conducted and a CO/H₂ mixture is readily available, it simply isn't necessary for the reaction. Desilication and dealumination of MOR do not necessarily scale well to an industrial catalyst production level either. There is also some evidence showing that it does not sufficiently enhance the stability enough to warrant the trouble of scaling it up [228,229,235]. Ion-exchange remains one of the simplest techniques to scale up to an industrial level, but it has been shown that Cu-exchanged H-MOR, while providing an enhancement to the selectivity, does not substantially enhance the stability [92,223,232]. Despite this, the use of Cu is still desirable. It is a known carbonylation catalyst as in its single oxidation state it activates CO [278–281,293,294] and it is considerably cheaper when compared with the precious metals, such as Rh, Pt, Ir, or Pd, that are often used in catalysts.

It is therefore highly desirable (and quite valuable) to find a means to stabilizing Cu/H-MOR especially as this catalyst is beginning to be used for other applications (see Section 2.4). The simplest way this could be achieved is by the ion-exchange of another metal with Cu onto MOR. There are an incredible number of options available here as nearly any other transition metal (and even the alkali and alkaline earth metals [295]) could be ion-exchanged onto MOR along with Cu, though some may be more difficult than others.

In an actually quite relevant reaction to the subject at hand, Cu is stabilized with Zn for the purpose of synthesizing methanol from syngas and already exists as a commercial catalyst (Cu-ZnO-Al₂O₃) [43–45,296,297]. As mentioned in Chapter 1, Cu and Zn based catalysts, whether the metals are deposited onto alumina or a zeolite, have seen increasing

research within the last decade as bifunctional catalysts for the purpose of synthesizing dimethyl ether directly from syngas [50,56,58,296–298]. The ZnO likely plays a role in the inhibition of the reverse water gas shift reaction, which produces undesired CO for that application. The ZnO was also shown to stabilize the Cu against reoxidation by either CO_2 or H₂O and prevent sintering [297]. As the results from BP Chemicals Ltd. on the activity of Cu/H-MOR after regeneration imply that Cu may be unstable on MOR [223], the addition of Zn as a stabilizer is an attractive idea. Zinc may also play some other role on MOR. As it has become widely believed that carbonylation of DME on MOR is a site-specific reaction [212,215,216], Zn²⁺ may be able to more effectively block unselective acid sites due in part to its stability against reduction. As Zn^{2+} is unlikely to reduce at the conditions of this study, it will continue to occupy the ion-exchange location during reaction and prevent it from potentially becoming an acid site that could lead to reactions that form coke. Zinc oxide often requires temperatures in excess of 600-700°C to reduce [299,300].

Bimetallic ion-exchange onto a zeolite is an area that is not well-explored, and there are many questions that require answering. Among them is the question of if the ion-exchanged metals interact directly with one another. In true ion-exchange, the Cu^{2+} and Zn^{2+} would not necessarily bind to each other directly. The other question is if the metals will simply block the true active sites for reaction. It has already been implied that Cu^{2+} ion-exchange may occur in the 8-MR of MOR [233,301–304], and if that is the case, Zn^{2+} may as well. If Zn^{2+} simply blocks the true active sites, it may do more harm than good. The other issue is if these properties are dependent on the ratio of Cu to Zn, in which case considerable time and effort must be spent to find the appropriate ratio.

The purpose of this study was to determine if Zn could sufficiently stabilize Cu/H-MOR for use at an industrial level. If a bimetallic Cu-Zn/H-MOR catalyst does turn out to be highly stable, the roles of each metal will be theorized on using extensive characterization.

4.2 Synthesis of H-MOR catalysts containing Cu and/or Zn

The as-received sodium form of MOR (Na-MOR, Si/Al = 6.5, Zeolyst, CBV-10A) was converted to the ammonium form (NH₄-MOR) via liquid-based ion-exchange using a 1 M solution of ammonium nitrate (NH₄NO₃, purity \geq 99.0%, Sigma-Aldrich). The solution was created using deionized water. Typically, the solution was mixed and heated to ~60°C and the Na-MOR was added at a ratio of 1 g Na-MOR/50 mL NH₄NO₃ solution. The resulting mixture was stirred using a magnetic stir bar for a period of 3 hours. The resultant MOR powder was retrieved by vacuum filtration and washed with deionized water. The recovered solids were then dried in an oven maintained at ~60°C overnight before repeating the procedure. The entire ion-exchange procedure was repeated four times so as to ensure that all Na⁺ was removed from MOR (since ion-exchange is an equilibrium-limited process [163,166]). Results from SEM-EDX confirmed that all Na⁺ was exchanged with NH_4^+ .

The ion-exchange of Cu²⁺ and Zn²⁺ was conducted in much the same manner. To produce monometallic Cu/NH₄-MOR, copper nitrate (Cu(NO₃)₂·2.5H₂O, purity 98%, Sigma-Aldrich) was dissolved in deionized water so as to produce a solution with 0.2 M Cu²⁺. This copper solution was stirred using a magnetic stir bar and heated to ~60°C on a hot plate. The dried NH₄-MOR powder was then added at a ratio of 1 g to 50 mL of solution. This mixture was then covered and stirred for a period of 3 hours. The resultant ion-exchanged MOR was retrieved by vacuum filtration and washed excessively with deionized water. The recovered solids were further dried in an oven maintained at ~60°C before the ion-exchange was repeated. To overcome equilibrium limitations and ensure the maximum amount of ion-exchange donto NH₄-MOR in precisely the same way using zinc nitrate (Zn(NO₃)₂·6H₂O, purity 98%, Sigma-Aldrich) in place of copper nitrate. The bimetallic Cu-Zn/NH₄-MOR catalysts were also prepared the same manner, only with solutions containing both Cu²⁺ and Zn²⁺ and a total metal ion concentration of 0.2 M. The ratio of Cu²⁺:Zn²⁺ in solution was varied to achieve different ratios of CuO:ZnO on the final catalyst.

The ion-exchanged catalysts were calcined to produce the final H-MOR forms. Calcination was conducted as described in Section 3.3.1. The final compositions of the calcined catalysts are given in Table 1, measured by SEM-EDX. The total ion-exchange is defined as the percentage of AI that would theoretically be occupied by the ion-exchanged metal (assuming that a divalent metal occupies two AI atoms). The average total ion-exchange was ~55%, which is consistent with what has been reported by other groups for the maximum ion-exchange of Cu²⁺ onto MOR [161,170–172,223]. This means ~45% of the negative charge introduced into the framework by the AI is being compensated for by protons (H⁺). There are small differences in the total metal loading among the ion-exchanged catalysts. With monometallic Cu/H-MOR, the total ion-exchange was 57.8%, while it was 52.2% on Zn/H-MOR. This difference was consistent on all spots taken for composition on the samples. While it is a small difference, it does imply that Cu²⁺ and Zn²⁺ behave differently in ion-exchange on MOR. The total ion-exchange over the bimetallic Cu-Zn/H-MOR catalysts varied between these values.

| Catalyst | Al wt.% | Si wt.% | Cu wt.% | Zn wt.% | Cu/Zn Ratio | Total ion-exchange |
|-----------------|---------|---------|---------|---------|-------------|--------------------|
| | | | | | (molar) | (mol%) |
| H-MOR | 5.09 | 35.66 | - | - | - | - |
| Cu/H-MOR | 4.72 | 33.26 | 3.21 | - | - | 57.8 |
| 2Cu-1Zn/H-MOR | 4.72 | 33.57 | 2.04 | 0.92 | 2.3 | 52.8 |
| 1Cu-1Zn/H-MOR | 4.73 | 33.35 | 1.61 | 1.57 | 1.1 | 56.1 |
| 1Cu-2.5Zn/H-MOR | 4.75 | 33.27 | 0.90 | 2.36 | 0.4 | 57.1 |
| 1Cu-4Zn/H-MOR | 4.76 | 33.13 | 0.57 | 2.47 | 0.2 | 53.1 |
| Zn/H-MOR | 4.82 | 33.66 | - | 3.05 | - | 52.2 |

Table 4.1. Compositions of H-MOR-based catalysts containing ion-exchanged Cu^{2+} and/or Zn^{2+} .

4.3 Bimetallic Cu-Zn/H-MOR catalysts in DME carbonylation

4.3.1 Selection of catalyst reduction temperature

As has been previously stated, the adsorption and activation of CO occurs preferentially on Cu^+ as compared to Cu^{2+} and metallic Cu [278–281,293,294]. While it is known that CO, given the proper conditions, can act as a reducing agent, it was desired to start the carbonylation reaction with Cu in the correct state for the proper adsorption of CO. This is assuming that Cu⁺ would be in the proper proximity to active methyl groups so that the CO addition to the methoxy site to create the acetoxy site would be facilitated and increase the overall reaction rate (see Section 2.3.1). Prior to conducting extensive reaction trials, the proper reduction temperature for the catalyst had to be determined. For this purpose, TPR using H_2 carried out as explained in Section 3.3.2 was conducted with results shown in Figure 4.1. Protonated MOR was used as the baseline signal, which showed limited to no interaction with H₂. From the TPR of Cu/H-MOR, two very strong reduction peaks are visible at 263°C and 625°C with what appears to be two other peaks present at ~521°C and ~700°C. It was assumed that the low temperature peak was associated with the reduction of Cu^{2+} to Cu^{+} while the high temperature peak is attributable to the further reduction of Cu⁺ to Cu. The presence of three distinct temperatures for the reduction of Cu⁺ to Cu may be an indication of the differing bonding strengths of the different ion-exchange sites in the MOR framework (recall that there are 4 unique tetrahedral Al locations in the MOR framework [140,197–200]). Interestingly, the TPR of Zn/H-MOR revealed a minor reduction peak at 384°C. As it is understood that ZnO does not typically reduce at these low temperature conditions and the peak area is small, this peak was not further investigated [299,300]. When Zn^{2+} was combined with Cu^{2+} over H-MOR, it had a significant effect on the reduction temperature of Cu²⁺. With regards to 2Cu-1Zn/H-MOR, it decreased both the low and high temperature reduction peaks to 234°C and 606°C respectively. On 1Cu-1Zn/H-MOR, it increased those reduction temperatures to 275°C and 650°C. This behaviour continued with 1Cu-4Zn/H-MOR, where the low temperature reduction peak increased to 387°C. The high temperature reduction peak for 1Cu-4Zn/H-MOR is very broad, and starts at 600°C. The climax of this peak was not reached before a temperature of 800°C at which point it can be assumed that the MOR framework begins to become damaged and the TPR results are likely no longer reliable [282–284]. Obviously there is some bimetallic effect between the Cu^{2+} and Zn^{2+} , but it cannot be stated yet that this is due to direct interactions of the two metals. The change in reduction temperature may be due to interactions with the MOR framework itself. With zeolites, a significant

portion of their acid strength may be related to the crystal structure. In other words, the bond angles and bond lengths, as well as the next nearest neighbours, around an acid site will have some influence on its strength [136,142,143]. It is also highly likely that the presence of an ion-exchanged divalent metal will lead to framework deformation. As the Zn²⁺ content is increased and Cu²⁺ content decreases, it may lead to increasing (or decreasing) framework deformation. This will have some influence on the strength of other ion-exchange locations, which may be presenting themselves as a change in the required Cu²⁺ and Cu¹⁺ reduction temperature. In this case, it is assumed there is no direct interaction between the two ion-exchanged metals, and they instead impact each other through the MOR framework. It also may be the case that the ion-exchanged metals directly interact through bonds between them. Regardless, to maintain consistency over all reactions, a reduction temperature of 325°C was selected. While this temperature is likely not enough to reduce all of the Cu²⁺ to Cu⁺ on 1Cu-4Zn/H-MOR, it would be high enough to reduce some of the Cu²⁺. The effect of varying reduction temperature on the performance of the catalyst was investigated using the DME carbonylation reaction itself.



Figure 4.1. Temperature-programmed reduction (TPR) of calcined H-MOR catalysts with ion-exchanged Cu^{2+} and/or Zn^{2+} .

4.3.2 DME carbonylation with bimetallic Cu-Zn/MOR catalysts

All synthesized catalysts listed in Table 4.1 were tested for the carbonylation of DME at the conditions described in Section 3.3.1. The results were processed as described in that same section. Prior to reaction, catalysts were stored in an oven maintained at \sim 60°C

since being synthesized. After calcination and reduction, catalysts were maintained at ambient temperature and pressure under a low flow rate of pure He for a period not longer than 12 hours. Results for the conversion of DME, the productivity of MeOAc, and the selectivity towards MeOAc, MeOH, and other compounds are shown in Figures 4.2, 4.3, and 4.4 respectively. Other details, such as the total MeOAc and MeOH produced, time before deactivation and the peak productivity of MeOAc are given in Table 4.2. The performance of H-MOR is consistent with what has been found by other groups [89–91,233,235,236]. The H-MOR catalyst has an approximate 4–6 h induction period before it achieves the maximum conversion of DME and productivity of MeOAc after which it quickly deactivates and by 30 h on stream the catalyst has dropped below 15% DME conversion. This actually appears to be at least 10 h longer than some groups' results. The peak selectivity towards MeOAc is quite high (\sim 97%) but as the catalyst deactivates this decreases to \sim 60%. This decrease in selectivity towards MeOAc is accompanied with increased production of MeOH and other hydrocarbons. Quite interestingly, under the conditions tested Cu/H-MOR actually performed more poorly compared to H-MOR. Its lifetime was 23% shorter compared to H-MOR and it produced 30% less MeOAc. The peak conversion of DME was higher, but this was not reflected in the peak activity of MeOAc. From the selectivity, more MeOH was produced at the start of reaction with Cu/H-MOR compared to H-MOR. The poor performance of Cu/H-MOR could be due to several factors. As found by Zhang et al. [232], if Cu/H-MOR was calcined at too high of a temperature, the catalyst performance was negatively affected. As the calcination temperature in this study is higher than their identified ideal temperature of 430°C, this may be the case.

Monometallic Zn/H-MOR proved to be a superior catalyst to H-MOR. Overall, it produced 68% more MeOAc despite also producing 65% more MeOH. These increases are not due to the peak activity, which wasn't much higher than that of H-MOR. Instead, Zn/H-MOR proved to be far more stable than H-MOR, lasting 54% longer before DME conversion dropped below 15%. From Figures 4.2 and 4.3, it is apparent that the catalyst induction period has been increased. The time before peak DME conversion and peak MeOAc productivity were achieved has been extended to 20 hours. During this extended induction period, more MeOH was produced as compared to either of H-MOR and Cu/H-MOR. During the entirety of the reaction with Zn/H-MOR, there were no other by-products detected and the selectivity to MeOAc only decreased to 75% with substantial catalyst deactivation.

The bimetallic Cu-Zn/H-MOR catalysts all outperformed H-MOR and Cu/H-MOR, but not all of them performed better than the Zn/H-MOR. The performance of the bimetallic

catalysts proved to be a strong function of the ratio of Cu to Zn on the MOR. The 2Cu-1Zn/H-MOR produced less MeOAc overall as compared to Zn/H-MOR, but did achieve a 9.4% higher peak productivity, which was also reflected with a higher peak conversion of DME compared to Cu/H-MOR. Compared to Zn/H-MOR, 2Cu-1Zn/H-MOR had a 13% shorter time before deactivation. The selectivity behaviour of the two catalysts was similar upon deactivation. The 1Cu-1Zn/H-MOR catalyst gave the highest peak activity of MeOAc and produced 19% more MeOAc and 20% less MeOH compared to Zn/H-MOR with only a marginally longer time before deactivation compared to 2Cu-1Zn/H-MOR. The selectivity behaviour with deactivation was similar to that of 2Cu-1Zn/H-MOR and Zn/H-MOR. However, the truly almost magical catalyst was obviously 1Cu-4Zn/H-MOR. Compared to 1Cu-1Zn/H-MOR, it produced 100% more MeOAc while only producing 27% more MeOH. The peak activity was similar to that of 1Cu-1Zn/H-MOR, or rather, similar enough that it could not be considered to be outside the error of the experiments. The 1Cu-4Zn/H-MOR was substantially stabilized, lasting 86 hours before deactivation. This is 187% longer when compared to H-MOR. The 1Cu-4Zn/H-MOR also produced 400% more MeOAc compared to H-MOR. Upon deactivation, the selectivity towards MeOAc was highly stabilized, only decreasing to \sim 85%. While the 1Cu-4Zn/H-MOR did take a longer period of time to reach maximum peak activity of MeOAc compared to all other catalysts, the production level of MeOAc was actually quite stable for a period of ~50 hours. This period of stability would be absolutely necessary for consideration for industrial implementation.

Table 4.2. Total MeOAc and MeOH produced, time before catalyst deactivation, and peak productivity of MeOAc for H-MOR catalysts containing ion-exchanged Cu^+ and/or Zn^{2+} used in DME carbonylation.

| Catalyst | Total MeOAc | Total MeOH | Catalyst | Peak Activity |
|---------------|--|---|----------|--|
| | (kg _{MeOAc} kg _{cat} -1) | (kg _{MeOH} kg _{cat} -1) | lifetime | (g _{MeOAc} kg _{cat} -1 |
| | | | (h) | h⁻¹) |
| H-MOR | 3.57 | 0.28 | 30 | 213.3 |
| Cu/H-MOR | 2.51 | 0.26 | 23 | 205.9 |
| 2Cu-1Zn/H-MOR | 5.53 | 0.39 | 40 | 237.7 |
| 1Cu-1Zn/H-MOR | 7.12 | 0.37 | 42 | 246.4 |
| 1Cu-4Zn/H-MOR | 14.24 | 0.47 | 86 | 240.1 |
| Zn/H-MOR | 6.00 | 0.46 | 46 | 217.2 |



Figure 4.2. Conversion of DME during the lifetime of H-MOR catalysts containing ion-exchanged Cu⁺ and/or Zn²⁺.

Figure 4.3. Productivity of MeOAc by DME carbonylation over H-MOR catalysts containing ion-exchanged Cu⁺ and/or Zn²⁺.

The outstanding performance of 1Cu-4Zn/H-MOR over the other catalysts is potentially related to its TPR profile. The two reduction peaks for this catalyst were higher than for any of the other bimetallics and monometallic Cu/H-MOR. A potential reason for the poor performance of Cu/H-MOR could be the instability of Cu^+ at the reaction conditions. With the increased pressure and amount of CO, Cu^+ may reduce to Cu metal during reaction. The same could be said of 2Cu-1Zn/H-MOR. Cu metal, and even Cu⁺, could sinter during reaction and cause pore blockage and premature catalyst deactivation as compared to H-MOR [79,234]. The temperature required for reducing Cu⁺ to Cu is substantially higher on 1Cu-4Zn/H-MOR compared to the other Cu-containing catalysts, indicating that Zn²⁺ is providing a more stable environment for monovalent Cu. At reaction conditions, it is unlikely that CO is able to further reduce Cu^+ and the bond of Cu^+ to its ion-exchange location may be strong enough that sintering is effectively hindered. Despite this stability enhancement, it doesn't appear that Cu⁺ has substantially increased reaction rates. While the peak productivity of MeOAc is 13% higher on 1Cu-4Zn/H-MOR compared to H-MOR, it is likely that the deactivation of H-MOR was so quick that it was unable to achieve the peak productivity level it was capable of. However, it is to be recalled that the ion-exchange level of Cu^{2+} and Zn^{2+} was ~55%. Based upon earlier works, protonated sites are required to form methyl groups that are the true active site [89,90,212,215–217]. On Cu/H-MOR, with Cu^{2+} reduced to Cu^+ it would still mean that ~29% of sites would be blocked by Cu^+ . With 1Cu-4Zn/H-MOR, the number of blocked sites is higher as Zn^{2+} is unlikely to reduce and will continue to block acid sites. Despite these blockages, catalyst activity was not reduced with metal loading, indicating Cu⁺ may be facilitating the reaction.



Figure 4.4. Selectivity to MeOAc, MeOH, and others in DME carbonylation performed over H-MOR catalysts containing ion-exchanged Cu^+ and/or Zn^{2+} .

The relation of DME conversion to MeOAc productivity must be discussed. The conversion of DME was only stabilized to a certain degree on 1Cu-4Zn/H-MOR, and the MeOAc productivity served as a reflection on that until after a time on stream of approximately 40 hours. After this time, DME conversion began decreasing rapidly, falling to below 60% by 50 hours. However, it was only at 50 hours that MeOAc productivity began to decrease rapidly. At the conditions tested, it is apparent that the conversion of DME does not necessarily reflect the MeOAc produced despite the seemingly high selectivity. During these periods, the mass spectrometer did not show any obvious by-products and none of the other signals in the mass spectrometer seemed to follow the behaviour of the raw DME signals. If it is assumed that the MeOAc productivity after 50 hours was a proper reflection of the conversion of DME, then not all DME conversion 0 and 40 hours can be attributed to MeOAc or MeOH production. With nothing substantial on the mass spectrometer indicating other species were forming, the selectivity was calculated as presented in Figure 4.4. During this time frame, the "lost" DME may be involved in coking reactions occurring over the MOR, which eventually cause the deactivation of the catalyst. A potential solution to this problem would be to simply decrease the amount of DME present. It has been theorized by other groups that the likely reaction order to DME in its carbonylation is 0 [90]. If that is truly the case, and as it seems that DME carbonylation on MOR is a somewhat slow reaction, not much DME would be required to facilitate the reaction. Excess DME may only contribute to catalyst deactivation. Another simple solution would be to decrease the residence time and give DME less opportunity to react.

The impact of the reduction temperature was studied on one catalyst with all reaction tests being conducted from the same synthesized batch. The catalyst 1Cu-2.5Zn/H-MOR was tested for DME carbonylation at the reaction conditions detailed in Section 3.3.1 with results for the production of MeOAc given in Figure 4.5. In the first reaction, the catalyst was only calcined with no reduction. In the second reaction, the catalyst was reduced at a temperature of 325°C, intended to reduce Cu²⁺ to Cu⁺ (labelled as half reduction). For the final reaction, the catalyst was reduced at a temperature of 650°C, intended to fully reduce Cu⁺ to Cu (labelled as full reduction). From the results shown in Figure 4.5, it is obvious that fully reducing the catalyst has a negative impact on its performance, showing a greatly decreased lifetime and substantially less MeOAc produced at 325°C are quite minimal, with only a minor shift in the data with regards to the time of reaction. It seems that the catalyst that is half reduced has a longer induction period compared to the catalyst that is not reduced at all. Despite this, peak and overall MeOAc

production levels were unchanged between the two. This somewhat confirms the theory that at the reaction conditions selected, if Cu^{2+} is present, the CO in the reaction gas will act as a reducing agent and reduce it to Cu^+ . The negative performance of the fully reduced sample may be due to sintering of Cu at the higher temperature, blocking some of the pores and channels. In addition to the sintering, the reduction may have caused acid sites to be created where the Cu^{2+} had been ion-exchanged. If that were the case, unselective acid sites that may have been blocked by Cu^{2+} and Cu^+ would become available again for reactions that lead to coking and subsequent catalyst deactivation.



Figure 4.5. Effect of different stages of reduction on the MeOAc productivity performance of 1Cu-2.5Zn/H-MOR in DME carbonylation.

4.3.3 TPO of selected used catalysts

To give a bit more information on the influence of the metals on the catalyst during DME carbonylation, TPO was carried out as described in Section 3.3.3. In these experiments, both the TCD signal from the Autochem and the ion signals of masses 0–75 amu in the mass spectrometer were measured. Unfortunately the TCD signal from the Autochem will include all species and is not necessarily representative of the coke that has formed on the catalyst from the reaction. Therefore, the ion signal for CO₂, 44 amu, was used from the mass spectrometer and normalized with the catalysts lifetime until deactivation in reaction (as reported in Table 4.2). The results are shown in Figure 4.6. On H-MOR, it appears that a very high temperature coke (or hard or heavy coke) has formed that required a temperature in excess of 700°C to remove. By this point the H-MOR itself would become damaged due to the high temperature. The addition of Cu^{2+}/Cu^+ to H-MOR significantly lowered the temperature required to remove the coke. The coke formed on

Cu/H-MOR may still be classified as high temperature coke, but it is significantly lighter (or softer) as it required a temperature of 400-450°C to remove. This is consistent with what has been found by other groups [295]. The coke formed on Zn/H-MOR is softer than the coke formed on H-MOR but not as soft as the coke formed on Cu/H-MOR, requiring a temperature of 600°C to fully remove it. The coke formed on the bimetallic 1Cu-4Zn/H-MOR appears to be more closely related to the coke formed on Zn/H-MOR but required a marginally lower temperature of 550°C to remove it. From these results, it may be inferred that the coke that is forming may consist of polyaromatic species that simply grow too large to desorb easily from the catalyst [260,261]. No characterization of the coke that formed was attempted and it will not be further theorized on. Regardless of the type of coke that forms, the cost associated with the ion-exchange of Cu^{2+} onto H-MOR is likely more than compensated for by the much lower temperature required for regeneration of the catalyst. Even if the presence of the ion-exchanged Cu^{2+} gave no benefit to activity or selectivity (which in the present study it did not, but in others it was shown to [92,223,232]), it would be worthwhile from the perspective of catalyst regeneration. Interestingly, Zn^{2+} , which should have minimal interaction with any of the reactants and should at the very least occupy space within the MOR framework, did not limit the weight of the coke formed to the same extent that Cu⁺ did. The Zn definitely reduces the rate at which the coke forms, and perhaps if the catalyst is regenerated before deactivation is nearly complete the coke formed will not be as heavy. However, catalyst regeneration was out of the scope of the current study. It must also be considered 1Cu-4Zn/H-MOR and Zn/H-MOR lasted much longer in reaction, giving more opportunity for coke to form and grow in weight.



Figure 4.6. TPO of selected used catalysts that had gone until full deactivation. The CO_2 ion signal from the mass spectrometer has been normalized with the catalyst reaction time.

4.4 Characterization of bimetallic Cu-Zn/H-MOR catalysts

From the TPR of calcined catalysts, reaction performance of calcined and reduced catalysts, and the TPO of spent catalysts, some very compelling observations were made. With the limited data, no real conclusions can be made aside from the fact that 1Cu-4Zn/H-MOR outshines all of the other catalysts. To more decisively determine what the roles of Cu^{2+}/Cu^+ and Zn^{2+} actually are in the catalyst and how they interact, extensive characterization must be performed. A more in depth understanding of the catalyst should allow for possible improvements to it before it finds use industrially.

4.4.1 XRD patterns of calcined catalysts

The XRD patterns of calcined H-MOR and catalysts based on H-MOR containing ionexchanged Cu^{2+} and/or Zn^{2+} were taken as described in Section 3.3.13 with results for 20 angles between 5 and 50° shown in Figure 4.7 (there were no important peaks past 50° 20). The profile for H-MOR matches the known XRD profile for H-MOR available from the IZA structure database [305,306]. From the patterns shown in Figure 4.7, it is obvious that there is very little impact on the XRD patterns due to the presence of ion-exchanged Cu²⁺ or Zn^{2+} . There are also no peaks visible due exclusively to the presence of CuO or ZnO, the primary peaks for CuO being at 35.77 and 38.77° 20 and for ZnO being at 36.14 and 34.31° 20. This is consistent with the understanding that a calcined sample of ionexchanged metal on a zeolite would not typically form XRD-visible nanoparticles of the metal itself, and instead the metal would be more atomically dispersed on the sites available for ion-exchange [167,174,233,307]. It could also be the case that the Cu or Zn is simply not present in a large enough quantity to be viewed by the XRD. For reference, if the crystallite size is below 20-30 Å, it may not be visible by XRD. Even full reduction of an ionexchanged metal on a zeolite may not produce nanoparticles of that size, given that most zeolites have pore sizes <12 Å which may restrict the size of the metal nanoparticles that are formed [95]. Instead, the presence of ion-exchanged metals may produce a shift in the XRD pattern peak positions and could be an indication of where the ion-exchanged metals are located [307,308]. However, in the present study no peak shift was observed that could be considered to be outside the error associated with the characterization (there may be minor peak shifts due to sample preparation). It could again be the case that Cu and Zn are not in high enough amounts to cause this to occur, given the approximate 55% level of ion-exchange. In fact, on first glance at Figure 4.7, it would appear that the presence of ion-exchanged metals made no impact to the XRD pattern of H-MOR. However, while the

peak positions may not have changed, one trend was observed in the relative peak intensities. The relative peak intensities of interest are summarized in Table 4.3. The ratio between the peak intensity at 29.84° 20 and the peak at 25.83° 20 shifts from 1.25 for H-MOR to 1.14 for Cu/H-MOR. The relative intensity continues to decrease with increasing Zn^{2+} content to 1.04 for Zn/H-MOR. The Miller indices for the peak at 29.84° 20 are (202) and for the peak at 25.83° 2 θ are (150). The ratio of the intensities of the other primary peaks of the XRD pattern (the peaks at 22.81° for (330), 30.57° for (350), and 32.24° for (511)) were also calculated. The other trend produced was between (202) and (511), with the ratio of intensities increasing with increasing Zn²⁺ content. For Cu/H-MOR the ratio of these two peak intensities was 2.42 and increased to 2.71 for Zn/H-MOR. The final trend observed was for the relation between (150) and (511). The relative peak intensities here again increased with increasing Zn²⁺ content, from 2.12 for Cu/H-MOR to 2.59 for Zn/H-MOR. From how much the relative intensities were altered, it is implied that there is a large degree of change in the h plane with a more minor change in the k plane with ionexchange. The directions of the *hkl* planes are shown in Figure 2.11. Interestingly, Cu does not seem to produce as great a change in either scenario, with more minor differences between the relative intensities of H-MOR and Cu/H-MOR. It is Zn^{2+} that produces the greatest degree of change in both those planes. Zn^{2+} must therefore be in a location with greater impact, perhaps in the 8-MR. Given how much smaller the 8-MR is compared to the 12-MR of mordenite (refer to Figure 2.11), the presence of an ion-exchanged transition metal would be much more strongly felt in the 8-MR. To that end, from the results it may be implied that Cu²⁺ prefers ion-exchange in the 12-MR where it has less of an impact on the overall crystallography (it would occupy much less of the volume of the 12-MR).

| Catalyst | (202)/(150) | (202)/(511) | (150)/(511) |
|---------------|-------------|-------------|-------------|
| H-MOR | 1.25 | 2.59 | 2.07 |
| Cu/H-MOR | 1.14 | 2.42 | 2.12 |
| 2Cu-1Zn/H-MOR | 1.11 | 2.51 | 2.27 |
| 1Cu-1Zn/H-MOR | 1.08 | 2.63 | 2.44 |
| 1Cu-4Zn/H-MOR | 1.09 | 2.61 | 2.39 |
| Zn/H-MOR | 1.04 | 2.71 | 2.59 |

| Table 4.3. | Relative peak | intensities | from XR | D patterns | s of Cu ²⁺ | and/or | Zn ²⁺ | ion-exchang | ed |
|------------|-----------------|-------------|---------|------------|-----------------------|--------|------------------|-------------|----|
| H-MOR cal | cined catalysts | | | | | | | | |





As visible in Figure 4.7, there are variations in the intensity of the peaks among the samples. XRD patterns were recorded for the different catalysts at different times, and minor variations in the operation of the machine may have occurred. Variations in intensity are attributed to this and will not be further theorized on here.

To eliminate some other possibilities for the reason for catalyst deactivation, the XRD pattern of a used 1Cu-4Zn/H-MOR catalyst that was completely deactivated was taken and compared against the XRD pattern for the fresh 1Cu-4Zn/H-MOR. The comparison is shown in Figure 4.8. As shown in the figure, there is nearly no crystallinity loss between the calcined and used samples. This eliminates dealumination as a possible deactivation mechanism for the catalysts (as some water was detected by the mass spectrometer during reaction, it was thought that dealumination could be a source of deactivation). There is little to no peak shift between the patterns for the calcined and used catalysts or, at least, no peak shift that could be considered to be outside the error of the XRD measurement. From the XRD pattern of the used catalyst, it would appear that the deactivation is indeed blockage of the active sites by coke deposits.



Figure 4.8. XRD patterns of calcined and used 1Cu-4Zn/H-MOR. Used 1Cu-4Zn/H-MOR did not have coke removed prior to XRD.

4.4.2 Surface area, pore volume, and pore distribution

For additional crystallographic information regarding the ion-exchanged Cu²⁺ and/or Zn^{2+} containing H-MOR catalysts, the surface area and pore volume were measured using the procedure and equipment described in Section 3.3.14. Results for surface areas and pore volumes are shown in Table 4.4. The pore size distribution of all catalysts as analyzed using the Horvath-Kawazoe (HK) method are shown in Figure 4.9. As the desire with this characterization was to effectively determine the pore size distribution from the data, full adsorption isotherms measured to P/P₀~1 were not taken. Only the micropore region was necessary, and as such it was not required to create a complete adsorption isotherm. A full isotherm would also not have been possible at the conditions tested. To have as much data created for the micropore region, a very low dose rate of Ar was used. By the time the data was created for the micropore region, the amount of liquid Ar in the dewar was already very low. It would not have been possible to create a full isotherm as the liquid Ar would have evaporated long before it could have been completed. Due to its low interactivity, using liquid Ar gives much better results for the micropore region as compared to the use of liquid N₂ [262,269,309].

Speaking quite generally, as shown in Table 4.4 the ion-exchange of Cu^{2+} and Zn^{2+} onto MOR resulted in a decrease in the Langmuir surface area. The surface area of H-MOR was determined to be 438.1 m²/g, decreasing to 428.4 m²/g for Cu/H-MOR and 414.4 m²/g for Zn/H-MOR. This trend continued with pore volume, where Zn/H-MOR had considerably
lower pore volume compared to both H-MOR and Cu/H-MOR. However, this was still only a 3.7% decrease in pore volume from H-MOR. There was hardly a decrease in pore volume between H-MOR and Cu/H-MOR. Among the bimetallics, the measured surface area seemed unique to each bimetallic combination. The bimetallic 2Cu-1Zn/H-MOR catalyst had a nearly identical Langmuir surface area compared to Cu/H-MOR, but had a 6% lower micropore volume as measured by the t-plot method. This decrease carried on to the micropore area, measured to be 383.9 m^2/q on Cu/H-MOR and 358.3 m^2/q over 2Cu-1Zn/H-MOR. The difference was in the external surface area, which increased over 58% between Cu/H-MOR and 2Cu-1Zn/H-MOR. The 1Cu-1Zn/H-MOR had a similar Langmuir surface area to Zn/H-MOR at 415.7 m^2/g , but a lower micropore volume as measured using the t-plot method. The 1Cu-1Zn/H-MOR also had a lower micropore area and higher external surface area compared to Zn/H-MOR. Despite having a large excess of Zn^{2+} over Cu^{2+} , the 1Cu-4Zn/H-MOR had very similar characteristics to Cu/H-MOR. The Langmuir surface area was measured to be identical, with only minor differences in micropore volume and in the micropore and external surface areas. However, the overall results are in good agreement with what was implied by XRD. From XRD, it seemed that Zn²⁺ had much more of an impact on the crystallography of MOR than Cu^{2+} did. This was confirmed by Ar physisorption. The pore volume as measured by the HK method did not followed the same general trend as the micropore volume measured by the t-plot method. H-MOR had the highest HK pore volume, with Cu/H-MOR and 2Cu-1Zn/H-MOR having only 1.4% lower volumes. 1Cu-1Zn/H-MOR and Zn/H-MOR had the lowest HK pore volume, being 5.4% lower than the measured pore volume of H-MOR.

| | Langmuir | | t-plot Data | Horvath-Kawazoe Data | | |
|---------------|------------------------|--|--------------------------|--|-------------------------------------|--------------------------|
| Catalyst | Surface Area (m²/g) | Micropore Volume (cm ³ /g) | Micropore Area (m²/g) | External Surface Area (m ² /g) | Pore Volume (cm ³ /g) | Median Pore Width (Å) |
| H-MOR | 438.1 | 0.149709 | 389.4 | 48.7 | 0.160789 | 6.83 |
| Cu/H-MOR | 428.4 | 0.148782 | 383.9 | 44.5 | 0.158399 | 6.84 |
| 2Cu-1Zn/H-MOR | 428.9 | 0.139957 | 358.3 | 70.5 | 0.158574 | 6.86 |
| 1Cu-1Zn/H-MOR | 415.7 | 0.140024 | 360.7 | 55.0 | 0.153273 | 6.85 |
| 1Cu-4Zn/H-MOR | 428.4 | 0.147600 | 382.9 | 45.5 | 0.157902 | 6.88 |
| Zn/H-MOR | 414.4 | 0.144205 | 375.3 | 39.1 | 0.152112 | 6.81 |
| | | | | | | |

Table 4.4. Surface area and pore volume measurements for Cu^{2+} and/or Zn^{2+} ion-exchanged H-MOR catalysts tested in DME carbonylation.

The question was therefore raised – what is the difference between Cu^{2+} and Zn^{2+} ion-exchange on MOR that causes the Zn^{2+} to have a greater impact on the crystallography? This is easily explained by the HK analyzed pore size distribution shown in Figure 4.9. The data below a pore width of 6 Å is attributable to the 8-MR channel and 8-MR side pockets while the data between pore widths of 6 and 9 Å is attributable to the 12-MR main channel. H-MOR shows very high initial adsorption of Ar, consistent with the filling of the small micropores in the 8-MR channel and 8-MR pockets. This behaviour was mimicked by Cu/H-MOR and 2Cu-1Zn/H-MOR (which both had even higher initial adsorption). However, on 1Cu-1Zn/H-MOR, this high initial adsorption was significantly reduced. The high initial adsorption returned for 1Cu-4Zn/H-MOR but was again reduced significantly on Zn/H-MOR. While Cu/H-MOR and 2Cu-1Zn/H-MOR had the same initial high adsorption in the 8-MR channel and 8-MR pockets as in H-MOR, the adsorption level in the 12-MR was reduced and caused the average pore width of the 12-MR to shift to ~6.9 Å from the ~6.8 Å pore width for H-MOR with no ion-exchanged metals. In addition to the decrease in initial adsorption, 1Cu-1Zn/H-MOR had significantly lower adsorption in the 12-MR with an average pore width of ~6.9 Å. 1Cu-4Zn/H-MOR again had similar adsorption levels compared to Cu/H-MOR and 2Cu-1Zn/H-MOR but had pushed the average pore width in the 12-MR to \sim 7.0 Å. Consistent with its initially very low adsorption of Ar below 6 Å, Zn/H-MOR again had the lowest level of adsorption in the 12-MR channels. As was implied by the XRD, it appears Zn^{2+} in higher quantities does ion-exchange in the 8-MR while Cu^{2+} does not. This does not mean Zn^{2+} does not ion-exchange in the 12-MR. It likely ion-exchanges there as well, indicated by the decreased adsorption capacity in that pore width region. It would appear from the pore size distribution analysis that Cu^{2+} does not ion-exchange in the 8-MR channels or 8-MR pockets, and instead chooses to ion-exchange preferably in the 12-MR. This is a simplified explanation. The reality of the situation may be different. Ion-exchange of metals, especially divalent metals, in a zeolite will have some effect on the zeolite framework [310–313]. A zeolite framework is flexible to an extent, and will adjust itself based on the extraframework cations present. This should certainly show itself in the pore size distribution. However, based on the decreases observed and the relative results among the catalysts, the results from pore distribution analysis indicate that Cu²⁺ ion-exchanges preferably in the 12-MR while Zn²⁺ will ion-exchange in the 8-MR channels, 8-MR pockets, and the 12-MR main channels. At least in the pore width region for the 12-MR, the channel itself does not appear to be deformed. The shape of the pore distribution curve in that region is the same for each catalyst, just shifted in position.



Figure 4.9. Horvath-Kawazoe pore distribution analysis in the micropore region for H-MOR and ion-exchanged H-MOR catalysts containing Cu²⁺ and/or Zn²⁺.

From the XRD and surface area, pore volume and pore distribution data, it is apparent that Cu^{2+} and Zn^{2+} have quite different behaviour when ion-exchanged onto MOR. While some groups may cite that the difference in ion-exchanged locations is due to the size of the ion-exchanged metal, the behaviour observed here cannot necessarily be attributed to size differences between Cu and Zn [233]. Cu and Zn are located beside one another in the periodic table, and their size is very similar. The Van der Waals radius for Cu is 140 pm and for Zn is 139 pm. The atomic radius between the two is also nearly the same at 145 pm for Cu and 142 pm for Zn. The difference in physisorption must then be related to something besides the size, likely having to do with the electronic structure of Cu^{2+} and Zn^{2+} . Interestingly, when both Cu^{2+} and Zn^{2+} are ion-exchanged together in the same solution, the ratio of Cu^{2+} to Zn^{2+} seems to have a very important influence on where the metals ion-exchange. Despite having less than 20% of the Cu^{2+} present in Cu/H-MOR as shown in Table 4.1, 1Cu-4Zn/H-MOR shows nearly the same physisorption behaviour. This also serves to partially explain the very unique behaviour in reaction this particular catalyst exhibited.

4.4.3 TEM images of calcined and spent catalysts

To give some more perspective on whether or not Cu and/or Zn nanoparticles are created on MOR in the zeolite synthesis, TEM images were taken of both the calcined and the deactivated (spent) catalysts. These are shown in Figure 4.10. The TEM images of H-MOR with no metals ion-exchanged did not show significant differences between the calcined and spent catalyst and are not shown. On calcined Cu/H-MOR, there are some very small nanoparticles of Cu visible (<5 nm in diameter). However, given the nanoparticle size, it is likely that they are formed on the external catalyst surface. Regardless, after reaction, TEM images of Cu/H-MOR showed significant sintering of Cu into larger clusters on the surface of the crystal. Excessive Cu sintering on Cu/H-MOR would lead to even faster deactivation of the catalyst compared to H-MOR as the larger Cu clusters would block the channels of MOR. As was stated earlier, on MOR it does not take much blockage before an entire channel becomes unusable for reaction [234]. On calcined 2Cu-1Zn/H-MOR, it appeared that the Cu and/or Zn nanoparticles that are shown in the TEM image are more highly distributed and smaller, perhaps indicating a higher dispersion of Cu. On the spent 2Cu-1Zn/H-MOR, compared to Cu/H-MOR, there has not been as great a degree of sintering of the metals into larger nanoparticles, indicating even the small amount of Zn²⁺ has helped to stabilize the Cu⁺. Calcined 1Cu-1Zn/H-MOR shows some small nanoparticles with a more uniform size distribution, though there are very few and it does not appear that they are on the surface. The real change between 2Cu-1Zn/H-MOR and 1Cu-1Zn/H-MOR is on the spent catalyst. On spent 1Cu-1Zn/H-MOR, there are hardly any metal clusters visible. Calcined 1Cu-4Zn/H-MOR again showed small metal clusters, but they were highly uniform in size and did not appear to be on the surface. In fact, it appears as if the metal clusters are lined up, showing the channel system of the MOR. While these may appear to be small nanoparticles, it is highly likely the TEM image is just showing the ion-exchanged metals. On the spent 1Cu-4Zn/H-MOR, there are no metal clusters visible at all. Whatever sintering behaviour Cu⁺ has previously shown on H-MOR has been completely suppressed by the presence of Zn^{2+} . Spent Zn/H-MOR was very much the same as spent 1Cu-4Zn/H-MOR, while calcined Zn/H-MOR seemed to have some larger clusters of Zn.





Zn/H-MOR Spent



The TEM images taken of the catalysts have very important implications for Cu/H-MOR catalysts. In one of the original patents from BP Chemicals Ltd. on DME carbonylation with H-MOR, it was shown that regenerated Cu/H-MOR did not give the same activity as the original fresh catalyst [223]. It is apparent that that behaviour is likely due to sintering of Cu metal, which is not redistributed in the regeneration process and continues to block channels in the next reaction cycle. While a considerable amount of Zn (at least equimolar or in molar excess) is required, it is highly beneficial as in fresh catalysts it appears to increase the dispersion of Cu or, at the very least, force it further apart from each other on the zeolite framework. The Zn maintains the dispersion of Cu during the reaction, and likely means that Cu has been stabilized in its monovalent state. This was also shown in the H₂-TPR results for the Cu²⁺ and/or Zn²⁺ ion-exchanged H-MORs.

4.4.4 DME adsorption and desorption

The analysis of the interaction of DME with a zeolite is important from several perspectives. In the present case, it is important to have a better understanding of how one of the reactants interacts with the catalyst, including how much is adsorbed and at what temperature it desorbs. In addition to this information, it should also reveal how many acid sites are actually accessible to DME and if there are any sites that are not utilized. It has been discussed that, theoretically, DME should interact with acid sites on a zeolite to ultimately produce methyl groups and water with a MeOH intermediate [82,83,90,137,201,212,215–217,314]. MeOH is more reactive with a zeolite and should more favourably form a methyl group and water [206–208]. From the characterization procedure as described in Section 3.3.4, it should be possible to calculate the amount of methyl groups created from the difference between the DME adsorbed and subsequently desorbed. While there are other means that this may be done, such as DME titration [314], the mass spectrometer used in this study did not prove to be sensitive enough to conduct titration of the acid sites by small pulsed injections of DME. In titrations, desorption would still need to be conducted in order to remove any physisorbed unreacted DME that would otherwise unintentionally be used in the calculation of the number of accessible acid sites. The number of acid sites that were methylated was calculated in this study assuming one molecule of DME will create two methyl sites (which would require two Al to be in the framework). If MeOH was detected in either the adsorption or desorption stage, the amount of MeOH was removed from the number of acid sites. See Equations 2.5 and 2.6 for the reaction schemes by which DME will create two methyl groups (or methoxy sites).

There were many sources of error in these experiments and they were compensated for as much as was possible. Correction was applied to the final results for the empty tube volume, intended to compensate for the initial filling of the system volume with the DME gas mixture. It was desired to track MeOH as well, however this was expected to be in low amounts and only the primary mass of 31 was thought to be useful for this purpose in the mass spectrometer. This mass is also one of those peaks associated with DME in the mass spectrum. The peaks were therefore deconvoluted but a source of error here still remains. Variations in the flow rate from day to day also had the potential for drastically affecting the results. For example, a 5% change in DME gas flow rate results in an equivalent 5% change in the calculation of the active sites populated. The flow rate of DME was therefore calibrated each day immediately before the characterization to eliminate this source of error. The mass spectrometer was also calibrated prior to each test and corrected for the variations in the baseline signal from day to day. Dependent on the perceived reliability, DME adsorption and desorption was repeated with fresh catalyst until consistent results were yielded. In early tests, catalysts from the same batch were run up to 4 times in order to ensure the procedure produced consistent results.

Results for the amounts of DME adsorbed, desorbed, and unaccounted for are presented in Table 4.5. The MeOH produced and the theoretical number of acid sites that are methylated is also presented in Table 4.5. No MeOH was detected in the desorption stage of the characterization and only very small amounts of it were detected in the adsorption stage. The amounts produced are likely not outside the error of the signals in the mass spectrometer but were still considered in the calculation of the number of acid sites methylated. The amount of MeOH produced seemed to be higher for the bimetallic Cu-Zn/H-MOR catalysts that contained equimolar or higher amounts of Cu⁺. The results for MeOH produced are consistent with the theory that MeOH will react more readily with an acid site on MOR compared to DME [206-208]. From Table 4.5, it is apparent that the ionexchanged metals, especially Zn²⁺, decreased the amount of DME adsorbed and, subsequently, the amount of DME desorbed. The bimetallic catalysts 2Cu-1Zn/H-MOR and 1Cu-1Zn/H-MOR actually behaved very similarly in these characterizations, adsorbing nearly the same amount of DME and desorbing very similar amounts of DME (only a 3.7% difference in desorption amounts, which could easily be within the error associated with the experiments). The amount of unaccounted for DME was nearly identical between these two catalysts. Among the metal ion-exchanged catalysts, Cu/H-MOR had the highest amount of DME adsorbed and desorbed. On Zn/H-MOR, the amount of DME adsorbed was ~14% less compared to Cu/H-MOR and the amount of DME desorbed was ~54% less. Despite these

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differences, Cu/H-MOR and Zn/H-MOR had very similar levels of unaccounted for DME. H-MOR had the highest level of unaccounted for DME, being 8% higher than the average for the ion-exchanged H-MOR catalysts. Among the ion-exchanged H-MOR catalysts, only 1Cu-4Zn/H-MOR had a somewhat distinct level of unaccounted for DME, being ~7% less than the other catalysts. To ensure this was a true result, this characterization was repeated 3 times for the 1Cu-4Zn/H-MOR catalyst.

| Table 4.5. | Amounts of DME adsorbed, | desorbed, and | d unaccounted | for over | Cu^+ | and/or Zn ²⁺ | ion-exchanged | H-MOR catalysts |
|------------|-----------------------------|-----------------------------|---------------|----------|--------|-------------------------|---------------|-----------------|
| along with | the theoretical number of a | cid sites meth [,] | ylated. | | | | | |

| Catalyst | Total DME Adsorbed | | Total MeOH Produced | | Total DM | 1E Desorbed | Unaccounted for DME | Acid sites methylated |
|---------------|-----------------------|---------------------------------------|-----------------------|---------------------------------------|-----------------------|---------------------------------------|---------------------------------------|--------------------------|
| | µmol/g _{cat} | mol _{DME} /mol _{Al} | µmol/g _{cat} | mol _{DME} /mol _{AI} | µmol/g _{cat} | mol _{DME} /mol _{Al} | mol _{DME} /mol _{Al} | % |
| H-MOR | 1054.1 | 0.557 | 4.85 | 0.003 | 311.7 | 0.165 | 0.392 | 78.1 |
| Cu/H-MOR | 922.9 | 0.528 | 7.27 | 0.004 | 292.5 | 0.167 | 0.360 | 71.6 |
| 2Cu-1Zn/H-MOR | 900.7 | 0.525 | 26.37 | 0.015 | 269.9 | 0.157 | 0.367 | 71.9 |
| 1Cu-1Zn/H-MOR | 902.5 | 0.516 | 16.35 | 0.009 | 259.1 | 0.148 | 0.368 | 72.7 |
| 1Cu-4Zn/H-MOR | 859.6 | 0.485 | 7.12 | 0.004 | 255.1 | 0.144 | 0.341 | 67.8 |
| Zn/H-MOR | 792.2 | 0.443 | 0 | 0 | 135.6 | 0.076 | 0.368 | 73.6 |
| | | | | | | | | |

The trend observed in the DME adsorption and desorption levels is consistent with the thinking that Zn^{2+} does more to block active sites as compared to Cu⁺. Prior to these characterizations, the catalyst was reduced so that Cu²⁺ became Cu⁺. It has been previously mentioned and shown by TPR that ZnO does not necessarily reduce in the presence of H₂ at the temperature of reduction used for the catalysts in the present study [299,300]. With similar ion-exchange levels as shown in Table 4.1, Cu⁺ would only block half as many acid sites as Zn^{2+} . This is especially shown in the levels of DME adsorbed with respect to the amount of Al in the Cu/H-MOR and Zn/H-MOR catalysts. However, this did not necessarily translate the same way in the amounts of DME desorbed. The amounts of DME desorbed between H-MOR and Cu/H-MOR were not substantially dissimilar with only a 6% difference between them. It could be possible that Cu⁺ has some interaction with DME, which would certainly explain the very similar levels of DME desorbed on all bimetallic Cu-Zn/H-MOR catalysts.

This site blockage issue with Zn²⁺ must be discussed further, given the calculation of the acid sites methylated and shown in Table 4.5. Based on the unaccounted for DME and the MeOH produced, it appears that 78.1% of acid sites are methylated on H-MOR. This is reasonable, as some acid sites may be in locations not easily accessible to DME. Interestingly, the acid sites methylated on Zn/H-MOR is 73.6%, despite that 52.2% of the sites are involved in the ion-exchange. The only substantially different value for the acid sites methylated among the catalysts is for 1Cu-4Zn/H-MOR with a slightly lower value of 67.8%. The theory that the unaccounted for DME will populate two acid sites with methyl groups did not seem to hold true here. Especially on Zn/H-MOR, if 52.2% of the acid sites are blocked with Zn^{2+} , the DME should not be able to populate 73.6% of the acid sites with methyl groups. Instead, the level of unaccounted for DME itself may be a better indication of the actual active sites for DME carbonylation. This showed only a moderate decrease from H-MOR to metal ion-exchanged H-MORs, and could serve as an indication that the metals are ion-exchanging onto acid sites that do not normally have a strong interaction with DME anyways. There are several implications of this. It could be that these experiments were not conducted long enough for DME to suitably methylate the active sites, which may explain the long induction period observed during reactions. The results could also be an indication of metal sintering and freeing of acid sites, which is unlikely given the results from TEM. It is to be noted that water was detected during the desorption stage of the experiments, which based on the reactions shown in Equations 2.5 and 2.6, could be an indication that DME has indeed methylated some of the acid sites.

For the catalysts in this study, DME was desorbed in a stepwise manner with results shown for the levels of DME desorption in each temperature range in Figure 4.11. For all catalysts, the majority of molecular DME was desorbed in the temperature range 160°C to 210°C (recall that DME adsorption was conducted at 210°C). For H-MOR, only a small amount of DME was desorbed in the range 210-250°C and none at higher temperatures. The TPD of DME from Zn/H-MOR was very much the same as H-MOR, just with smaller amounts of DME desorbed. The TPD of DME from Cu/H-MOR was somewhat different. With this catalyst, much more of the molecular DME was desorbed at the higher temperature ranges with some even desorbing at 250-300°C. This behaviour continued with the bimetallic Cu-Zn/H-MOR catalysts, with small amounts of DME requiring temperatures in excess of 300° C to desorb. With the Cu⁺-containing H-MOR catalysts, in addition to the levels of DME adsorption decreasing, the DME also appears to be more strongly adsorbed as unreacted molecules. This serves to potentially explain the impact Cu⁺ has on the formation of coke during DME carbonylation as shown in Section 4.3.3. Cu⁺-containing H-MOR catalysts produced lighter (or softer) coke than both H-MOR and Zn/H-MOR. If DME is more strongly adsorbed as a whole molecule, it would be less inclined to participate in coking reactions since it is more stable. It may then be more likely to participate in DME carbonylation as opposed to contributing to the coking. While the presence of Cu^+ does not stop the coking from occurring over H-MOR, it does substantially limit the coke formed to lower weights. Zn^{2+} , on the other hand, likely limited the amount of DME that adsorbed. Both effects combined would explain the stability increase shown by the bimetallic Cu-Zn/H-MOR catalysts.



Figure 4.11. Amounts of DME desorbed in different temperature ranges over H-MOR catalysts containing ion-exchanged Cu⁺ and/or Zn²⁺.

4.4.5 CO TPD and isotherms

The interaction of the reactant CO with the catalysts was evaluated using both CO adsorption and desorption. CO TPD was carried out according to the procedure detailed in Section 3.3.5. CO TPD results were not used to evaluate the dispersion of Cu on the catalyst, as the difference between chemisorbed and physisorbed CO could not be discerned. This issue was also apparent when attempting to perform CO chemisorption experiments with pulsed CO. Due to competing physisorption and chemisorption, CO adsorption isotherms were carried out as described in Section 3.3.6, measured at both 30°C and 200°C. CO isotherms at 30°C could not be used for determination of Cu dispersion as it appeared physisorption and chemisorption were still competing, and as such the data for those isotherms will not be presented here. Using data from the CO isotherms measured at 200°C appeared to be far more useful for differentiating chemisorbed and physisorbed CO.

Results regarding the interaction of each catalyst with CO are presented in Table 4.6 for both CO TPD and isotherms. The values for the different temperatures at which CO desorbed were obtained from peak deconvolution using Origin software. The CO TPD TCD signals are shown in Figure 4.12 for each catalyst. For the bimetallic catalysts, the deconvoluted CO TPD signals are shown in Figure 4.13. The adsorption of CO as measured by CO isotherms is shown in Figure 4.14. Interestingly, H-MOR and Zn/H-MOR did have some interaction with CO. From TPD measurements, the level of CO adsorbed was very nearly the same on those two catalysts, which served to indicate that Zn²⁺ likely had no interaction with CO. However, from isotherms, it was predicted that there was much higher physisorption of CO on Zn/H-MOR compared to H-MOR, shown very prominently in Figure 4.14. This in part has to do with the sources of CO used for the experiments. For the CO isotherms, a 99.5% pure source of CO was used, while for the CO TPD experiments the source of CO was a 3% CO/He mixture. It could be the case that some physisorption of CO due to ZnO does occur, but requires CO to be at a higher partial pressure in the gas mixture. Another difference between H-MOR and Zn/H-MOR is the temperatures at which the CO desorbs. For H-MOR, all of the CO desorbs at a temperature of 357°C, while on Zn/H-MOR 15% of the CO desorbs at 143°C while the rest desorbs at 491°C. Whatever the interaction of CO may be with H-MOR, Zn^{2+} has obviously altered it considerably. With regards to the Cu⁺-containing H-MOR catalysts, the amount of CO adsorbed/desorbed was commensurate with the amount of Cu^+ contained in the catalyst. Cu/H-MOR had the

highest level of CO adsorbed, with most of the CO desorbing from it at 389°C and the remaining ~36% desorbing at 485°C. The behaviour of the bimetallics in CO TPD is quite interesting, as they did not seem to produce a trend with regards to Cu content. With the lowest amount of Zn^{2+} , 2Cu-1Zn/H-MOR showed increased desorption temperatures of 418°C and 487°C with the majority of CO desorbing at 418°C. With 1Cu-1Zn/H-MOR, both the medium and high temperatures of desorption decreased by an average of 27°C compared to 2Cu-1Zn/H-MOR. However, on 1Cu-1Zn/H-MOR more than 75% of the CO was desorbed at the higher temperature with the remaining less than 25% desorbed at the medium temperature. This is the reverse of what occurred on the 2Cu-1Zn/H-MOR. Increased Zn²⁺ content on 1Cu-4Zn/H-MOR created a low temperature desorption peak at 138°C, although only 1.6% of adsorbed CO was desorbed at this temperature. The trend again reversed between 1Cu-1Zn/H-MOR and 1Cu-4Zn/H-MOR for at what temperature most of the CO desorbed. The medium desorption temperature for 1Cu-4Zn/H-MOR was the same as for 1Cu-1Zn/H-MOR, but more than 78% of the adsorbed CO was desorbed at this point. The high temperature desorption peak for 1Cu-4Zn/H-MOR was 23°C higher than that of 1Cu-1Zn/H-MOR, and accounted for approximately 20% of the CO desorption. As was stated earlier, there is not a consistent trend in the temperatures at which the bulk of CO desorbs among the Cu-containing catalysts, which may serve as an indication that not all of the Cu^+ and Zn^{2+} may interact indirectly with each other through the MOR framework in the bimetallic Cu-Zn/H-MOR catalysts. It may be the case that some of the Cu⁺ and Zn²⁺ do interact more directly with each other. The measured dispersion Cu on Cu/H-MOR was 42.2%, while for the bimetallics it was more or less consistent at an average 62.7%.



Figure 4.12. CO TPD profiles for H-MOR catalysts containing Cu⁺ and/or Zn²⁺.

Table 4.6. Total CO adsorbed and Cu dispersion as measured by isotherms and total CO desorbed in each temperature zone as measured by TPD.

| | Total CO Adsorbed | | Desorpt | | | | | | |
|---------------|-------------------|----------|---------|--------|--------|--------|--------|--------|------------|
| Catalyst | (mmol CO/g) | | Low | | Medium | | High | | Dispersion |
| | From | From | | CO Amt | | CO Amt | | CO Amt | of Cu (%) |
| | TPD | isotherm | T (*C) | (%) | T (°C) | (%) | T (°C) | (%) | |
| H-MOR | 0.067 | 0.034 | - | - | 357 | 100.0 | - | - | - |
| Cu/H-MOR | 0.799 | 0.722 | - | - | 389 | 64.3 | 485 | 35.7 | 42.2 |
| 2Cu-1Zn/H-MOR | 0.604 | 0.600 | - | - | 418 | 71.4 | 487 | 28.6 | 62.5 |
| 1Cu-1Zn/H-MOR | 0.422 | 0.441 | - | - | 384 | 24.5 | 468 | 75.5 | 63.6 |
| 1Cu-4Zn/H-MOR | 0.178 | 0.270 | 138 | 1.6 | 384 | 78.6 | 491 | 19.8 | 62.0 |
| Zn/H-MOR | 0.069 | 0.164 | 143 | 15.2 | - | - | 491 | 84.8 | - |



Figure 4.13. Peak deconvolution of the CO TPD TCD signal for the bimetallic Cu-Zn/H-MOR catalysts.



Figure 4.14. CO isotherms measured at 200°C for H-MOR catalysts containing Cu⁺ and/or Zn^{2+} .

From Figure 4.13, the interesting behaviour of the bimetallic Cu-Zn/H-MOR catalysts can be more easily observed as opposed to from data in a table. The 2Cu-1Zn/H-MOR had much more in common with Cu/H-MOR compared to the other bimetallics, which was also observable in Figure 4.12. This implies that there may be minimal interaction between Cu and Zn at that ratio. The behaviour is completely different when Cu⁺ and Zn²⁺ are at equimolar amounts (1Cu-1Zn/H-MOR), implying that now Cu⁺ and Zn²⁺ are having more of an impact on each other. With the CO adsorbed amount being lower (due to lower Cu⁺ content), most of the CO is now desorbed at 468°C with a more minor amount desorbed at 384°C. What is quite interesting, and wasn't immediately visible from Table 4.6, is that the

amount desorbed at 384°C is quite similar between 1Cu-1Zn/H-MOR and 1Cu-4Zn/H-MOR. Between the two catalysts, only the amount of CO desorbed at the higher temperature appears to have decreased with the increasing Zn²⁺ content, leaving the CO desorbing at 384°C the same. This certainly implies that Cu⁺ is occupying different ion-exchange locations on MOR, and the increased amount of ion-exchanged Zn²⁺ between 1Cu-1Zn/H-MOR and 1Cu-4Zn/H-MOR is simply forcing Cu²⁺ to ion-exchange only at its more preferable locations. Zn²⁺ likely does adsorb some small amount of CO, but this is limited to physisorption as implied by the CO isotherm shown in Figure 4.14.

As mentioned in Section 2.2.4, zeolites are often used as a means to producing very small and somewhat uniform in size nanoparticles through ion-exchange [174]. This was not the intent of the current study, where it was desired to leave Cu⁺ at ion-exchange locations and keep it atomically dispersed. From the dispersion measured by CO isotherms, it is likely that much of the Cu may be atomically dispersed. For all that a zeolite can do with regards to ion-exchange, just because a metal is ion-exchanged does not mean it is fixed in place [308,315–320]. The metals do migrate and can form nanoparticles if given the right conditions. Given the pretreatment, small Cu nanoparticles do likely form, indicated by the lower than 100% Cu dispersion on Cu/H-MOR. The presence of Zn^{2+} appears to help stabilize Cu^+ against sintering in all cases, with a very consistent 62-64% dispersion of Cu on the bimetallic Cu-Zn/H-MOR catalysts. Pretreatment at milder or more controlled conditions may mean the Cu⁺ could be more highly dispersed [232]. Variation of the pretreatment conditions was outside the scope of the current study. However, there are potentially other reasons why the dispersion is not 100%. As indicated by TPR, at the reduction conditions selected perhaps not all of the Cu²⁺ has been reduced to Cu⁺, especially on 1Cu-4Zn/H-MOR. As it is Cu⁺ that is active for CO chemisorption, incomplete reduction of Cu^{2+} to Cu^{+} would give a falsely lower value for Cu dispersion [278– 281,293,294].

4.4.6 NH₃-TPD

A quite often used measure of the relative and absolute acidity of zeolites is the adsorption and succeeding desorption of NH₃. Given the relatively small size of NH₃, it can reach nearly every point of a zeolite framework. Consequently, without detailed and thorough mathematical treatments of the TPD profile, typically through peak deconvolution methods, it is nearly impossible to differentiate the different acid sites on the zeolite. However, even by these methods, error will be introduced as the individual peaks for different acid sites will superimpose on each other. It may also be possible to combine the

TPD with further simultaneous characterization or modeling work to differentiate between the different Al locations [321-324]. However, these processes can be rather complex and the value of the information obtained may not be worth the time and effort required. In the present study, the desorption of adsorbed NH₃ was used as an overall indication of the acidity, as well as an indication of possible site blockage due to the presence of ionexchanged metals.

The amounts of adsorbed/desorbed NH₃ for the low temperature and high temperature NH_3 -TPD regimes are shown in Figure 4.15. To more accurately represent the acidity of the zeolite and any potential site blockage, the amount of NH₃ is presented relative to the amount of Al in the catalyst (this also normalizes the results). The raw TCD signal from the NH_3 -TPD tests is shown in Figure 4.16. The apex of the TPD curves (the peak T) for each region is shown in Figure 4.17. The low temperature and high temperature regions were defined as below and above 400°C and were based on analysis of the raw TPD profiles. This is consistent with what other groups have observed [322,325,326]. Due to the stability of mordenite at high temperatures, data past 700°C should be considered to be potentially inaccurate [282-284]. Quantification of results proceeded via curve fitting of both the low temperature region and high temperature region TPD signals. The area was then calculated under these curves and, used together with the calibration of the TCD signal for NH_3 content, the amount of desorbed NH_3 was determined. The NH_3 in the low temperature region is assumed to be very weakly physisorbed to parts of the framework and is not necessarily an indication of the zeolite acidity. However, from Figure 4.15, it is obvious that the presence of ion-exchanged metals increased this physisorbed NH₃. This is potentially due to adsorption of NH₃ on the ion-exchanged metals themselves and not necessarily changes to the electron density of the zeolite framework [327–329]. In fact, if it is considered that one NH_3 molecule adsorbs on one Cu^+ , and if the dispersion of Cu in Cu/H-MOR as shown in Table 4.6 is considered, the amount of low temperature NH_3 adsorbed on Cu/H-MOR is 1.57 mol NH₃/(mol Al+mol Cu) while the value for adsorption of low temperature NH₃ on H-MOR is 1.55 mol NH₃/mol Al. For monometallic Zn/H-MOR, if the same calculation is performed assuming a 100% dispersion of Zn, the amount of low temperature NH₃ adsorbed is 1.64 mol NH₃/(mol Al+mol Zn). It is obvious from Figure 4.15 that Zn/H-MOR has a much greater affinity for physisorbed NH₃ than Cu/H-MOR, though this could be due to metal dispersion and not simply alteration of the H-MOR framework electron density. This is merely a theory, and it is likely both factors come into play. The TCD signals for Cu/H-MOR and 2Cu-1Zn/H-MOR during the TPD show an obvious shoulder in the low temperature peak at ~217°C that was not present with H-MOR, which may indicate

physisorbed NH₃ on Cu⁺ centres. The Zn/H-MOR and 1Cu-4Zn/H-MOR had a shoulder in the low temperature peak at ~332°C. Again, this shoulder was not present with H-MOR, and is likely due to physisorbed NH₃ on Zn²⁺. With the bimetallic Cu-Zn/H-MOR catalysts, the amount of low temperature adsorbed NH₃ increases with increasing ZnO content.



Figure 4.15. Amounts of NH_3 adsorbed/desorbed in the low temperature and high temperature regions during NH_3 -TPD for H-MOR and ion-exchanged Cu⁺ and/or Zn²⁺ H-MORs.



Figure 4.16. Raw TCD signals from each NH_3 -TPD characterization of H-MOR and ionexchanged Cu⁺ and/or Zn²⁺ H-MORs.

The high temperature adsorbed NH_3 is a different story. Over H-MOR, the amount of high temperature adsorbed NH_3 (hereafter referred to as chemisorbed NH_3) was 1.92 mol NH₃/mol Al. The presence of nearly 2 moles of NH₃ adsorbed per mol of Al is due to the theorized formation of NH_4^+ $\cdot nNH_3$ associations [330,331]. The amount of chemisorbed NH_3 did not change much with Cu^{2+} ion-exchange. This is likely due to Cu^{2+} being reduced to Cu⁺, which should mean only ~28% of acid sites are blocked by Cu. This would certainly not account for the lack of a decrease in NH_3 chemisorption, but the possibility also exists that NH_3 is chemisorbed to Cu^+ . This would compensate for a potential decrease in the number of zeolite acid sites accessible to the NH₃. The level of chemisorbed NH₃ decreased on Zn/H-MOR to 1.70 mol NH₃/mol Al. This implies that Zn^{2+} has done more to block acid sites than Cu⁺ has, again stemming from its inability to reduce at the reduction conditions in the study [299,300]. However, even though Zn^{2+} has blocked ~52% of zeolite acid sites, the level of NH₃ chemisorption has not decreased appropriate to that blockage. Again, this implies that there is some chemisorbed NH_3 on ZnO (or, if not chemisorbed, requires temperatures in excess of 400°C to desorb). The possibility does exist, though, that multiple NH₃ molecules could be adsorbed in the $NH_4^+ \cdot nNH_3$ associations. These groups could have sterically limited each other prior to metal ion-exchange. With Cu^+ or Zn^{2+} blocking some acid sites, this may decrease this limitation and >2 NH₃ molecules could be chemisorbed to one zeolite acid site location. No further investigation was conducted to determine if this was the case. With the bimetallic Cu-Zn/H-MOR catalysts, 2Cu-1Zn/H-MOR had a higher amount of chemisorbed NH_3 than Cu/H-MOR. The difference was not necessarily outside the error of the experiments, and should not be considered to be substantially different. The level of chemisorbed NH_3 decreased with increasing Zn content.

The impact of Cu⁺ and Zn²⁺ ion-exchange onto H-MOR had a very significant impact on the desorption temperatures in both the low temperature and high temperature regions. For clarification, the temperatures reported in Figure 4.17 are the temperatures at which the highest amount of NH₃ was being desorbed from the catalyst. Quite generally, the required temperature of desorption increased from H-MOR for all ion-exchanged H-MOR catalysts. Cu/H-MOR showed the largest increase in desorption temperature, being 32°C higher for the low temperature desorption and 49°C higher for the high temperature desorption over H-MOR. For Zn/H-MOR, the increase was much more moderate over H-MOR, with only a 12°C higher desorption temperature in the low temperature region and 7°C higher in the high temperature region. With the bimetallic Cu-Zn/H-MOR catalysts, the desorption temperatures decreased with increasing Zn content. Between 1Cu-4Zn/H-MOR and Zn/H-MOR, the required desorption temperatures cannot be considered to be outside the experimental error of each other (only a 3-6°C difference). The increase in desorption temperature could be due to blockage of acid sites by the ion-exchanged metals. If the ion-exchanged metals were to block the weaker acid site locations of H-MOR, the overall desorption temperature may appear higher. The higher desorption temperatures are also likely due to differing MOR framework characteristics, potentially electron density shifts, due to the ion-exchanged metals.



Figure 4.17. Peak desorption temperatures in the low temperature and high temperature regions of NH_3 -TPD of H-MOR and ion-exchanged Cu⁺ and/or Zn²⁺ H-MORs.

4.4.7 Py-TPD

Adsorption and subsequent desorption of pyridine (Py) has been done for decades for zeolites for much the same purpose as NH₃-TPD – determination of absolute and relative acidity. However, Py-TPD is a bit trickier than NH₃-TPD. A Py molecule is significantly larger than an NH₃ molecule, and as such it can only access a portion of the acid sites on MOR (and for that matter, many other zeolites). For MOR, it is generally believed Py can access acid sites located in the 12-MR main channel and in the interconnecting 8-MR side pockets of MOR. It is not typically thought that Py can access the 8-MR of MOR, though some evidence indicates that, given enough time, it may be able to diffuse to those locations as well [218,219,254,332]. It has been well studied and is generally known that the rate-limiting step of Py chemisorption on a zeolite is diffusion and not the actual interaction of Py with acid sites, which is relatively quick [332,333]. Given that, in the present thesis, the adsorption of Py was carried out at ~60°C for a period of an hour, it may

be assumed that the Py adsorbed is more representative of the 12-MR and the 8-MR interconnecting side pockets and is not necessarily reflective of the 8-MR channel. However, this is an assumption and no evidence will be presented to support it.

The raw TCD results from Py-TPD, carried out as detailed in Section 3.3.8, are shown in Figure 4.18 for H-MOR and Cu^+ and/or Zn^{2+} ion-exchanged H-MORs. The Py that is desorbed at low temperatures (<400°C) may be assumed to be physisorbed Py and may not be properly indicative of the acid sites of MOR [218,334]. Quantitative evaluation of the results from Py-TPD proved to be quite difficult for the present study on H-MOR catalysts containing ion-exchanged Cu⁺ and/or Zn²⁺ and was not attempted. This was for several purposes. Due to the difficult diffusion of Py in MOR, very high temperatures (in excess of those required for NH_3 removal) are required to desorb Py. At these high temperatures, as in the NH₃-TPD study, the MOR framework can be potentially damaged and the TCD signal observed may not be solely due to desorbing Py [282-284]. Another reason for not quantifying the data is the treatment of the samples. While the procedure outlined in Section 3.3.8 was followed for each catalyst, minor changes in the procedure may have occurred that could have affected Py adsorption levels. It should also be noted that the sample, after Py adsorption, was exposed to the lab atmosphere which contained water vapour. Zeolites quickly adsorb any water present, and desorption of this water upon TPD will alter the TCD signal. Based upon the TPD curves shown in Figure 4.18, it was difficult to ascertain how quantification should be done. Obviously desorption of Py is not finished, even at 800°C. While for H-MOR the amount of Py that would desorb at those high temperatures could be estimated based on curve fitting and assuming a typical Gaussianstyle curve, the TPD of Py was so substantially different over Cu⁺ and/or Zn²⁺ ionexchanged H-MOR samples (see Figure 4.18) that it made estimation of the Py amount quite difficult. It also appeared from the metal ion-exchanged H-MOR catalysts that desorption of physisorbed and chemisorbed Py could not necessarily be differentiated. While H-MOR by itself provided a very nice distinction, the other catalysts did not. It is obvious from the data that several peaks could be deconvoluted from the data over metalexchanged H-MOR, but this data would have little value and meaning in the context of the current study.



Figure 4.18. Raw TCD signals from each Py-TPD characterization of H-MOR and ionexchanged Cu^+ and/or Zn^{2+} H-MORs.

While quantitative evaluation of the Py-TPD results proved too difficult for the perceived benefit of having it, qualitatively the data is incredibly useful. From Figure 4.18 it is obvious that there is a substantial decrease in the total Py uptake between H-MOR and the metal-exchanged H-MORs (based on area under the curves). This could mean that the channels are blocked by metals, especially any metal nanoparticles that may have formed. Metals that are ion-exchanged and blocking acid sites will also prevent Py chemisorption (and potentially physisorption). However, pore distribution analysis showed that the 12-MR main channels were not completely blocked, and were, in the worst case, just obstructed. The large changes in Py uptake are hence not likely due to blockage of the channels by nanoparticles. The Py-TPD results are more likely indicative of metal ion-exchange blocking some acid sites and the altered acidity of the remaining available sites. Each metalexchanged H-MOR sample acts quite differently in Py-TPD. As was seen with Cu/H-MOR in NH_3 -TPD, it would appear that the acidity of remaining acid sites has increased as even at 800°C desorption of chemisorbed Py has not completed (has not even climaxed). While the same could be said for the other metal-exchanged H-MOR catalysts, Cu/H-MOR was also distinct in that, more than any of the other catalysts, it showed no delineation between physisorbed and chemisorbed Py. The uniqueness between Cu/H-MOR and Zn/H-MOR shows that the two metals interact with the MOR very differently, likely both in acidity and in ion-exchange location. The bimetallic Cu-Zn/H-MOR catalysts have incredibly varied responses in Py-TPD. For 2Cu-1Zn/H-MOR, it appears that there are several unique high

temperature desorption peaks. 1Cu-1Zn/H-MOR seems to have several unique peaks as well, but in substantially different locations from 2Cu-1Zn/H-MOR. The behaviour of 1Cu-4Zn/H-MOR seems to have much in common with Zn/H-MOR, which is not surprising due to the high Zn content. Both have an initially much higher level of physisorbed Py, which could indicate some weak interaction of Py with ZnO. With 1Cu-4Zn/H-MOR, it appears that physisorbed Py is removed even at ~500°C, although this could potentially be a combination of physisorbed and weakly chemisorbed Py. Regardless of the accuracy of the results for Py-TPD, what is shown by the data is a substantially different interaction of the ion-exchanged metals with the MOR. The NH₃-TPD showed a general increase in acidity with Cu and Zn ion-exchange. The results from Py-TPD are in agreement with this, but more aptly show that Cu⁺ and Zn²⁺ affect Py adsorption in significantly different ways. This is most likely due to different ion-exchange locations of the two metals, given that even a very small obstruction in the channels of MOR has the potential to greatly influence the diffusion of Py into the framework of MOR (due to the bulky size of Py).

4.4.8 Py-DRIFTS

Pyridine may offer some other insights aside from the overall acidity of the zeolite. Pyridine will chemisorb differently onto a Lewis acid site and a Brønsted acid site as outlined in Section 3.2 [271]. Py-DRIFTS with MOR has been well studied and enough work has been done that the contribution of Brønsted acid sites (BAS) and Lewis acid sites (LAS) can be separated and an approximate ratio developed between the two based on peak areas [218,219,270,335,336]. The three peaks of interest for Py-TPD over H-MOR occur at ~1545 cm⁻¹ for BAS, ~1490 cm⁻¹ for both LAS and BAS, and ~1450 cm⁻¹ for LAS. Typically, only the 1545 cm⁻¹ and 1450 cm⁻¹ are used for direct quantitative comparison of the number of BAS and LAS. Using what are referred to as molar extinction coefficients, an approximate ratio of the number of BAS to LAS can be determined, though this will not be done for the present work. As was mentioned in the previous section on Py-TPD and what is known for H-MOR and Py chemisorption, the chemisorbed Py is not necessarily indicative of all of the acid sites of MOR and, in the Py-TPD, the amount of chemisorbed Py could not be determined to within any level of accuracy and only a qualitative discussion was made [169,218,219,332]. The discussion on the results of Py-DRIFTS will again be limited to a qualitative discussion with only the very obvious trends addressed.

The results from DRIFTS of the Cu⁺ and/or Zn²⁺ ion-exchanged H-MOR catalysts are shown in Figure 4.19. Very obviously, H-MOR with no ion-exchanged metals has the highest amount of accessible Brønsted and Lewis acid sites as was also indicated in Py-TPD.

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The peak for the LAS for H-MOR is guite broad, and is very likely not due completely to Py chemisorption on the LAS. It could be the case that the LAS have varied acidity, which would cause the peak to shift/broaden. As expected from Py-TPD, all ion-exchanged H-MOR catalysts had significantly less BAS and LAS accessible to Py indicated by the much decreased peak areas. From the results, it would appear that Cu/H-MOR and 1Cu-4Zn/H-MOR had nearly the same amount of Py chemisorbed on BAS, while the 1Cu-4Zn/H-MOR had much more Py chemisorbed to LAS. Evidently 2Cu-1Zn/H-MOR had the most acid sites accessible to Py among the ion-exchanged H-MOR catalysts. Coincidentally, 2Cu-1Zn/H-MOR also had one of the lowest ion-exchange levels (see Table 4.1). Zn/H-MOR had the lowest ion-exchange level, but this was not reflected in the amount of chemisorbed Py shown in DRIFTS. From DRIFTS, it appears that there is almost no chemisorbed Py on Zn/H-MOR. From Py-TPD, it is obvious that Zn/H-MOR does have chemisorbed Py present and not necessarily in the lowest amount. It may be the case that ion-exchanged Zn²⁺ does more to block access for Py to the interior of the zeolite framework. It should be noted that, even with the odd LAS peak for H-MOR, it can be inferred that the metal-loaded H-MOR catalysts have significantly fewer LAS. As mentioned earlier, a perfect zeolite crystal may not necessarily have any LAS. A LAS is typically created as an imperfection in the framework that is caused by high temperature treatment (calcination), steaming, or acid leaching [136,137,185,337,338]. With so much fewer LAS indicated by Py-DRIFTS, it could be that the ion-exchanged metals have stabilized H-MOR during the calcination procedure and somewhat protected the framework from damage. However, the significantly lower amounts of Py chemisorbed onto the Metal/H-MOR catalysts as indicated by Py-TPD cannot be dismissed as having an impact on what Py-DRIFTS shows.



Figure 4.19. Results from Py-DRIFTS for H-MOR and Cu⁺ and/or Zn²⁺ ion-exchanged H-MOR catalysts.

The techniques based on pyridine adsorption in the context of the present catalyst did not seem to provide much valuable information. There are a few ways in which the results may have been improved. Higher temperatures for Py adsorption could have been used so as to overcome diffusion limitations and obtain the maximum chemisorption of Py possible. In addition to the higher temperatures, a longer period for Py adsorption could have been used, again to overcome the diffusion limitations [169,332]. However, even with these changes, the sample would still be exposed to the lab atmosphere after Py adsorption and temperatures in excess of the thermal stability of MOR may be required to properly desorb all Py. These issues could have only been resolved with newly designed equipment. Several issues would still have to be kept in mind. When the experimental set up for Py adsorption was dismantled, it was apparent that residual Py was adsorbed in the stainless steel lines (discoloration and odour). While Py adsorption could be done in the Autochem 2920, it would not be preferable due to the "poisoning" of the gas lines, which would no doubt have an influence on the quality of the other characterizations. To overcome the thermal limitations of MOR, the samples with Py adsorbed could be put under vacuum. This is commonly done with Py and NH_3 desorption over zeolites [323,324,334]. It would absolutely have been possible to build such a set up in the laboratory. However, due to time and financial limitations, it was not possible to do this during the course of this thesis.

4.4.9 CO-DRIFTS: 2200-2000 cm⁻¹

DRIFTS analysis was also performed on CO-adsorbed H-MOR and Cu⁺ and/or Zn²⁺ containing H-MOR catalysts with results shown in Figure 4.20 for the carbonyl stretching region located between wavelengths of 2200 and 2000 cm⁻¹. As shown in Figure 4.20, there is very little/no CO chemisorption on H-MOR or Zn/H-MOR, which is consistent with the results from CO isotherms shown in Figure 4.14. The CO isotherms had suggested that CO was only physisorbed on these two catalysts. As for the Cu-containing H-MOR catalysts, there is one solitary peak observed at \sim 2127 cm⁻¹. A peak at 2120-2136 cm⁻¹ is typically assigned to linearly chemisorbed carbonyl species, or Cu⁺-CO [339–343]. However, if the Cu is very highly dispersed such as in the present case, Cu⁰ species can chemisorb CO and will adsorb at a nearly identical frequency as the Cu⁺-CO carbonyl [339,342]. There are likely none of these species present, as the Cu^{2+} present in Cu/H-MOR was only partially reduced to Cu⁺. It may also be the case that two CO molecules chemisorb to one Cu⁺ centre. These Cu^+ -(CO)₂ dicarbonyl species would have their vibrational modes at 2160 and 2115 cm⁻¹, which are associated with their symmetric and antisymmetric vibrations respectively [344]. These are not observed here, and it may be the case that these species are only observed at very low temperatures (~ 100 K). Otherwise, the peak at 2127 cm⁻¹ seems to scale somewhat with total Cu⁺ content of the catalyst, which would be expected as CO adsorption increased with increasing Cu^+ content (from CO-TPD shown in Figure 4.12). As the catalysts were not analyzed by DRIFTS at the same time and the amount of KBr mixed with the catalyst may have been varied, a relationship was not developed between the peak area or intensity and total Cu⁺-CO species. This would also be inappropriate, as half-reduced CO-Cu/H-MOR catalysts were exposed to the laboratory atmosphere while being taken for the DRIFTS tests. In this scenario, the possibility exists that Cu⁺ may oxidize to Cu^{2+} using the O₂ present in the air.



Figure 4.20. CO-DRIFTS spectra in the carbonyl stretching region for H-MOR and Cu⁺ and/or Zn^{2+} ion-exchanged H-MOR catalysts.

As for there being Cu-Zn interactions that would affect the frequency at which Cu⁺-CO would be observed, there do not appear to be any. There is no shift in position with the peak at 2127 cm⁻¹ with increasing Zn content. Other groups have observed some CO interaction with Zn, but these are at very low temperatures (~77 K) and were not observed in the present work [345,346]. From the CO-DRIFTS results in the carbonyl stretching region, it is not possible to ascertain whether or not there is any interaction between Cu and Zn directly.

4.4.10 CO-DRIFTS: 3700-3500 cm⁻¹

While the carbonyl stretching region may not have revealed much useful information about the catalysts, the hydroxyl region, specifically between 3500 and 3700 cm⁻¹, may contain some information regarding the ion-exchange and where the Cu⁺ or Zn²⁺ may be located [270]. The term "hydroxyl" refers to an –OH group. These will be located at ionexchange locations on a zeolite when it is activated by ion-exchange with NH₄⁺ and subsequent heating (creates a SiOHAI active site, see Section 2.2.1). When metals are ionexchanged onto the zeolite, they force the proton (or any other cation) from the negatively charged SiOAI bridge and replace it. This would remove any signal for the –OH group from the IR spectrum, and would serve to show that the ion-exchange has occurred and could potentially, dependent on the zeolite, show where the metal has ion-exchanged. Work is still ongoing on the quantification of the IR spectrum of these zeolitic –OH groups, but at this point in time it is generally agreed that the spectrum wavelength range ~3650-3660 cm⁻¹ is due to extraframework AI (Al_{ef}) regardless of the type of zeolite [270,335,347,348]. A smaller peak located at ~3745 cm⁻¹ is usually attributed to terminal silanol groups. More specifically for MOR, it is believed that the hydroxyl groups located in the 12-MR have their vibrational wavelength at ~3610 cm⁻¹ and the hydroxyl groups in the 8-MR at ~3585 cm⁻¹ [213,214,270,347,349–353]. These larger peaks may consist of several smaller ones, meaning that each –OH group at the different locations of MOR will have a different wavelength (and by extension, a slightly different acidity). In recent work, the band for hydroxyl groups in the 12-MR was expanded to include the wavelengths from 3609 to 3625 cm⁻¹. In the same work, the IR band for hydroxyl groups in the 8-MR was theorized to extend from at least 3581 to 3590 cm⁻¹ [347]. Each MOR sample may be different, and the acidity may also be influenced by the presence of Al_{ef} and even by Si/Al ratio.

The results from DRIFTS in the hydroxyl region for the catalysts in this study are shown in Figure 4.21 and the ratios of peak areas are listed in Table 4.7. The wavelengths obtained in this work by peak deconvolution of the large hydroxyl peak were in agreement with the literature detailed above. There is a small amount of Al_{ef} present in each sample, indicated by a peak between 3654 and 3660 cm⁻¹. A larger peak present at 3623 – 3631 cm⁻¹ was assumed to be indicative of the 12-MR BAS. The last peak at 3583 – 3587 cm⁻¹ was assigned to 8-MR BAS. The ratio of the areas of the peaks for 12-MR BAS and 8-MR BAS is given in Table 4.7. This ratio decreased substantially between H-MOR and Cu/H-MOR, serving as a strong indication that Cu^{2+} was preferably ion-exchanging in the 12-MR. Between H-MOR and Zn/H-MOR, the ratio increased, giving a strong suggestion that Zn²⁺ preferred to ion-exchange in the 8-MR. This is not to say that Cu²⁺ would not ion-exchange in the 8-MR channel or Zn^{2+} would not ion-exchange in the 12-MR channel. It is simply implied by the IR spectroscopy data that there is a preference for one ion-exchange location over another and is different for the two metals. It should be noted that the implication for preferred ion-exchange locations of Cu²⁺ and Zn²⁺ from pore distribution analysis detailed in Section 4.4.2 is the same as the implication from DRIFTS. The bimetallic Cu-Zn/H-MOR catalysts demonstrated unique behaviour. From 2Cu-1Zn/H-MOR, it appears most of the ion-exchange is occurring in the 12-MR, but there is a considerable amount of ion-exchange in the 8-MR as well as the ratio of 12-MR BAS to 8-MR BAS was not as low as for Cu/H-MOR. The ratio increased for 1Cu-1Zn/H-MOR to 1.43, which was still lower than the original H-MOR ratio of 1.57, indicating again that higher ion-exchange was occurring in the 12-MR. Quite differently, the ratio decreased substantially to 1.18 for 1Cu-4Zn/H-MOR. This is nearly the same as the ratio for Cu/H-MOR. Again, this shows highly preferred ionexchange in the 12-MR. These results are consistent with results from other

characterizations and the reaction results. It had been theorized by other groups that deactivation of the H-MOR catalyst in DME carbonylation was mostly caused by the acid sites in the 12-MR [90,212,215–217]. The higher the ion-exchange in the 12-MR, the more hindered deactivation should be. Cu/H-MOR should therefore have been the best catalyst, but in this study it turned out to be the very worst. This was due to sintering of Cu into larger nanoparticles during reaction, which would block access to the active sites in the zeolites and cause even faster deactivation than with H-MOR. Zn helped to stabilize the Cu in place, and it appears from IR spectroscopy that Cu²⁺ forced Zn²⁺ to ion-exchange in the 12-MR as opposed to the 8-MR.

| Catalyst | 12-MR BAS/8-MR BAS | | | | |
|---------------|--------------------|--|--|--|--|
| H-MOR | 1.57 | | | | |
| Cu/H-MOR | 1.14 | | | | |
| 2Cu-1Zn/H-MOR | 1.34 | | | | |
| 1Cu-1Zn/H-MOR | 1.43 | | | | |
| 1Cu-4Zn/H-MOR | 1.18 | | | | |
| Zn/H-MOR | 1.8 | | | | |

Table 4.7. Approximate ratio of the number of hydroxyl groups (Brønsted acid sites) located in the 12-MR and 8-MR of MOR on Cu^+ and/or Zn^{2+} ion-exchanged H-MORs.

From Figure 4.21, it appears that the amount of AI_{ef} created by calcination is reasonably consistent among all the samples, though may be considerably less for 1Cu-4Zn/H-MOR, keeping in mind the scales for each plot. For the Cu/H-MOR and 1Cu-4Zn/H-MOR samples, the intensity of the peak was nearly double the other samples. As each sample had its spectrum taken on different days, it is possible that the amount of KBr mixed with the sample was varied or the sample amount itself changed. As such, the intensities of the peaks should not be used as an indication of the number of -OH groups, but rather the ratios should be used as was done with the data presented in Table 4.7. It should be kept in mind that these DRIFTS patterns are from the CO-DRIFTS experiments, in which Cu²⁺ was reduced to Cu⁺. If the linearly bound CO on Cu⁺ managed to stabilize Cu in its monovalent state, it would mean that if the catalyst was simply calcined with Cu²⁺, the ratio of 12-MR BAS to 8-MR BAS would be considerably lower, showing incredibly high preference of Cu²⁺ for ion-exchange in the 12-MR. While Zn²⁺ may have a preference for the 8-MR, based on the increase of the ratio of BAS it is likely it ion-exchanges in both the 12-MR and 8-MR. This is obvious from Figure 4.21, where a clear shoulder is observed at 3583 - 3587 cm⁻¹ for H-MOR and Cu/H-MOR while for Zn/H-MOR this shoulder is hardly visible. The shoulder is again visible in 1Cu-4Zn/H-MOR, but was harder to see for the 2Cu-1Zn/H-MOR and 1Cu-1Zn/H-MOR.

While it may have been possible, through detailed mathematical treatments and highly controlled experiments, to distinguish the many different –OH groups on the different samples as Lukyanov et al. [347] did, it was more desirable to obtain a general idea of the ion-exchange locations as opposed to a highly detailed one. While there are advantages to being able to analyze each –OH group separately, it would not have provided noticeably useful information in this study and would have required too much effort for the benefit.



Figure 4.21. The deconvoluted IR spectrum in the hydroxyl group region for H-MOR and Cu⁺ and/or Zn²⁺ ion-exchanged H-MOR catalysts.

4.4.11 UV-Vis

As a further means of gathering information about the state of Cu on the ionexchanged Cu-containing H-MOR catalysts, UV-Vis was performed on calcined catalysts as detailed in Section 3.3.10. Results are shown in Figure 4.22. For ZnO nanoparticles, an absorption band at ~355 nm may occur in UV-Vis [354–356]. In the present case, there is nearly no difference between the spectra of H-MOR and Zn/H-MOR. This may be due to the size of ZnO nanoparticles (if any) which are created on H-MOR. It may be the case that they are simply too small to be viewed using this technique. With regards to Cu, Cu^{2+} complexes have absorption bands in the visible region that are related to d-d transitions. No information may be gained from UV-Vis of Cu^+ as it has a $3d^{10}$ electronic configuration [357]. Among the Cu^{2+} ion-exchanged H-MOR spectra, a peak was consistently produced at 500 nm, though this peak was even somewhat present in H-MOR and Zn/H-MOR. On Cu/H-MOR, a very broad band with peak at 675 nm was present which was not produced by the other Cu²⁺-containing H-MOR catalysts. This is potentially attributable to electron d-d transitions in Cu²⁺ in a distorted octahedral orientation in CuO particles [358]. This is understandable, given the lower dispersion of Cu on Cu/H-MOR and the presence of nanoparticles as seen by TEM. 2Cu-1Zn/H-MOR and 1Cu-1Zn/H-MOR also produced a small peak at ~366 nm. This band could be due to the formation of a mono (μ -oxo) dicopper core, $[Cu_2O]^{2+}$, but was interestingly not present on the Cu/H-MOR catalyst [357,358]. Overall, the more Cu contained on the H-MOR, the lower the reflectance. Due to the distinct differences between the spectra obtained in this study and what is known for Cu/MOR and CuO, no further analysis of the UV-Vis spectra was conducted [357,359,360].



Figure 4.22. UV-Vis spectra of calcined H-MOR and Cu²⁺ and/or Zn²⁺ containing H-MOR catalysts.

4.4.12 XPS

XPS was used as a means of ascertaining additional information about how Cu and Zn were bonded to the MOR before and after reaction (otherwise referred to as calcined and spent) and was conducted as detailed in Section 3.3.11. Results for determined binding energies are detailed in Table 4.8 for all Cu⁺ and/or Zn²⁺ ion-exchanged H-MOR catalysts and in Figures 4.23 and 4.24 for Cu and Zn binding energies respectively. Comparison of the deconvoluted binding energies and assignments of the peaks were conducted using the NIST XPS database [361]. For comparison, the 2p3/2 spectral line for Cu and Zn were used. Results were not quantified for determination of how much of each metal state was present. With regards to XPS of the Cu-containing H-MOR catalysts, each catalyst, both calcined and spent, had the largest peak at a binding energy of ~933.2 eV and is due to CuO (catalysts were calcined with no reduction, so no Cu_2O should be present) [357]. With increasing Zn²⁺ content, the binding energy on the calcined catalysts for CuO increased from 933.10 eV to 933.32 eV. On the used catalysts, the CuO binding energy sometimes increased and sometimes decreased with no consistent trend was produced. A second peak was also present in all the Cu-containing H-MOR catalysts at 935.65 - 936.12 eV. In Figure 4.23, this is labelled as $CuSiO_2(OH)_2$. The higher degree of ion-exchange of Cu^{2+} over Zn^{2+} as detailed in Table 4.1 could indeed be due to Cu binding to terminal silanol groups. However, the possibility exists that this peak may also be due to $mono(\mu-oxo)$ dicopper (II)

species, though no reference spectra for this Cu species is available [357]. As the peak is always present, even at very high Zn content, it is assumed to be due to $CuSiO_2(OH)_2$ species. The binding energy for this peak decreases slightly with increasing Zn content on both calcined and spent catalysts. Whereas on calcined catalysts it only decreases from 936.00 eV to 935.82 eV, the change is more pronounced on spent catalysts, decreasing from 936.12 eV to 935.65 eV. Generally, the binding energy of this species decreased from calcined to spent catalysts. On Cu/H-MOR, there is another deconvoluted peak occurring at 934.20 eV on calcined and 934.31 eV on the spent catalyst. This is likely a shake-up satellite peak. From the NIST database, the binding energy for Cu₂O would be expected to be at ~932.20 eV. This peak was not observed in any of the XPS spectra. The peak for Cu metal alone would normally be observed at 932.60 eV, and was also not seen in any of the XPS spectra. This seems inconsistent with other characterization results. From TEM, it appeared that large Cu clusters were formed on the surface of the MOR crystals during reaction on Cu/H-MOR and 2Cu-1Zn/H-MOR. It was not expected that these clusters would be CuO, as the large amount of CO at the reaction conditions was thought to reduce Cu^{2+}/Cu^{+} . It could be the case that not enough of these other species are produced and they are simply hidden in the large CuO peak. It could also be the case that these clusters do not consist of Cu metal, and instead are composed mostly of CuO.

The ratio of the peak areas due to Cu oxides and $CuSiO_2(OH)_2$ was calculated and is shown in Table 4.8. In all cases, this ratio increases between the calcined and spent catalysts. This would imply that these $CuSiO_2(OH)_2$ species are mobile during reaction, and may convert to CuO species during reaction. From Figure 4.23, it is obvious that the increase of this ratio is less likely due to the increased formation of CuO and more likely related to the disappearance of this $CuSiO_2(OH)_2$ species. From the data available from XPS, it would thus appear that CuO does not necessarily reduce during reaction, and that the Cu clusters consist mostly of CuO. However, this is difficult to believe. The only oxygen present during reaction is from CH_3OCH_3 (DME) and CO. While it may be believable that a reaction may occur where DME gives up its O to Cu, it is not believable that CO would do this. CO is a known reducing agent, and would rather remove O. However, it could also be the case that Cu stays in its monovalent state during reaction, and after removal of the used catalyst from the reactor and exposure to lab atmosphere, the Cu⁺ simply oxidizes to Cu^{2+} . An in situ technique would be required to observe the changes of Cu state during reaction. The ZnO binding energies are detailed in Table 4.8 and shown visually in Figure 4.24. The binding energy did not shift excessively between calcined and spent catalysts and produced no discernible trend nor were any other peaks observed due to the presence of Zn. Among the bimetallic samples, the ZnO binding energy did increase with increasing Zn content. For 2Cu-1Zn/H-MOR, the measured binding energy on the calcined catalyst was 1022.74 eV, which shifted to 1023.09 eV for 1Cu-4Zn/H-MOR. The trend did not scale with Zn content, as for calcined Zn/H-MOR the binding energy was 1022.75 eV, which was nearly the same as for 2Cu-1Zn/H-MOR – the bimetallic catalyst with the lowest Zn content. The ZnO binding energy for spent catalysts did show a trend, decreasing from 1022.86 eV for 2Cu-1Zn/H-MOR to 1022.80 eV for Zn/H-MOR. This is not a large shift and ZnO binding energy was more consistent as compared to CuO binding energy. This implies that ZnO is not particularly mobile during reaction, does not sinter, and stays at the ion-exchange locations.
| | | Cu oxides/ | | | |
|---------------|--------|------------|--------------------------------------|-----------|--------------------------------------|
| Catalyst | Cı | OL | CuSiO ₂ (OH) ₂ | ZnO 2p3/2 | CuSiO ₂ (OH) ₂ |
| | 2р | 3/2 | 2p3/2 | | |
| Cu/H-MOR | | | | | |
| Calcined | 933.11 | 934.24 | 936.00 | - | 3.96 |
| Spent | 933.03 | 934.31 | 936.12 | - | 19.20 |
| 2Cu-1Zn/H-MOR | | | | | |
| Calcined | 933.15 | - | 935.99 | 1022.74 | 6.24 |
| Spent | 933.26 | - | 935.73 | 1022.86 | 7.50 |
| 1Cu-1Zn/H-MOR | | | | | |
| Calcined | 933.29 | - | 935.91 | 1023.06 | 12.06 |
| Spent | 933.32 | - | 935.66 | 1022.83 | 20.43 |
| 1Cu-4Zn/H-MOR | | | | | |
| Calcined | 933.33 | - | 935.82 | 1023.09 | 3.60 |
| Spent | 933.12 | - | 935.65 | 1022.81 | 9.05 |
| Zn/H-MOR | | | | | |
| Calcined | - | - | - | 1022.75 | - |
| Spent | - | - | - | 1022.80 | - |

Table 4.8. Binding energies of Cu and Zn species on calcined and spent Cu and/or Zn containing H-MOR catalysts.



Figure 4.23. Cu species binding energies as determined from XPS for calcined and spent Cu^{2+} and/or Zn^{2+} ion-exchanged H-MOR catalysts.



Figure 4.24. Zn species binding energies as determined from XPS for calcined and spent Cu^{2+} and/or Zn^{2+} ion-exchanged H-MOR catalysts.

The results from XPS are difficult to gather a conclusion from regarding what happens to Cu^{2+}/Cu^+ and Zn^{2+} during reaction. In the case of 2Cu-1Zn/H-MOR, the binding energy for both CuO and ZnO increases during reaction. This could simply be due to the formation of the methyl groups (or other adsorbed species) on H-MOR during reaction. For 1Cu-1Zn/H-MOR, the binding energy shift for CuO is not nearly as large as the decrease in binding energy for ZnO between the calcined and spent catalysts. The binding energy change from calcined to spent for 1Cu-4Zn/H-MOR is the opposite of 2Cu-1Zn/H-MOR: the binding energy decreases for both CuO and ZnO during reaction. These results are based on peak deconvolution, and cannot be considered perfect. The changes in binding energy are only on the order of ~0.2 eV, and for all that is going on during reaction, may even be meaningless.

4.4.13 Brief summary of Cu-Zn/H-MOR characterizations

After extensive characterization of the H-MOR and Cu and/or Zn containing H-MOR catalysts, some consistent trends have emerged that have lent some understanding of just what Cu and Zn are doing and how they interact. Quite generally, Cu^{2+} and Zn^{2+} ionexchange have increased the acidity of the leftover protonated sites. There could be considered to be several reasons for this, but the root of all the behaviour lies in the strength of an acid site being at least partially influenced by the next nearest neighbours of the site (see Section 2.2.1) [136,141–143]. With ~55% ion-exchange and a Si/Al ratio of 6.5, it is reasonable to assume that some of the next nearest neighbours are Al atoms with bridging O atoms that are involved in the ion-exchange. This does not appear to have had much of an influence on the rate of reaction. On some of the Cu⁺ and/or Zn²⁺ containing H-MOR catalysts, it appeared that the induction period was extended. While this may have been influenced by the acidity change of the ion-exchanged catalysts, it may also be the case that Zn has introduced additional diffusion limitations. From pore distribution analysis, it was apparent that Zn²⁺, in the right quantities, at least partially obstructed the 8-MR channels of MOR. From DME adsorption/desorption, it appeared that DME could still access those sites without much difficulty, and perhaps the difficulty lies in the insertion of CO to create the acetoxy group. While interpretation of the Py-TPD results was difficult, it was apparent that Py was either blocked from getting to acid sites or that significant diffusion limitations had been introduced by the metal. Given the size of Py, it is not unreasonable to assume that even a bit of blockage by ion-exchanged metals could introduce significant limitations. Pore distribution analysis did show some decrease in micropore volume with ion-exchange.

What is quite fascinating is how the ratio of Cu to Zn on the bimetallic Cu-Zn/H-MOR catalysts so greatly affects its characteristics. XPS did not reveal much information that would lead one to believe that there were direct Cu-Zn interactions. The binding energy of CuO did increase with increasing Zn content. TPR seemed to show this as well, as increasing Zn content caused the reduction temperature of Cu^{2+} to increase substantially. Pore distribution analysis showed some indications of possible differing ion-exchange locations of Cu^{2+} and Zn^{2+} . DRIFTS analysis also showed that Cu^{2+} seemed to have a strong preference for ion-exchange in the 12-MR, while Zn^{2+} seemed to prefer the 8-MR but would also ion-exchange in the 12-MR. To understand this in more detail, modeling of the ion-exchange locations using quantum-chemical methods was used.

4.5 Hartree-Fock modeling of Cu²⁺ and Zn²⁺ ion-exchange locations on MOR

A brief introduction and some general procedures regarding the modeling have been presented in Sections 3.4.1 and 3.4.2. The original hope of the modeling work was that it could shed some light on the preferential ion-exchange locations for Cu^{2+} and Zn^{2+} . This is not the first time characterization and modeling has been used to try and ascertain the preferable ion-exchange locations of divalent metals. XRD data is available that suggests Cu^{2+} prefers to ion-exchange in the 8-MR, coordinated to 6 framework oxygen atoms and two water molecules. Following this, the Cu²⁺ would ion-exchange between T1 and T2 AI atoms, coordinated to 4 framework oxygens. A final location was determined to be between T2 and T4 Al atoms, where it would be bound to three oxygens [302]. In other works, Cu²⁺ was suggested to be coordinated in a square planar or square pyramidal coordination [362]. Further characterizations seemed to suggest that Cu²⁺ would only occupy the 8-MR in MOR at low Cu loadings, and be coordinated with six framework oxygens. At higher loadings, Cu would again be bound to four framework oxygens between the T1 and T2 Al atoms in the 12-MR [304,363]. Contrary to these works, a DFT modeling study was conducted where it was determined that at low Cu loadings Cu²⁺ would be coordinated to the smaller 6-MR with two AI atoms that make up part of the 12-MR (the 6-MR is made up of T1 and T2 AI atoms). At higher loadings, it was determined Cu(OH)⁺ would preferentially ion-exchange at the 6-MR or 5-MR with only one Al atom. Calculations also seemed to indicate that the 8-MR was not occupied by Cu²⁺ [301]. Other work showed that Cu clusters would likely form around the mouth of the 8-MR pockets connecting the 8-MR and 12-MR [169]. A similar result was obtained for Cu^{2+} in ferrierite [364]. By comparison, there is little work done on modeling Zn^{2+} ion-exchange on MOR. One DFT study has shown that Zn^{2+} could ion-exchange in the

smaller 5-MR and 6-MR that contain two Al atoms. It was also shown that Zn^{2+} could ionexchange with Al sites at greater distances from each other, but that the Zn^{2+} seemed to interact more with one Al site than the other [365].

From this small literature review on the determination of Cu²⁺ ion-exchange locations on MOR, it is apparent that just about every possible ion-exchange location has had some evidence presented for it at some point. The very limited studies on Zn²⁺ ion-exchange on MOR effectively stated that Zn²⁺ ion-exchange could take place nearly anywhere on MOR (as the framework is assembled from smaller 5-MR and 6-MR). It could be the case that every MOR is different, and ion-exchange over one sample could be different from over another sample. The ion-exchange behaviour would also be different with different Si/Al ratios. With the next nearest neighbours affecting the acidity of any given site, they would no doubt have some influence over any potential ion-exchange behaviour [136,141–143].

4.5.1 Initial models – the siliceous MOR framework and basis set selection

Prior to modeling of the ion-exchange of Cu^{2+} and Zn^{2+} onto MOR, it was necessary to build a suitably sized portion of the MOR framework that was consistent with available information on the bond lengths and angles [140,366–368]. Some models used for ionexchange are very small, in which case DFT methods can be used (computationally expensive) [301]. This was deemed not to be suitable, given the argument for how the next nearest neighbours in the framework can influence acidity. It is likely that some framework bending and deformation will occur in ion-exchange [310-313], and smaller models may allow this to too great an extent. Additional framework atoms around the ionexchange location will limit the amount of distortion that occurs to accommodate the ionexchanged metal. In the present case, two separate models were built: one for the 8-MR channel and the other for the 12-MR channel. These are shown in Figure 4.25. The models were terminated with H atoms where they would normally connect with the rest of the MOR framework. These terminal H atoms were frozen in place during optimizations. These models were built based on the excellent information available in Dominguez-Soria et al. [140] for bond lengths and angles. The 8-MR model consisted of 231 total atoms (with 68 Si atoms and 1878 electrons total) while the 12-MR model consisted of 284 total atoms (with 84 Si atoms and 2328 electrons total). The naming convention for atoms in this study was the same as used by Dominguez-Soria et al. [140].



Figure 4.25. Purely siliceous models built of the a) 8-MR of MOR and the b) 12-MR of MOR.

The models were then optimized to determine what the best method was for the further optimization of models containing ion-exchanged Cu^{2+} or Zn^{2+} . Optimizations were first conducted with semi-empirical methods, and while the models successfully ran, they all failed to maintain the appropriate bond angles and lengths between framework atoms. Specifically, these methods could not maintain the $\sim 180^{\circ}$ T2-O8-T2 angle. The bond angles predicted by semi-empirical methods were generally less than what the reality is for MOR. When using HF methods, a basis set must be selected. A basis set is a mathematical description of all of the orbitals within a system. These help to approximate the electronic wavefunction [290]. Basis sets vary in the number of equations that are assigned to each atom to describe the orbitals. They therefore have a huge impact on the amount of computational resources required for a model to run. In the present case, the models shown in Figure 4.25 were optimized with several basis sets until one was found that produced a suitably optimized MOR structure. The results are shown in Table 4.9 for bond lengths and Table 4.10 for bond angles for the optimized 8-MR model. The same results for the 12-MR are shown in Tables 4.11 and 4.12. Surprisingly, the comparatively small basis set STO-3g produced results in very good agreement with what is known for synthetic MOR, with average error on the bond lengths at 0.48% and on bond angles of 3.92%. This error on the bond angles was consistent with the error obtained by DFT methods by other groups, showing that DFT methods may not necessarily give a better prediction for bond lengths and angles for stable structures [140]. Moving to a 6-31G basis set introduced significantly more error in both bond lengths and angles. Adding extra polarization ability to the 6-31G basis set, 6-31G(d) decreased error from 6-31G. Using this basis set, the error on bond lengths was 0.45% while for bond angles was 3.3%. Adding further polarization functions (6-31G(2d)) further decreased the error on bond lengths to 0.39% and on bond angles to

3.04%. It may be noticed in Tables 4.10 and 4.12 that the bond angle T1-O7-T1 was badly predicted compared to synthetic MOR. In the work of Dominguez-Soria et al. [140] who used DFT methods with a similar basis set, the error in the prediction of this angle was 6.7% compared to the >7.2% error in this work. Introducing diffuse functions only increased computational requirements and did not provide much benefit.

| Bond | Synthetic MOR | STO-3g | Error (%) | 6-31G | Error (%) | 6-31G(d) | Error (%) | 6-31G(2d) | Error (%) |
|---------|------------------|--------|--------------|-------|--------------|----------|--------------|-----------|--------------|
| T1-01 | 1.623 | 1.620 | 0.18 | 1.639 | 0.99 | 1.628 | 0.31 | 1.624 | 0.06 |
| T1-03 | 1.609 | 1.611 | 0.12 | 1.632 | 1.43 | 1.622 | 0.81 | 1.619 | 0.62 |
| T1-06 | 1.620 | 1.623 | 0.19 | 1.636 | 0.99 | 1.628 | 0.49 | 1.624 | 0.25 |
| T1-07 | 1.629 | 1.612 | 1.04 | 1.626 | 0.18 | 1.619 | 0.61 | 1.616 | 0.80 |
| Average | 1.620 | 1.617 | 0.38 | 1.633 | 0.90 | 1.624 | 0.56 | 1.621 | 0.43 |
| | | | | | | | | | |
| T2-02 | 1.616 | 1.621 | 0.31 | 1.628 | 0.74 | 1.623 | 0.43 | 1.621 | 0.31 |
| T2-03 | 1.606 | 1.610 | 0.25 | 1.634 | 1.74 | 1.623 | 1.06 | 1.619 | 0.81 |
| T2-05 | 1.615 | 1.598 | 1.05 | 1.644 | 1.80 | 1.620 | 0.31 | 1.614 | 0.06 |
| T2-08 | 1.618 | 1.610 | 0.49 | 1.625 | 0.43 | 1.617 | 0.06 | 1.614 | 0.25 |
| Average | 1.614 | 1.610 | 0.53 | 1.633 | 1.18 | 1.621 | 0.47 | 1.617 | 0.36 |
| | | | | | | | | | |
| T3-01 | 1.634 | 1.618 | 0.98 | 1.635 | 0.06 | 1.626 | 0.49 | 1.622 | 0.73 |
| T3-04 | 1.612 | 1.601 | 0.68 | 1.640 | 1.74 | 1.618 | 0.37 | 1.612 | 0.00 |
| Т3-09 | 1.632 | 1.621 | 0.67 | 1.631 | 0.06 | 1.626 | 0.37 | 1.625 | 0.43 |
| Average | 1.626 | 1.613 | 0.78 | 1.635 | 0.62 | 1.623 | 0.41 | 1.620 | 0.39 |
| | | | | | | | | | |
| T4-02 | 1.627 | 1.623 | 0.25 | 1.631 | 0.25 | 1.626 | 0.06 | 1.623 | 0.25 |
| T4-04 | 1.605 | 1.603 | 0.12 | 1.641 | 2.24 | 1.619 | 0.87 | 1.613 | 0.50 |
| T4-010 | 1.620 | 1.627 | 0.43 | 1.624 | 0.25 | 1.626 | 0.37 | 1.627 | 0.43 |
| Average | 1.617 | 1.618 | 0.27 | 1.632 | 0.91 | 1.624 | 0.43 | 1.621 | 0.39 |

Table 4.9. Optimized bond lengths of 8-MR model using HF theory with different basis sets (bond lengths are in Å).

| Bond | Synthetic MOR | STO-3g | Error (%) | 6-31G | Error | 6-31G(d) | Error | 6-31G(2d) | Error |
|------------------|------------------|--------|--------------|-------|-------|----------|-------|-----------|-------|
| | | | | | () | | () | | () |
| T1-01-T3 | 146.0 | 152.0 | 4.10 | 156.0 | 6.83 | 152.6 | 4.50 | 151.2 | 3.53 |
| T1-03-T2 | 158.0 | 161.3 | 2.07 | 162.4 | 2.78 | 159.9 | 1.19 | 158.5 | 0.33 |
| T1-06-T1 | 149.0 | 149.6 | 0.39 | 151.9 | 1.95 | 149.1 | 0.07 | 148.5 | 0.31 |
| T1-07-T1 | 138.7 | 154.1 | 11.12 | 158.2 | 14.02 | 155.1 | 11.82 | 154.1 | 11.10 |
| T2-02-T4 | 143.6 | 148.6 | 3.45 | 152.6 | 6.30 | 148.3 | 3.29 | 147.0 | 2.33 |
| T3-04-T4 | 164.8 | 165.5 | 0.39 | 175.3 | 6.38 | 169.7 | 2.97 | 166.7 | 1.17 |
| Т3-09-Т3 | 149.7 | 156.3 | 4.40 | 149.6 | 0.05 | 152.4 | 1.81 | 153.8 | 2.76 |
| T4-010-T4 | 150.3 | 156.5 | 4.10 | 149.0 | 0.88 | 152.3 | 1.34 | 153.8 | 2.30 |
| Average Error | | | 3.75 | | 4.90 | | 3.38 | | 2.98 |

Table 4.10. Optimized bond angles of 8-MR model using HF theory with different basis sets (bond angles are in °).

| Bond | Synthetic MOR | STO-3g | Error (%) | 6-31G | Error (%) | 6-31G(d) | Error (%) | 6-31G(2d) | Error (%) |
|---------|------------------|--------|--------------|-------|--------------|----------|--------------|-----------|--------------|
| T1-01 | 1.623 | 1.614 | 0.55 | 1.634 | 0.68 | 1.622 | 0.06 | 1.620 | 0.18 |
| T1-03 | 1.609 | 1.610 | 0.06 | 1.629 | 1.24 | 1.620 | 0.68 | 1.618 | 0.56 |
| T1-06 | 1.620 | 1.621 | 0.06 | 1.632 | 0.74 | 1.624 | 0.25 | 1.620 | 0.00 |
| T1-07 | 1.629 | 1.616 | 0.80 | 1.632 | 0.18 | 1.621 | 0.49 | 1.619 | 0.61 |
| Average | 1.620 | 1.615 | 0.37 | 1.632 | 0.71 | 1.622 | 0.37 | 1.619 | 0.34 |
| T2-02 | 1.616 | 1.623 | 0.43 | 1.625 | 0.56 | 1.625 | 0.56 | 1.624 | 0.50 |
| T2-03 | 1.606 | 1.610 | 0.25 | 1.632 | 1.62 | 1.622 | 1.00 | 1.619 | 0.81 |
| T2-05 | 1.615 | 1.598 | 1.05 | 1.644 | 1.80 | 1.619 | 0.25 | 1.613 | 0.12 |
| T2-08 | 1.618 | 1.614 | 0.25 | 1.624 | 0.37 | 1.620 | 0.12 | 1.618 | 0.00 |
| Average | 1.614 | 1.611 | 0.50 | 1.631 | 1.09 | 1.622 | 0.48 | 1.619 | 0.36 |
| T2 01 | 1.624 | 1 (10 | 0.00 | 1.620 | 0.24 | 1.624 | 0.61 | 1 (22 | 0.70 |
| 13-01 | 1.634 | 1.618 | 0.98 | 1.630 | 0.24 | 1.624 | 0.61 | 1.622 | 0.73 |
| T3-04 | 1.612 | 1.601 | 0.68 | 1.635 | 1.43 | 1.617 | 0.31 | 1.612 | 0.00 |
| T3-09 | 1.632 | 1.625 | 0.43 | 1.629 | 0.18 | 1.626 | 0.37 | 1.626 | 0.37 |
| Average | 1.626 | 1.615 | 0.70 | 1.631 | 0.62 | 1.622 | 0.43 | 1.620 | 0.37 |
| | | | | | | | | | |
| T4-02 | 1.627 | 1.627 | 0.00 | 1.629 | 0.12 | 1.628 | 0.06 | 1.626 | 0.06 |
| T4-04 | 1.605 | 1.602 | 0.19 | 1.639 | 2.12 | 1.618 | 0.81 | 1.613 | 0.50 |
| T4-010 | 1.620 | 1.633 | 0.80 | 1.622 | 0.12 | 1.629 | 0.56 | 1.632 | 0.74 |
| Average | 1.617 | 1.621 | 0.33 | 1.630 | 0.79 | 1.625 | 0.48 | 1.624 | 0.43 |

Table 4.11. Optimized bond lengths of 12-MR model using HF theory with different basis sets (bond lengths are in Å).

| Bond | Synthetic MOR | STO-3g | Error (%) | 6-31G | Error (%) | 6-31G(d) | Error (%) | 6-31G(2d) | Error (%) |
|------------------|------------------|--------|--------------|-------|--------------|----------|--------------|-----------|--------------|
| T1-01-T3 | 146.0 | 155.1 | 6.20 | 157.7 | 7.99 | 155.8 | 6.71 | 154.7 | 5.94 |
| T1-03-T2 | 158.0 | 159.3 | 0.80 | 160.2 | 1.39 | 157.2 | 0.49 | 155.9 | 1.32 |
| T1-06-T1 | 149.0 | 149.0 | 0.01 | 153.0 | 2.66 | 150.1 | 0.72 | 149.4 | 0.24 |
| T1-07-T1 | 138.7 | 150.9 | 8.80 | 150.6 | 8.60 | 148.8 | 7.30 | 148.7 | 7.17 |
| T2-02-T4 | 143.6 | 154.2 | 7.35 | 153.8 | 7.08 | 149.6 | 4.21 | 148.3 | 3.24 |
| T3-04-T4 | 164.8 | 166.0 | 0.73 | 176.5 | 7.07 | 169.8 | 3.02 | 166.9 | 1.28 |
| Т3-09-Т3 | 149.7 | 156.6 | 4.61 | 148.3 | 0.95 | 152.6 | 1.96 | 154.2 | 2.97 |
| Т4-О10-Т4 | 150.3 | 156.6 | 4.17 | 148.3 | 1.31 | 152.8 | 1.65 | 154.3 | 2.67 |
| Average Error | | | 4.08 | | 4.63 | | 3.26 | | 3.11 |

Table 4.12. Optimized bond angles of 8-MR model using HF theory with different basis sets (bond angles are in °).

From the results, it would appear that HF with a basis set 6-31G(2d) would be suitable for further optimization work of ion-exchange locations. Unfortunately, this basis set proved to be too computationally expensive for the size of the models and the computational resources available. Runtimes for the models became too long and file sizes became excessively large. The 6-31G(2d) basis set also did not provide significantly better results over 6-31G(d). The basis set 6-31G(d) seemed to provide a happy equilibrium between model run times and bond length and angle accuracy. For these reasons, HF theory with 6-31G(d) basis set was used for all ion-exchange modeling. The 6-31G basis set is what is called a split-valence double-zeta basis set while the d indicates extra d functions are added for heavy atoms. Altogether, 6-31G(d) may be referred to as a polarized split-valence double-zeta basis set, and such basis sets have been used by other groups when working with the modeling of zeolites [140,301].

4.5.2 Cu²⁺ ion-exchange

Once reliably optimized models for the 8-MR and 12-MR had been developed, active sites were introduced into the MOR framework by replacing Si atoms with Al atoms as described in Section 3.4.2. In all cases, Al atoms were separated by at least one Si atom

(AI–O–Si–O-AI) as dictated by Löwenstein's rule [98,99]. Two models were optimized for each ion-exchange location. The first model included the framework with the two AI atoms, no ion-exchanged metal, and a net -2 charge placed on the framework. The second model included the ion-exchanged metal with a net neutral charge placed on the model. The purpose of this was to observe how the presence of the ion-exchanged metal would distort the framework. The purely siliceous models could not be used for this purpose as AI-O bonds in the framework are longer than Si-O bonds [140,369].

Recently a great deal of research has been conducted into the state of ionexchanged Cu^{2+} on MOR. This has included $Cu(OH)^+$, Cu_2O^{2+} , and even $Cu_3O_3^{2+}$ clusters that may be formed on MOR during ion-exchange [169,251,253,254,301]. These will not be explored here. In the present case, only true Cu^{2+} ion-exchange requiring two Al atoms in the zeolite framework was modeled. No argument is being made here for whether or not these other species are formed during ion-exchange, but under the ion-exchange conditions used in this study and detailed in Section 4.2, it was not expected that $Cu(OH)^+$ species would be present. If they were, it was thought that a much greater degree of ion-exchange would have occurred (from Table 4.1, ion-exchange levels were at \sim 55%). The goal in this study was to determine, in the bimetallic ion-exchange, if Cu²⁺ and Zn²⁺ would compete for the same ion-exchange locations or if the two metals would force each other to move to different areas of the framework. Also, the argument has been brought forth several times about how the next nearest neighbours to an AI atom will influence the site acidity [136,141–143]. For this work, all of these were assumed to be Si atoms. If Al atoms were introduced to these locations, it would simply introduce too many degrees of freedom into the modeling. In the future, modeling work could be done with one specific ion-exchange location and the influence of next nearest neighbour Al atoms could be explored.

Other groups have made the comment that Cu²⁺ will try to be more highly coordinated in the ion-exchange [302,362]. There are not many locations on MOR where Cu²⁺ would be able to take on a higher coordination comfortably. One of the very few locations is located between two T1 Al atoms in reasonable proximity to each other, shown in Figure 4.26, in the 6-MR formed by the T1 and T2 tetrahedral locations accessed from the 12-MR. In Figure 4.26a, the T1 atoms are separated by a single T1 Si atom. In this arrangement, Cu²⁺ can successfully achieve a somewhat deformed square planar coordination with bond lengths varying between 1.87 Å and 2.00 Å. However, for the ionexchange to be possible at this location, a significant amount of deformation to the MOR framework is required. The bond angle between T1-O1-T3 may seem quite reasonable at 142.1°, and may seem even quite similar to the angle when only Si atoms are used of 136.1°. However, it is apparent from Figure 4.26a that the angle became inverted so as to bring the O1 atom closer to Cu²⁺, and introduced an admittedly small but significant change to the T3 atom location. If possible, this would also introduce deformation to the 4-MR composed of T3 and T4 atoms. It is by this logic that the ion-exchange shown in Figure 4.26b would be considered to be much more likely to occur. The two T1 Al atoms are now separated by a T3 Si atom. In this scenario, the bond lengths between Cu²⁺ and the framework O atoms are now nearly constant at 1.98 Å and Cu^{2+} can achieve a very nearly perfect square planar coordination. There is a minimal amount of deformation to the framework and the bond angle T1-O1-T3 is minimally impacted. Bond lengths and angles are nearly symmetric between the two opposing sides of the 6-MR. Regardless of how the T1 Al atoms are located relative to each other, it is highly probable that they serve as the primary location of Cu²⁺ ion-exchange if only from the perspective of they are one of the few locations to provide an environment in which Cu^{2+} can have a higher coordination number. It has been mentioned by other groups that Cu^{2+} could take on a square pyramidal or octahedral orientation in ion-exchange. If this were to occur at the 6-MR, the O1 atoms between T1 and T3 would have to be involved. This was not simulated as it was thought to be not realistic.



Figure 4.26. Cu^{2+} ion-exchanged in the 12-MR in square planar coordination between two T1 Al atoms a) separated by a T1 Si atom and b) separated by a T3 Si atom at the smaller 6-MR (bond lengths shown are in Å).

As T1 atoms are shared between the 8-MR and 12-MR, it is possible that Cu^{2+} could potentially ion-exchange into the 8-MR. However, the orientation of T1 O atoms (especially the O7 atoms, which point towards the 12-MR) would not permit Cu^{2+} to have a higher coordination between two T1 Al atoms. Rather, it may be possible that Cu^{2+} could ionexchange between a T1 Al atom and a T3 Al atom, shown in Figure 4.27. However, there are some interesting problems with this location. From Figure 4.27, it could be assumed that Cu^{2+} in a trigonal planar coordination would be more suitable. However, as was stated earlier, only models that have successfully converged are being presented. The models where Cu²⁺ was placed in a trigonal planar coordination here did not converge, even when the basis set was reduced from 6-31G(d) to STO-3G. Models with the STO-3G basis set were more likely to converge, based on previous experience with Gaussian. It is apparent in Figure 4.27 though that a square planar orientation may not be realistic, or at the very least not preferable to the ion-exchange location presented in Figure 4.26. While 3 of the bond lengths between Cu²⁺ and O atoms are realistic at 1.90 Å and 1.96 Å, the bond between Cu^{2+} and the O1 atom of length 3.14 Å is likely not feasible, but the model converged regardless. With the model shown in Figure 4.26a, the O1 atom was drawn much closer to the Cu²⁺ during the optimization, even forcing the angle to be inverted from the starting model. There must be a higher amount of the negative charge placed in that O as compared to the others, and indeed this may be the case in the model shown in Figure 4.27 as well. The O7 atoms in Figure 4.27 remained where they were and were not drawn to the Cu²⁺ ion, and as such the bulk of the negative charge must not be placed there in this particular orientation of atoms. In the case of the ion-exchange between T1 Al atom and T3 Al atom locations, the framework was hardly disturbed. One must then use intuition to determine if this is a reasonable ion-exchange location. In terms of space restrictions, this location is far more restricted and inaccessible compared to approaching a set of T1 Al atoms from the 12-MR. What may be more likely here, if Cu^{2+} did ion-exchange in this location, is that it is unstable, and may intermittently change which O atoms it primarily binds to. As T1 Al atoms are quite likely one of the primary locations for ion-exchange, it must be remembered that there would be competing ion-exchange between the 12-MR and 8-MR locations for it. In the case of Cu²⁺, it would seem much more probable that the ionexchange would occur in the 12-MR as opposed to the 8-MR, if only for the reasons of Cu^{2+} being less confined in the 12-MR.



Figure 4.27. Cu^{2+} ion-exchanged in the 8-MR in a deformed square planar coordination between a T1 Al atom and a T3 Al atom in a smaller 5-MR (bond lengths shown are in Å).

There are some locations where models converged with Cu^{2+} at lower coordination. For example, shown in Figure 4.28 is a T1 Al atom located near to a T4 Al atom where a Cu^{2+} ion was optimized in a bent coordination (in the 12-MR). With this particular orientation of Al atoms, Cu^{2+} would not be able to obtain a tetrahedral or square planar orientation, at least not without significant deformation to the framework. The 010 atom at T4 is too far from the Cu^{2+} for it to be useful in allowing a trigonal planar coordination. However, the model did converge and perhaps this could be a feasible location for ionexchange to occur. The bond lengths between Cu^{2+} and the framework O atoms are both approximately 1.88 Å, which is generally shorter than the bond lengths for Cu²⁺ in the square planar coordination between T1 Al atoms. The bond angle for Cu^{2+} is very small at 78.8°, and could be a likely source for instability of the ion-exchange at this location. That said, the deformation to the framework due to the ion-exchange at this location is minimal. The bond length between the T4 Al atom and O2 is a little larger at 1.88 Å but is not entirely unreasonable, given the average bond length between AI and O atoms in the framework has been consistently optimizing at 1.80 Å to 1.84 Å. Bond angles are not substantially altered in the framework. This model is consistent with the impression that ion-exchange preferentially occurs at T1 Al atoms, regardless of whichever additional Al atom provides the other balancing charge.



Figure 4.28. Cu^{2+} ion-exchanged in the 12-MR in a bent coordination between a T1 Al atom and a T4 Al atom located in a smaller 5-MR (bond lengths shown are in Å).

The final model for Cu^{2+} ion-exchange that converged is between a T2 Al atom and a T4 Al atom in the 12-MR, shown in Figure 4.29. In this particular situation, Cu²⁺ took on a less intense bent coordination, which is assumed to be a bit more stable as compared to the bent coordination presented previously in Figure 4.28. However, in comparison to the previously discussed ion-exchange involving T1 and T4 Al framework atoms, the ionexchange between the T2 and T4 Al atoms has introduced a higher amount of framework deformation. The bond lengths between Cu^{2+} and the framework O2 atoms are 2.00 Å and 2.11 Å, which are the longest bond lengths so far discussed in Cu^{2+} ion-exchange. The angle between the bonds at Cu^{2+} is 158.1°, which seems much more reasonable as compared to the 78.8° bond angle for Cu^{2+} ion-exchanged at the T1 and T4 Al atoms presented in Figure 4.28. To achieve this bond angle and bond lengths for Cu²⁺, the bond angles T2-O2-T4 decreased considerably to 125.5°. Normally this bond angle would be in the order of 148.6°. The bond lengths between the T4 Al and O2 and T2 Al and O2 had to extend to 1.86 Å and 1.89 Å respectively (from ~1.75-1.78 Å). However, the bond lengths and angles in the T4-O10-T4 were relatively unaffected. Indeed, it is highly likely that the Cu^{2+} could be stable here as any negative charge focused at the O10 atom would also help to compensate for the Cu^{2+} cation. It is noted here that Cu^{2+} in a trigonal planar coordination did not optimize successfully. This can be extended to all locations, as Cu²⁺ in a trigonal planar coordination did not optimize successfully in any location, even when using the smaller, more likely to converge, basis sets.



Figure 4.29. Cu^{2+} ion-exchange in the 8-MR side pocket connecting the 12-MR to the 8-MR in a deformed linear coordination between a T2 Al atom and a T4 Al atom (bond lengths shown are in Å).

To summarize the Cu²⁺ ion-exchange models, based on these computational results it is highly likely that Cu^{2+} ion-exchange occurs preferentially in the 12-MR of MOR. This is not to say that ion-exchange of Cu²⁺ would not occur in the 8-MR, but that given the choice, Cu²⁺ would prefer the 12-MR. The likely location would be between T1 Al atoms in the 6-MR, where Cu²⁺ can successfully achieve a square planar coordination (and potentially higher coordination) and have enhanced stability. The framework deformation here, dependent on the orientation of the T1 Al atoms, is minimized and framework symmetry is maintained. There are other locations where Cu^{2+} ion-exchange occurs in a bent coordination, but these are assumed to be less stable as Cu^{2+} typically shows an inclination towards becoming more highly coordinated [301]. If the Cu/H-MOR material were to be stored in an environment where water could be adsorbed, these lower coordinated Cu²⁺ cations would likely migrate and sinter with other Cu²⁺ cations (or form copper hydroxide complexes). Based on the idea that Cu^{2+} ion-exchange could occur in the 8-MR side pockets joining the 8-MR and 12-MR channels, this could lead to Cu nanoparticles forming at these side pockets and blocking access to the 8-MR. It has been previously theorized that the T3 Al site, specifically the O9 atom, is the primary location of DME carbonylation [212,215,216]. If Cu nanoparticles were to block the adjoining side pockets, this site would become inaccessible and lead to losses in activity and acceleration of catalyst deactivation. These results are consistent with what other groups have theorized for the preferential ionexchange locations of Cu^{2+} [169,301].

It should also be stated here that it was considerably more difficult to converge Cu^{2+} ion-exchange models as compared to Zn^{2+} ion-exchange models. Cu^{2+} ion-exchange models often resulted in model termination due to annihilation of the first spin contaminant. This is not an uncommon issue when dealing with Cu models in the modeling program Gaussian, and steps were taken in an attempt to help these models converge. These steps were often not enough to make the models converge. That said, the presented results must be taken with some degree of uncertainty as all modeling results should be. The locations for Cu^{2+} ion-exchange that have been presented may not be all the locations possible, but should be taken as an indication of where it is preferred and not preferred.

4.5.3 Zn²⁺ ion-exchange

The modeling of Zn^{2+} ion-exchange was carried out in an identical fashion to the modeling of Cu^{2+} ion-exchange. All previous models of Cu^{2+} ion-exchange, including those that had not successfully converged at smaller basis sets, simply had the Cu^{2+} replaced with Zn^{2+} and the models were ran again. In the cases where the models again failed, the bond lengths and angles were changed slightly so as to determine if a different starting point would allow the model to converge successfully. No additional assumptions regarding Zn^{2+} coordination number were made.

In an identical orientation of T1 atoms as shown in Figure 4.26a with Cu^{2+} , the ionexchange of Zn^{2+} in a bent coordination between two T1 Al atoms accessed from the 12-MR is shown in Figure 4.30. While the angle O7–Zn–O3 is entirely reasonable at 121.3° for a bent coordination, the bond lengths are longer but still reasonable at 2.00 Å for Zn–O7 and 2.07 Å for Zn–O3. When comparing Cu^{2+} and Zn^{2+} ion-exchange at this location, the ionexchange of Zn^{2+} introduces a significantly higher amount of framework deformation, especially in the T1–O7–T1 bond angles. These angles are normally closer to 150°, and in the case of Cu^{2+} ion-exchange were approximately this value. While not deformed to the same extent, the T1–O1–T3 angle (not shown in Figure 4.30, shown in Figure 4.26a) is decreased to 141.3° from approximately 155°. Based on the amount of deformation to the surrounding framework required to ion-exchange and stabilize the Zn^{2+} suitably, this is not considered to be a primary location for Zn^{2+} ion-exchange but is believed to be feasible. Interestingly, the O7 atom not bound to Zn was still drawn to it. The model where this bond was formally made did not converge.



Figure 4.30. Zn^{2+} ion-exchanged in a bent coordination between T1 Al atoms at the smaller 6-MR located as part of the 12-MR (bond lengths are in Å).

In the same 6-MR, the situation could exist where a T1 Al atom and a T2 Al atom are separated by a T1 Si atom. In this case, the only possibility for ion-exchange at this location would have to involve using the O7 and O3 atoms. Cu²⁺ did not successfully optimize at this location, but Zn^{2+} did with results shown in Figure 4.31. However, this could be considered to be another improbable location for ion-exchange. The bond lengths between Zn–O7 and Zn–O3 at 2.33 Å and 2.21 Å respectively are longer compared to other ion-exchange locations. The angle between the bonds is very small for a bent molecule at 59.3°, and would bring with it a high degree of instability. For the ion-exchange to occur at this location, the framework must be distorted significantly. This means the bond angles at T1-O7-T1 and T1-O3-T2 have been decreased to 133.4° and 137.2° respectively. Under more normal circumstances these bond angles would have been in the order of 150° and 158° respectively. The bond lengths between the Al and nearby O atoms are also extended considerably beyond what they should be, and are approximately 1.90 Å. Due to the deformation required of the framework and the strange coordination of the ion-exchanged Zn^{2+} , this is again considered to be an improbable location for ion-exchange of Zn^{2+} to occur.



Figure 4.31. Zn^{2+} ion-exchanged in a bent coordination between a T1 Al atom and T2 Al atom at the smaller 6-MR located as part of the 12-MR (bond lengths are in Å).

In an identical orientation of Al's as shown in Figure 4.28 for Cu²⁺ ion-exchange, ionexchange of Zn^{2+} can occur in the same location albeit with a significantly different result as shown in Figure 4.32. For the case of Zn^{2+} , the angle between bonds is smaller at 72.2° (as compared to 78.8° for Cu²⁺). Due to this smaller angle, the bond lengths are longer between Zn-O2 and Zn-O3 at approximately 1.95 Å each but are still reasonable. As expected, there is deformation to the bond angles as the framework O atoms are drawn closer to the ion-exchanged Zn^{2+} . This angle deformation is to about the same extent as occurred for Cu²⁺. The Al–O bond lengths are reasonable, with the largest being between T1 and O3 at 1.80 Å. The biggest difference between Zn^{2+} and Cu^{2+} being ion-exchanged at this location is the Cu^{2+} did not seem to be drawn to any other O atoms besides the primary points for ion-exchange. The Zn^{2+} seems to be drawn to the other O2 bonded to the T4 Al. The framework has also deformed so that specific O2 is brought closer to the Zn²⁺. Indeed, rather than having a coordination number of 2, it may be more feasible for Zn^{2+} to have a coordination number of 3 and take on a more trigonal planar orientation at this ionexchange location. However, the model where this structure was put in place did not converge. Rather, the deformation of bonds here may be due more to the Zn^{2+} cation drawing a larger part of the negative framework charge present at O atoms to itself, though this does not seem realistic as Cu²⁺ should have done the same. Regardless, this is considered to be one of the more likely ion-exchange locations for Zn^{2+} as compared to the situations presented in Figures 4.30 and 4.31.



Figure 4.32. Zn^{2+} ion-exchanged in a bent coordination between a T1 Al atom and T4 Al atom at the smaller 5-MR located as part of the 12-MR (bond lengths are in Å).

In an identical scenario as posited in Figure 4.29 for Cu^{2+} ion-exchange, Figure 4.33 shows the results from placing Zn^{2+} in the same location. Again, the results between Cu^{2+} and Zn^{2+} ion-exchange are markedly different. Zn^{2+} seems to be drawn much more strongly towards the O2 atom bonded to the T2 Al, with a bond length of only 1.81 Å. This is in stark contrast to the bond between Zn^{2+} and the other O2 atom bonded to the T4 Al, which has a length of 2.86 Å. It is obvious from Figure 4.33 that the O10 atom has been drawn much closer to the Zn^{2+} . This did not occur with Cu^{2+} being placed here. This result would give the impression that the Zn^{2+} should instead be using the O10 atom as one of the primary bridging O atoms for ion-exchange. However, the model in which this scenario was set up did not converge. The as-expected decrease in bond angles at which the ion-exchange was assumed to occur has happened here as well. While this may be considered to be a reasonable location for ion-exchange to occur, it is likely that if it does occur here it would more likely involve the T4–O10 atom rather than the T4–O2 atom.



Figure 4.33. Zn^{2+} ion-exchanged in a bent coordination between a T2 AI atom and T4 AI atom at the mouth of the 8-MR side pocket connecting the 8-MR and 12-MR channels (bond lengths are in Å).

The rest of the Zn²⁺ ion-exchange that will be discussed is with respect to the ionexchange occurring in the 8-MR or involving atoms in the 8-MR. Figure 4.34a shows Zn²⁺ with a coordination number of 2 bonded to O1 atoms located at a T1 Al and a T3 Al. The Zn^{2+} in this scenario appears to have taken on a bent coordination once again with a bond angle of 111.9° and bond lengths between the Zn and O1 atoms of 1.95 Å and 2.10 Å. However, in this scenario the Zn²⁺ has drawn the O6 atom closer to itself as it did with the O10 atom in Figure 4.33. The Zn^{2+} ion-exchange in Figure 4.34a led to a moderate amount of framework deformation. The T1-O7-T1 angle is normally in the order of 150°, and here it has been reduced to 140°. Considerably worse, the T1-O6-T1 atom is also normally in the order of 150° and has been decreased to 136.6°. A much more plausible ion-exchange scenario in this location for Zn^{2+} is presented in Figure 4.34b, where the Zn^{2+} has taken on a more trigonal planar/trigonal pyramidal coordination. In this scenario, the bond lengths are more consistent and vary between 1.93 Å for Zn-O6 and 2.02 Å for Zn-O1. The amount of deformation to the framework is significantly reduced, with bond lengths between T1 Al atoms and neighbouring O atoms being between 1.78 Å and 1.84 Å. All bond angles have been kept much nearer to what was optimized for MOR without the ion-exchange. For example, the T1-O6-T1 angle was optimized without ion-exchange to be approximately 148°. Here, with the ion-exchange, it has only been reduced to 143.9°. The T1-O7-T1 angles are also much nearer to the approximately 150° they are in reality. Based on the minimization of the impact to the framework and the bond lengths and angles of the ionexchanged Zn²⁺, for this location it is much more feasible that Zn²⁺ would take on a coordination number of 3. While any ion-exchange that may occur in the 8-MR could be considered to be much more difficult than the 12-MR (due to steric restrictions and accessibility issues), this seems to be a highly plausible location for Zn²⁺ to ion-exchange.



Figure 4.34. Zn^{2+} ion-exchanged into the smaller 5-MR as part of the 8-MR channel in a) bent, and b) trigonal planar coordination between a T1 Al atom and a T3 Al atom (bond lengths shown are in Å).

Similar to the case of Cu²⁺ being able to ion-exchange in the 8-MR side pocket, Zn²⁺ can also ion-exchange at the mouths of those side pockets as well. The difference between the two, however, is the Cu^{2+} ion-exchanges where the 8-MR side pocket meets the 12-MR main channel and Zn^{2+} ion-exchanges where the side pocket meets the 8-MR smaller channel. This is shown in Figure 4.35. In Figure 4.35a, the Zn^{2+} is ion-exchanged directly at the T3–O9 site with a coordination number of 3. The primary points of ion-exchange are the T3-O9, T3-O1, and T1-O1 sites. In this scenario, the Zn-O bond lengths are between 1.96 Å and 2.05 Å, which are reasonable and in line with results presented previously. No O atom has been drawn towards the Zn more than the others, making for a greater degree of symmetry. The framework bond angles have changed considerably. The T1-O1-T3 angle is normally in the order of 150°. In the case presented here in Figure 4.35a, these angles have been decreased to 125.7° and 130.7°. The T3-O9-T3 angle has been left relatively unchanged. The bond lengths between the Al and O atoms have been increased as is expected, the largest being between the T1 Al and O1 at 1.87 Å. This is consistent with previous results and, though somewhat larger, is again not unrealistic. With a different orientation of the T1 and T3 Al atoms as shown in Figure 4.35b, ion-exchange of Zn²⁺ in the

8-MR side pockets is again possible, though perhaps to a lesser degree compared to the situation presented in Figure 4.35a. Here the Zn²⁺ again has a coordination number of 3 but with much greater variance in bond lengths. The primary points of ion-exchange are the T1-O1, T1-O6, and T3-O1 atoms with bond lengths varying between 1.86 Å and 2.32 Å. The framework bond angle T1-O1-T3 has been considerably decreased to approximately 126° while the bond angle T1-O6-T1 is relatively unchanged. Bond lengths between the Al atoms and O atoms are extended as before, with maximum bond length again being 1.87 Å. Regardless, both locations and scenarios presented in Figure 4.35 are considered to be feasible ion-exchange locations for Zn.



Figure 4.35. Zn²⁺ ion-exchanged into the mouth of the 8-MR side pockets at the 8-MR channel between a T1 Al and T3 Al atom with the T1 Al located at different positions relative to the T3 Al atom (bond lengths shown are in Å).

To summarize the Zn^{2+} ion-exchange modeling results, it appears that Zn^{2+} can ionexchange in the 8-MR channel and 12-MR main channels along with the 8-MR side pockets. From the modeling results, it appears that Zn^{2+} does not care to take on a higher coordination as Cu^{2+} did, with many of the converged models for Zn^{2+} being with it in a highly bent coordination or a deformed trigonal planar/trigonal pyramidal coordination. No models converged with Zn^{2+} at a higher coordination number than 3. In terms of preference, it would appear that Zn^{2+} is much more comfortable ion-exchanging in the 8-MR channel and 8-MR side pockets.

4.5.4 Competitive ion-exchange between Cu²⁺ and Zn²⁺

From the individual discussions of Cu^{2+} and Zn^{2+} ion-exchange, there are some very simplified conclusions that can be drawn. Even though the Cu^{2+} ion-exchange models did not converge as easily as the Zn^{2+} models, all models that successfully converged and had what could be considered believable results had Cu^{2+} ion-exchange taking place primarily in the 12-MR channel with a minor possibility of it occurring in the 8-MR channel. Most of the believable models for Zn^{2+} ion-exchange placed Zn^{2+} in the 8-MR channel and at the mouth of the 8-MR side pocket where it connects with the 8-MR channel. Not all Zn^{2+} model results were presented as many were redundant, but it is important to point out that all converged Zn^{2+} models in the 12-MR were presented while only about half of the results for ion-exchange in the 8-MR were presented.

With that in mind, there are locations where there is direct competition between Cu²⁺ and Zn^{2+} for the negative framework charge. As mentioned earlier in Section 3.4.2, the energies that were calculated from the models were considered to be quite unreliable and were not used for the determination of whether Cu^{2+} or Zn^{2+} were more likely to ionexchange at a particular location. Aside from this, even if these results were reliable, they would not be representative of reality. The MOR used for the determination of the experimental/characterization data above had a Si/Al ratio of 6.5. This means there are many Al's present in the framework. The models presented assumed that only two Al atoms were present in the framework. The influence of other nearby Al atoms (at next nearest neighbour positions) was not considered as this would have created far too many models to conceivably run. The scenario may also exist where more than two framework Al atoms are involved in the ion-exchange. With the negative charge introduced by the Al being potentially shared by more than one neighbouring O atom, the possibility exists where three AI atoms could be involved in the ion-exchange of a single divalent cation [140]. One framework AI atom could be involved in the ion-exchange of more than one divalent metal due to this splitting of the charge amongst the neighbouring O atoms. Also, the likelihood of one metal being at a certain location would also be influenced by its concentration in the ion-exchange solution and the conditions (i.e., temperature, pH) of the ion-exchange. Therefore, inferences will be made from the models that were run and should not be considered as absolute truth. It should be kept in mind that only ~55% of the theoretical ion-exchange limit is reached on MOR with divalent metal ion-exchange as shown in Table 4.1 and by several other groups [161,170–172]. Enough scenarios have been presented above that all tetrahedral atom locations were included in the ion-exchange at some point.

Whether some of these ion-exchange scenarios were feasible or not, due to the sharing of Al atoms in ion-exchange or framework Al atoms simply being too far apart from one another, not all Al atoms on MOR will be involved in divalent transition metal ion-exchange

The overall summarized results from the modeling of Cu^{2+} and Zn^{2+} ion-exchange are shown in Figure 4.36. It is assumed based on the results that Cu^{2+} does not ionexchange in the 8-MR. While converged results were shown for Cu^{2+} for ion-exchange between T1 and T3 Al atoms in the 5-MR as part of the 8-MR, this is considered very unlikely as Cu²⁺ would have a much more suitable coordination and minimal impact on the framework when ion-exchanged between two T1 AI atoms in the 12-MR, or between T1 and T4 Al atoms. If the Cu^{2+} preferentially ion-exchanged in these locations, it would mean it would draw the negative framework charge away from the 8-MR and further ion-exchange may not be possible there. With regards to the Zn^{2+} models, many of those that converged in the 12-MR seemed to have highly stressed bond angles or long bond lengths. While it is not going to be argued here that ion-exchange of Zn^{2+} in the 12-MR is not possible (because it very likely does occur), it is simply going to be assumed that Cu^{2+} ion-exchange is preferable to it. In fact, if Zn^{2+} were given the option of ion-exchange at a T1 Al site, it is more likely it would choose to ion-exchange in the 8-MR channel or even in the 8-MR side pocket as compared to the 12-MR. Those locations for Zn^{2+} showed reasonable bond lengths and angles and a minimization of framework distortion. The one location in the 12-MR where Zn^{2+} and Cu^{2+} may more directly compete is between the T2 AI atom and T4 AI atom. Both models converged at that location but had slightly different locations of the ionexchanged metal. The Cu²⁺ had shorter bond lengths and a larger angle between the bonds, which is why it was assumed to be more preferable at that location as compared to Zn²⁺.



Figure 4.36. Possible ion-exchange locations of Cu^{2+} and Zn^{2+} on MOR (Al atoms not shown).

Based on the results, there are many important insights that can be made about Cu^{2+} and Zn^{2+} simultaneous bimetallic ion-exchange. With only ~55% of the possible theoretical ion-exchange limit met on MOR, about half of the acid sites created by the presence of framework AI atoms are exposed for either adsorption or catalysis. This does not include the potential for reduction of Cu^{2+} to Cu^{+} , which should lead to the creation of an acid site from the reduction. The principle of the ion-exchanged metals competing for the negative framework charge becomes very important in understanding why only ~55% of the possible ion-exchange is achieved. Firstly, from the modeling results one of the primary locations for ion-exchange is believed to be at the T1 Al atom. In the greater majority of models that converged, an Al atom at the T1 location was usually involved. The T1 atom location is shared between the 8-MR and 12-MR. This means that if its negative charge is compensated for via ion-exchange in the 12-MR channel, the ion-exchange will not likely occur in the 8-MR channel and the remaining Al atom located in the 8-MR channel that would have been involved in the ion-exchange is left free. The opposite can also be considered to be true. Secondly, the T1 atom location is not the most likely location for Al atoms to be; the T3 location is. It had been previously mentioned in Section 2.3.2 that the distribution of T1:T2:T3:T4 Al atoms would be 36:20:42:29 [197-200]. While models were set up to simulate ion-exchange occurring between T3 Al's and T4 Al's, none of these models converged. These Al atoms are simply too far apart and not in the proper orientation for ion-exchange to conceivably occur (T3 is pointed towards the inside of the 8MR channel; T4 is pointed to the inside of the 12-MR channel). Therefore, ion-exchange must nearly always involve the T1 and T2 Al's. If it is assumed that every T2 atom is involved in ion-exchange with other locations and not itself, it means that, based on the ratios from Ban et al. [200], 31.5% of the theoretical ion-exchange limit is already reached, just with T2 Al atoms. While this is a poor assumption to say the least, it does lend credence to the idea that the T1 and T2 atoms are the locations of ion-exchange. The T2 atom location is not shared between the 8-MR and 12-MR, but it can provide an ion-exchange location together with another T1 atom for divalent metals and take the T1 away as a potential ion-exchange location for the 8-MR. The competitive ion-exchange that occurs for the T1 atoms therefore becomes the dictating factor for where the ion-exchanged Cu^{2+} and Zn^{2+} finally settle. In some situations, it becomes highly possible that the 8-MR could become blocked off, while in other situations most of the ion-exchange would occur in the 12-MR, dependent upon the ratio of Cu^{2+} and Zn^{2+} .

4.6 Discussion

When taking the experimental/characterization and modeling results together, the data all seems to support the same conclusion about how Cu and Zn together help to make MOR more stable for DME carbonylation. There have already been published studies utilizing monometallic Cu/H-MOR for DME carbonylation and claiming Cu by itself helps to improve the stability [92,223,232,233]. The accuracy of the data in these studies is not being called into question. As these studies were performed at slightly different reaction conditions and with different catalyst pretreatments, monometallic Cu/H-MOR may indeed be better as compared to H-MOR, particularly if the residence time is decreased. However, even in the latest BP Chemicals Ltd. patents, it has been shown that H-MOR by itself under their reaction conditions lasts as long if not longer than Cu/H-MOR [223,230]. In the present case, Cu/H-MOR actually performed even more poorly compared to H-MOR. It showed little to no enhancement in selectivity, and deactivated more quickly (23 hours vs. 30 hours for H-MOR). This is quite unexpected, as it was shown from HF modeling, pore distribution analysis, DRIFTS, and XRD (to some extent) that Cu²⁺ strongly preferred ionexchange in the 12-MR channels. It had been previously theorized that the acid sites in the 12-MR were predominantly responsible for the creation of coke and the subsequent deactivation of the catalyst [212,215–217]. If Cu²⁺ were ion-exchanging preferably in the 12-MR, it means the deactivation should be, at the very least, hindered and the selectivity towards MeOAc should be improved. The problem is then that Cu^{2+}/Cu^{+} sintered during the reaction, collecting into larger nanoparticles on the surface (and likely in the channels) of H- MOR. This was shown by comparison of the TEM images from before and after reaction. These large nanoparticles could easily block the microporous channels of H-MOR. It had been previously known that only a small amount of blockage in a channel of H-MOR can deactivate the entire channel [234]. If the Cu^{2+}/Cu^{+} had stayed ion-exchanged during reaction, not changed position, and maintained the high dispersion shown by CO isotherms, the lifetime of the catalyst would likely have been considerably longer and selectivity upon deactivation improved. The argument could be made that Cu sintering may be beneficial: if the 12-MR could be blocked off completely, that should stop the deactivation. The problem, though, is that the 8-MR channel and the active sites for DME carbonylation may not be directly accessible. Given the size of DME and MeOAc, it is far more likely that the reactants and products access and leave the active site in the 8-MR channel through the 8-MR side pockets that connect the two channels. The sintering behaviour of Cu under the reaction conditions is also likely the reason regeneration of the catalyst does not result in a completely restored activity level [223]. TEM images also seemed to show that a carbonaceous shell formed around the Cu clusters. In addition to the sintering of Cu accelerating catalyst deactivation, it may also unintentionally increase the coking rate, though TPO shows that the coke that is formed on Cu/H-MOR is considerably lighter than that formed on H-MOR.

Under the reaction conditions used, monometallic Zn/H-MOR performed considerably better as compared to H-MOR and Cu/H-MOR even though Zn is not a carbonylation catalyst. Rather, what Zn²⁺ likely does is ion-exchange and, based on its electronic configuration and the results from TPR, not leave the ion-exchange sites. This is supported by the TEM images of calcined and spent catalysts, which showed no sintering of Zn²⁺ into larger nanoparticles. XPS also showed little change in the binding energy of ZnO between the calcined and spent catalysts. The role of Zn^{2+} is simply to just block active sites that may lead to MOR coking and subsequent deactivation. This was shown by TPO. The presence of ZnO did not limit the creation of heavier coke as Cu did, but it certainly hindered the rate at which it was formed. The presence of Zn^{2+} would decrease the density of acid sites in the 12-MR, and potentially prevent polymerization reactions that lead to formation of heavy coke [221,222]. Ion-exchanged Zn^{2+} did not change the acidity of the H-MOR to any great extent, indicated by NH₃-TPD and DME-TPD. It did limit how much DME was non-dissociatively adsorbed, which is a likely explanation for the decreased coking rate. From the modeling results, there exists a possibility that ion-exchanged Zn^{2+} may actually block the active sites for carbonylation in the 8-MR channel. This is seemingly supported by the pore distribution results as well. The Ar used for the physisorption was almost

completely blocked from getting into the 8-MR side pockets and 8-MR channels. The 12-MR was also deformed and partially blocked on monometallic Zn/H-MOR. DRIFTS analysis along with the modeling results also indicated that Zn^{2+} seemed to have a preference for ion-exchange in the 8-MR channel, though all results also indicated that it ion-exchanged in the 12-MR as well. This blockage does not seem to have impacted the peak productivity towards MeOAc. However, the "induction period" before peak DME conversion and MeOAc productivity were achieved was extended considerably - almost double what it was for H-MOR and Cu/H-MOR. In all cases, the ion-exchange of Zn²⁺ on H-MOR seemed to increase the time required to achieve peak productivity. This may indicate some level of blockage that either decreases with reaction time (which would be an indication that Zn, like Cu, does migrate to new locations under reaction conditions) or simply that the presence of Zn has introduced additional steric limitations (and therefore, diffusion limitations) that must be overcome. The presence of ion-exchanged Zn^{2+} at the mouths of the 8-MR side pockets, indicated by modeling results, may have introduced considerably higher diffusion limitations, which could be responsible for this extended induction period. While under certain circumstances Zn may be leeched from the catalyst, based on analysis of used catalyst there is no evidence to support that Cu or Zn metal leeching is happening during the pretreatment or the reaction.

The question is therefore raised as to the primary roles of Cu^{2+} and Zn^{2+} in the bimetallic Cu-Zn/H-MOR catalysts. As a reminder, not all bimetallic combinations provided an enhancement over the monometallic Zn/H-MOR. When Cu^{2+}/Cu^{1+} was in molar excess of Zn²⁺ in the 2Cu-1Zn/H-MOR catalyst, a higher productivity rate as compared to Zn/H-MOR was achieved but the catalyst deactivated more quickly, leading to an overall lower total production of MeOAc. At approximately equimolar amounts of Cu and Zn, the 1Cu-1Zn/H-MOR catalyst had higher peak and total MeOAc productivity than Zn/H-MOR, but deactivated at a very fast rate when deactivation began at approximately 26 hours. The 1Cu-4Zn/H-MOR catalyst more than doubled the total MeOAc production of any other catalyst tested. This is likely due to several stabilizing factors and not just a single one. First of all, and possibly the easiest to comprehend, is the impact on the reduction temperature of Cu⁺ and Zn^{2+} 's ability to keep the atoms of Cu isolated. It is interesting to note that the Cu²⁺ in 2Cu-1Zn/H-MOR reduced more easily than monometallic Cu/H-MOR as indicated by TPR results. With increasing Zn^{2+} addition the required reduction temperature of Cu^{2+} kept increasing. It should be recalled here that the dispersion of Cu was very high at ~63% for all bimetallics. The reason for this is likely that ion-exchange of Zn^{2+} has led to either increased or decreased deformation of the MOR framework itself. Deformation to the

framework would potentially lead to changes in the ion-exchange behaviour by either increasing or decreasing bond lengths and angles. Changes in these parameters would lead to changes in the reduction behaviour of Cu^{2+} and Cu^{1+} . There were not always significant changes in reduction temperature, as was the case with 2Cu-1Zn/H-MOR and 1Cu-1Zn/H-MOR. With these two catalysts, it may simply be that there was not enough Zn²⁺ to make a substantial difference or it was not located close enough to where Cu²⁺ was ion-exchanging to impact it. At low ion-exchange levels, Zn²⁺ may have preferred ion-exchange in the 8-MR channel or in the side-pockets, which would have had minimal impact on the preferred ion-exchange of Cu^{2+} in the 12-MR. While modeling supports this conclusion, the pore distribution analysis does not. Either way, based on modeling, at very high Zn²⁺ loadings Cu^{2+} would be forced to ion-exchange at T1 Al's in the 12-MR, where it can take on a higher coordination and be more stable, thereby requiring a higher reduction temperature. Based on the TPR results for 1Cu-4Zn/H-MOR, Cu⁺ may not even reduce to Cu metal before the MOR framework begins being damaged by the high temperature (occurs at 700-800°C [282–284]). By TEM imaging, it was also shown that with 2Cu-1Zn/H-MOR, Cu still sintered. By 1Cu-1Zn/H-MOR, the sintering appears to have been stopped and on 1Cu-4Zn/H-MOR the ion-exchanged metals are hardly even visible. The role of Zn is therefore to prevent Cu sintering and stabilize it in its monovalent state. This is done by both isolating it and increasing its reduction temperature to the point where it is guaranteed that it will not fully reduce, or leave, the ion-exchange location. While Cu⁺ may not assist in the reaction (there isn't much evidence in the present case to support that it would), it can at least block sites that would normally contribute to coking.

There are additional reasons as to why the 1Cu-1Zn/H-MOR did not perform as strongly as either of 1Cu-2.5Zn/H-MOR and 1Cu-4Zn/H-MOR. Of all the catalysts tested, there were only two that seemed to have severe blockage of the 8-MR channels and side pockets as indicated by pore distribution analysis: the Zn/H-MOR and the 1Cu-1Zn/H-MOR. This was also hinted at by the relative peak intensities in the XRD patterns for those two catalysts. This behaviour is only possibly understood by analysis of the results from modeling. There were not as many preferred ion-exchange locations in the 12-MR as in the 8-MR channels and side pockets for Zn^{2+} . In fact, Cu^{2+} ion-exchange in the 8-MR channels did not seem to be favoured at all. At this particular ratio, what may have occurred is that Zn^{2+} forced Cu^{2+} away from its comfortable position at the T1 Al sites in the 12-MR by ion-exchanging at the T1 Al's from the 8-MR channels and side pockets. Cu^{2+} would be forced to its other possible ion-exchange sites in the 12-MR. This is supported by the DRIFTS results, where among the bimetallics 1Cu-1Zn/H-MOR had the highest ratio of 12-MR BAS

to 8-MR BAS. With Cu²⁺ in excess in the 2Cu-1Zn/H-MOR catalyst, it may have forced Zn²⁺ into its other less favourable locations. Therefore, with regards to the 1Cu-1Zn/H-MOR, additional stability is achieved with the Zn but, due to the competitive ion-exchange, the metals did not block the proper sites to achieve the stability that is realized when Zn is in molar excess of Cu on the MOR. This explanation does not necessarily explain why the smaller channels and pores were so open in 1Cu-4Zn/H-MOR compared to 1Cu-1Zn/H-MOR. Experimentally, Cu^{2+} ion-exchange does occur more readily compared to Zn^{2+} ion-exchange (the ratio of Cu:Zn in solution to produce 1Cu-4Zn/H-MOR was ~0.1). With such low Cu^{2+} in solution and Zn^{2+} not preferring ion-exchange at Cu^{2+} 's favourite exchange location [301], perhaps Cu²⁺ ion-exchanged first and refused to move from its position, even with all the Zn^{2+} ion-exchange going on. This is another factor in the ion-exchange. When the next nearest neighbours can influence the acidity of a particular Al site, and ion-exchange of a metal will have some influence on those neighbours, perhaps at different ratios of Cu:Zn the strength of the ion-exchange locations is changed and Cu^{2+} and Zn^{2+} change their preferences. This is an area of research that could be explored both theoretically and experimentally to almost no end.

Another important point has been mentioned earlier but will now be discussed directly. The role of Zn is easy to understand, but what of the role of Cu? In what was an unexpected conclusion, it would seem Cu^{2+}/Cu^{+} does not actually assist in facilitating the reaction under the conditions of the current study. Rather, the role of Cu²⁺ is twofold: to prevent and force Zn²⁺ to ion-exchange at locations it would not normally if it was ionexchanged by itself, and to *block* sites that would not have normally aided in the carbonylation of DME. The two metals by themselves cannot achieve these goals, and it is quite obvious that the two need to be together. Therefore, the true source of the stabilization of MOR using ion-exchanged Cu^{2+} and Zn^{2+} is selective site blockage. The two metals can even prevent each other from moving around. While Zn was required in substantial molar excess of Cu for the optimum catalyst performance to be achieved, Zn is far less likely to sinter into larger nanoparticles when compared to Cu. With Cu in such low amounts on the catalyst, the individual atoms would be isolated enough from each other that the probability of sintering would be minimized, and instead Cu would keep Zn from excessively ion-exchanging in the 8-MR. That all said, it may be apparent that the key metal in this scenario is not necessarily the Cu, but the Zn. The Cu²⁺ could likely be replaced with other metals in the ion-exchange, such as Co^{2+} or Fe^{2+} , and the same enhancement may be achievable.

While discussing this topic, the comparison of modeling results and experimental results will be summarized. The modeling of zeolites is non-realistic from many perspectives. While many reasonable assumptions can be made as to where the Al's actually are in the MOR framework, it is nearly impossible to know for certain. It is also not unreasonable to assume that every synthesized batch of MOR will be a little bit different, even those with the same Si/Al ratio. The bond lengths between Al and O atoms in the framework are also considerably longer as compared to the Si-O bonds. With more and more Al included in the framework, the framework will become increasingly distorted from the purely siliceous framework. A truly realistic model would include enough Al's to account for this distortion and have the compensating cations present as well. However, this would substantially increase the processing time for the models and greatly increase their complexity. In the case of the modeling presented in this paper, model convergence proved to be an issue with just two Al's present, and often times models had to be rerun with slightly different conditions to achieve convergence. Putting Al's at the next nearest neighbour positions as well would have introduced an almost overwhelming number of possibilities in the modeling. With that said, the models have agreed quite well with what was observed experimentally. The ultimate, and simplified, conclusion of the modeling work was that Cu²⁺ ion-exchange was preferred in the 12-MR and was nearly an impossibility in the 8-MR channel. Zn²⁺ ion-exchange was preferred in the 8-MR channel and 8-MR side pockets, but could also easily occur in the 12-MR. The experimental characterizations which are the strongest supporters of this conclusion (as they directly verify it) are the pore distribution analysis, DRIFTS, and XRD. To some extent, TPO also supports the conclusion from modeling. Ignoring the bimetallic combinations of Cu and Zn for the purposes of the present argument, Cu/H-MOR, as compared to H-MOR, showed a decrease in the pore volume due to the 12-MR but did not change the initially very high adsorption of Ar onto the sample. The initial high levels of adsorption would be due to Ar physisorbing in the 8-MR channels and side pockets. Unfortunately these two could not be separated into two distinct peaks as the limit of the equipment had been reached. When Zn/H-MOR and H-MOR were compared, those initial high levels of adsorption had been nearly completely removed and the pore volume due to the 12-MR was also lowered. This directly shows preferential Cu²⁺ ion-exchange in the 12-MR and Zn^{2+} ion-exchange in both the 8-MR and 12-MR. The earlier results from XRD simply showed that the presence of ion-exchanged Cu²⁺ had much less of an impact than ion-exchanged Zn^{2+} . One of the few places an ion-exchanged metal could make such a considerable difference in the XRD pattern would be the 8-MR. In this location, the presence of an ion-exchanged metal would significantly affect the pore volume

available there and could prevent the constructive interference of the X-rays. Due simply to total pore volume, ion-exchanged metals in the 12-MR would have much less of an impact. DRIFTS analysis in the hydroxyl region more directly showed the preference of Cu²⁺ ionexchange in the 12-MR and Zn^{2+} preferential ion-exchange in the 8-MR with some occurring in the 12-MR. TPO results were less of an indication, but showed that the presence of Cu decreased the weight of the coke that was formed substantially. Coke formation in the 8-MR (if it was occurring) would be sterically limited to lower molecular weight. By decreasing the molecular weight of the coke formed, and with the theories that deactivation of MOR occurs in the 12-MR for this particular application [212,215-217], it is implied that Cu²⁺ ionexchange was occurring in the 12-MR. With the moderate molecular weight coke that formed on Zn/H-MOR, it is insinuated that there was some Zn^{2+} ion-exchange in the 12-MR but not as much as Cu²⁺. It is therefore assumed that, for the purposes of this study and despite the difficulty, the models were actually a very strong indication of what was actually occurring in the ion-exchange procedure. Of course this is relevant only from the perspective of when equilibrium is achieved and a stable structure is produced. If different methods were to be used for getting the Cu^{2+} and Zn^{2+} onto the MOR, such as impregnation, the models may not be so relevant.

The purpose of this work was not to theorize on the potential reaction mechanism. However, there is one characterization result which seemingly directly contradicts what has been theorized previously. One of the original assumptions about the interaction of DME with protonated MOR is that DME will interact with two acid sites to produce two adsorbed methyl groups (or methoxy sites) and water. These methoxy sites have been theorized to be the true active site for the reaction [82,83,90,212,215–217]. In the DME adsorption experiments, the results were calculated based on this assumption. The problem therein is that the amount of active sites populated with methyl groups did not seem to accurately reflect how much metal was ion-exchanged and blocking the acid sites. The metal loading was consistently ~55% of the theoretical limit. This means ~55% of Al's were blocked with metal. While Cu²⁺ may reduce off of these ion-exchange sites and the location could again serve as a site for DME to interact with, Zn²⁺ would not. The difference in sites accessible to DME, with the assumption that DME can interact with two active sites, is only $\sim 6\%$ between H-MOR and the metal-exchanged H-MOR catalysts. While it may be believable that, on protonated MOR (H-MOR), DME may interact with 78.1% of the sites, it is not believable that on Zn/H-MOR, where Zn^{2+} is occupying 52% of the active sites, that DME could still interact with 73.6% of them. For this to be feasible, it would imply that, even with a metal blocking the site, the DME could interact with it. Now, it must be stated that

there is a certain degree of error associated with the DME adsorption experiments. However, the DME adsorption experiments were performed until a consistent number was achieved, and many corrections were applied. If there had been a considerable source of error, the numbers should not have been as consistent as they were over the four times the experiment was repeated for Zn/H-MOR. The numbers for DME activation make more sense if one assumes that DME, by itself with nothing else to force a reaction, only interacts with one site. In this case, on H-MOR only 39% of sites would be interacted with by DME, and for Zn/H-MOR it would be 37%. For comparison, Cu/H-MOR would be 36%. No further work was conducted on this to explain the observed trend with DME adsorption/desorption and the unaccounted for DME. It is perhaps that the reaction of DME with active sites to produce methyl groups is slow without increased pressure and not enough time was provided for DME to form methyl groups. This has been previously used as an explanation for the reason the MOR catalysts have an induction period [90].

4.7 Conclusions

While MOR is well-known to facilitate the carbonylation of DME to MeOAc, the problem has remained that it is quite unstable and protonated MOR by itself has a useful lifetime of only approximately 15 hours, dependent on reaction conditions. Of course the MOR can be regenerated by well-known means, but this requires time and significant energy. There is considerable value, both from an energy perspective and being able to industrialize this technology, to providing a stabilized MOR for reaction that does not have to be regenerated once a day. Despite the discovery of MOR for this reaction occurring nearly 10 years ago, the solutions so far presented have either involved quite complicated catalyst alterations, which would have problems with scale-up, or significant changes to the reaction conditions (higher temperature and pressure, substantial H₂ in the feed). Ion-exchange is a very simple procedure used to make industrial catalysts and scale-up problems are minimal.

The simultaneous ion-exchange of Cu²⁺ and Zn²⁺ onto MOR can provide a far superior catalyst to H-MOR alone. While Cu/H-MOR has been worked on by other groups, in the current study this catalyst was found to have even worse performance than H-MOR alone. This was likely due to the migration of Cu on the surface of the MOR during reaction and excessive sintering leading to active site blockage. Monometallic Zn/H-MOR was more stable and produced more MeOAc as compared to H-MOR and even some of the bimetallic Cu-Zn/H-MOR combinations. The true value of the bimetallic combinations is shown when Zn is in molar excess of Cu on the MOR. With the 1Cu-4Zn/H-MOR (Cu:Zn ratio of 0.25),

the catalyst lifetime and MeOAc produced were increased to 4 times that of H-MOR. The addition of Zn also suppressed the formation of MeOH and other products. Even during catalyst deactivation, the selectivity towards MeOAc remained high. Extensive characterization revealed that Cu²⁺/Cu⁺ and Zn²⁺ likely do not take part in the reaction, and instead the advantage of the Cu-Zn bimetallic combination lies in selective site blockage. With Zn in molar excess, the nature of Cu to sinter is limited and Cu likely stays at ion-exchange locations in its monovalent state. ZnO does not sinter due to its stable electronic configuration. With particular Cu-Zn combinations (Zn being in molar excess), both metals stay at their ion-exchange locations and simply block acid sites.

The competitive ion-exchange around the T1 Al site between Cu^{2+} and Zn^{2+} was found to be the most important determining factor for the ideal ratio of ion-exchanged Cu^{2+} to Zn^{2+} . Cu^{2+} prefers to ion-exchange at T1 Al's from the 12-MR, while Zn^{2+} prefers to ionexchange at T1 Al's from the 8-MR. Including only a small amount of Cu^{2+} allowed the 8-MR of MOR to remain clear and accessible to the reactants while also removing some of the negative framework charge from the 8-MR channel location. This also forced Zn^{2+} to move to ion-exchange locations in the 12-MR of MOR, where it could more effectively prevent any reactions that would lead to formation of coke and subsequent deactivation of the catalyst. This conclusion was only possible due to the combination of extensive characterization and theoretical modeling work.

The bimetallic ion-exchange of Cu^{2+} and Zn^{2+} onto MOR is a simple procedure that can significantly enhance the stability of commercially available MOR for use in DME carbonylation and makes its industrialization a far more attractive venture.
Chapter 5

Dealumination of mordenite by acid leaching for stability enhancement

Carlson's Consolation: Nothing is ever a complete failure; it can always serve as a bad example.

--Variant of Murphy's Law

5.1 Introduction

Ion-exchange remains one of the simplest and easiest means to modify the stability and other characteristics of a zeolite. For the case of where the zeolite itself serves as a catalyst as it does in the present case, it unfortunately isn't necessarily feasible or practical to use ion-exchange. This could be due to an assortment of reasons. The metal to be used for the ion-exchange may be too costly, as can potentially be the case for metals such as Au, Rh, Pt, Pd, or Ir. In some cases, if the pore and channel sizes of the zeolite are too small, bulkier cations cannot possibly ion-exchange due to steric limitations or complete ionexchange may otherwise be impossible [161,167,170–172,370,371]. In still other cases, the exchanged cations may have a large impact on the effective pore size. For example, the zeolites 3A, 4A, and 5A are all zeolite type A with different exchanged cations for tuning of the pore size: 3A is the K-exchanged form with pore size 3.3 Å, 4A is the Na-form with pore size 4.1 Å, and 5A is the Ca-form with 4.4 Å pore size [167]. While the process of ionexchange is simple and rather well understood, it can be quite time consuming to find the appropriate metal which gives the correct catalytic qualities for a process of interest. Even after a suitable metal is found for ion-exchange, the correct level of ion-exchange must also be determined and the best method of achieving it.

One of the more popular alternatives to ion-exchange for modification of a synthesized zeolite is desilication and/or dealumination. Zeolites (or other zeotypes) that have been modified in this way are typically referred to as hierarchical zeolites nowadays [177,178,372–375]. This was detailed in Section 2.2.5 and is just briefly introduced here. The main objective being sought after with these treatments is the additional mesoporosity created by the physical removal of either Si or Al from the zeolite framework. This helps to remove the configurational diffusion limitations thought to plague these materials [148–150,375]. For obvious reasons, desilication of highly siliceous materials creates substantially more mesoporosity as compared to dealumination. However, desilication is only relevant at certain Si/Al ratios, and even in those cases care must be taken to ensure that the entire zeolite crystal is not dissolved or otherwise destroyed [182,184,186,189]. In the present case, with the starting MOR purchased from *Zeolyst* with a Si/Al ratio of 6.5, which is outside the optimal ranges for any kind of presently known desilication procedure, dealumination was the only option available.

Historically, dealumination is usually performed by steaming at high temperature (~500°C) but can also be performed by acid leaching using a variety of strong acids (typically HCl or HNO₃). Acid leaching is sometimes performed on steamed zeolites, as steaming does not remove the Al completely from the crystal. Instead, the Al is left as an extraframework species or as a Lewis acid site [163,176,179–185]. Dealumination does not necessarily create substantial mesoporosity as is the case with desilication. This is due, quite simply, to the fact that most zeolites have much less Al compared to Si in the framework. Instead, little pockets of mesoporosity or other cavities may be formed within the zeolite, which can still aid in removing or reducing diffusion limitations [186]. Other effects of dealumination are a decrease in acid site density and potential overall decrease in acidity of the zeolite with increasing Si/Al ratio [163,176,182,184,185,376,377].

In one of the original studies of DME carbonylation on H-MOR, Cheung et al. [90] suggested that perhaps the proximity of acid sites was important for the reaction. This was used as an explanation for the monotonic increase of MeOAc synthesis rates with increasing H⁺ concentration and proximity. No further explanation was provided for this behaviour at the time and only this observation was provided. Nonetheless, it was this observation that spurred on the theory regarding the selective carbonylation of DME to MeOAc on the T3-O33 (see Figure 2.12, otherwise known as T3-O9) acid site in the 8-MR. Modeling and

experimental studies have proven this to an extent, as well as showed that the acid sites in the 12-MR were unselective and more likely to form other hydrocarbons [212,215–217]. It would thus make sense to use dealumination as a means to removing these unselective acid sites that contribute to deactivation.

The effect of selective dealumination of MOR on its catalytic activity in DME carbonylation has already been explored in a couple of isolated studies. BP Chemicals Ltd. has taken out a patent on the selective dealumination of H-MOR by steaming at 400 -600°C [229]. In this method, partial ion-exchange of Ag⁺ was used to protect the acid sites in the 8-MR from being removed. The metal-loaded dealuminated MOR was then converted back to the hydrogen form (removal of the ion-exchanged metal via ion-exchange). While some enhancement was shown, the dealuminated H-MOR was still unstable and there was no optimization of the extent of dealumination for best performance in DME carbonylation. The difficulty presented in this study is control: the amount of Ag⁺ ion-exchange has to be strictly controlled so as to obtain the best benefit. While the approximate amount of ionexchange for any given MOR sample may be known and a rough approximation may be fine, this method relies heavily on the idea that in all cases and conditions the monovalent metal will preferably ion-exchange at acid sites in the 8-MR. Along the same principles, Xue et al. [235] selectively ion-exchanged the 8-MR with Na⁺ to protect it from dealumination by steaming in what may be a more guaranteed way as compared to the method proposed by BP Chemicals Ltd. Xue et al. [235] first blocked the 12-MR with Py, and then treated this Py-H-MOR sample with a low concentration NaOH solution in which they assumed the protons in the 8-MR of the Py-H-MOR sample would be substituted with Na⁺. This material was then calcined to remove the Py and steamed at 750°C. The resultant solids were then ion-exchanged to replace the Na^+ with NH_4^+ and then calcined to produce the final dealuminated H-MOR sample. This procedure is quite complicated, and would likely not be feasible at an industrial level. While the dealuminated H-MOR did show enhanced selectivity to MeOAc, approximately the same amount of stability enhancement as BP Chemicals Ltd. [229] had achieved by selective dealumination was shown. At 15 hours on stream at the conditions tested, the dealuminated H-MOR was obviously deactivating.

Despite the considerable effort that has been put into identifying the primary means of deactivation of H-MOR in DME carbonylation, it does not appear that the acid sites in the 12-MR are the only reason for the deactivation. At this point, it is reasonable to assume that the acid sites in the 12-MR do lead to reactions that form coke and may be one of the means by which the H-MOR is deactivated. However, in both of the previous studies on selective dealumination, most of the 12-MR framework AI had been removed and the H-MOR's stability was not significantly enhanced. This would imply that the deactivation of the H-MOR catalyst is not as simple as had been hitherto believed and some catalyst deactivation may be attributable to other acid sites.

The purpose behind this study of dealuminated H-MOR for DME carbonylation was to better understand what was really going on in the reaction and shed further light on the catalyst deactivation issue. This was done by the stepwise dealumination via acid leaching of H-MOR, meaning that many H-MOR catalysts were prepared with varying degrees of dealumination. Neither further information nor theories regarding the mechanisms of deactivation will be offered – only the more macroscopic observations. Consequently, due to the stepwise nature of the dealumination procedure, it was possible to observe how the framework AI (Al_f) and extraframework AI (Al_{ef}) concentrations varied.

5.2 Dealumination procedures and catalyst syntheses

5.2.1 Dealumination of Na-MOR and creation of H-MOR catalysts

As-received Na-MOR (Si/Al=6.5, *Zeolyst*, CBV-10A) was used directly for acid-based dealumination. In a typical acid treatment, 3 g of Na-MOR was added to 50 mL of HNO₃ (70% solution, Sigma-Aldrich) solution of varying molarity to achieve the desired amount of dealumination. The molarity and temperature of the solutions required to achieve each of the Si/Al ratios tested are given in Table 5.1. For each solution, a condensing column was placed over the flask so that any vapours were captured and returned to the mixture. The slurry mixture of HNO₃ solution and solid Na-MOR was stirred for a period of one hour after which the mixture was vacuum filtrated and the recovered solids washed excessively with warm deionized water until the pH of the filtrate was approximately neutral. The collected solids were dried overnight in an oven maintained at ~60°C before any further experiments or procedures were conducted with them. The compositions of the dealuminated Na-MORs are given in Table 5.1 and were measured by SEM-EDX in accordance with the procedure detailed in Section 3.3.15. In addition to the removal of the Al, some of the Na⁺ also appears to have been ion-exchanged with the H⁺ in the solution.

| Catalyst | HNO₃ Sol′n | Sol'n Temp. | Si | Al | Na | Si/Al molar |
|-------------|------------|-------------|-------|------|------|-------------|
| Catalyst | Conc'n (M) | (°C) | wt.% | wt.% | wt.% | ratio |
| Na-MOR 6.5 | - | - | 35.03 | 4.92 | 4.32 | 6.84 |
| Na-MOR 7.7 | 0.080 | 60 | 35.40 | 4.39 | 1.87 | 7.72 |
| Na-MOR 8.6 | 0.139 | 60 | 35.97 | 4.01 | 1.56 | 8.62 |
| Na-MOR 10.1 | 0.343 | 60 | 36.19 | 3.42 | 1.13 | 10.16 |
| Na-MOR 11.2 | 0.550 | 70 | 36.96 | 3.18 | 0.54 | 11.16 |
| Na-MOR 13.0 | 0.550 | 85 | 37.60 | 2.77 | 0.44 | 13.04 |
| Na-MOR 15.4 | 0.550 | 100 | 37.73 | 2.36 | 0.40 | 15.36 |

Table 5.1. Compositions of the original and dealuminated Na-MOR materials after acid treatment.

The Na⁺ form of the MOR samples was converted to the NH₄⁺ form via liquid-based ion-exchange using NH₄NO₃ (purity \geq 99.0%, Sigma Aldrich). For a typical ion-exchange, a 1 M solution of NH₄NO₃ was mixed together with the original or dealuminated Na-MOR at a ratio of 50 mL of solution to 1 g of material. The mixture was covered and heated to 60°C and stirred for a period of 3 hours, after which it was vacuum filtrated, washed excessively, and placed in an oven at 60°C to dry. The procedure was repeated 3 more times to ensure all Na⁺ was removed.

Prior to all characterizations, the NH₄-MOR was calcined to yield the protonic H-MOR. This was typically done in a Micromeritics Autochem II 2920. The powder was put under a flow of 10% O₂/He (Praxair) and heated from ambient temperature to 110°C for 3 hours. This was followed by heating to 350°C for 1.5 hours and a final heating to 550°C for 3 hours. Heating between the steps was conducted at 20°C/min. The calcined catalyst was cooled to ambient conditions and either kept in the equipment for further analysis or removed. SEM-EDX was performed on the H-MOR with Si/Al of 6.5, which has the highest initial Na content, to confirm that the NH₄⁺ ion-exchange was effective and all Na⁺ had been removed.

5.2.2 Characterization of acid site concentration by metal probing

In addition to the characterizations of the dealuminated H-MOR catalysts as have been described in Chapter 3, an additional characterization was performed as part of this MOR dealumination study.

To give some indication as to the acid site proximity along with an evaluation of which framework Al's were being removed in dealumination, the cation exchange capacity was quantified using the liquid-based ion-exchange of Cu^{2+} . The ion-exchange was conducted on the NH₄⁺ form of the MOR catalysts. In a typical ion-exchange, a 0.2 M solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ (purity 98%, Sigma-Aldrich) was mixed with 1 g of the NH₄- MOR powder at a ratio of 1 g of powder to 50 mL of solution. The mixture was covered and stirred using a magnetic stir bar and kept at approximately 60°C for a period of 3 hours before being vacuum filtrated and washed excessively with deionized water. The recovered solids were dried in an oven maintained at ~60°C overnight. The ion-exchange was repeated twice to ensure a near maximum amount of ion-exchange of Cu^{2+} had occurred. In the Cu-Zn/H-MOR study detailed in Chapter 4, the ion-exchange was repeated four times. This was deemed to be unnecessary for the purposes of this study.

Samples were then pressed into a thin disk with 16 metric tons of force and placed on the SEM support grid with conductive tape. The composition was measured using SEM-EDX as has been detailed in Section 3.3.15.

5.3 Dealuminated H-MOR performance in DME carbonylation

The protonated version of received MOR (Si/Al=6.5) and dealuminated MOR samples were used as catalysts for the carbonylation of DME under the reaction conditions detailed in Section 3.3.1. To properly compare the effects of dealumination, the total amount of Al was kept constant in the reactor at 10 mg, meaning that the total catalyst weight was different in the reactor for each test. The total catalyst weight along with the inert-exclusive weight hourly space velocity (WHSV) is detailed in Table 5.2 for H-MOR with the received Si/Al ratio and for the dealuminated H-MOR catalysts. Catalyst designations consist of "H-MOR" followed by the numerical value for the molar Si/Al ratio and will be referred to in this manner for the remainder of this thesis. If the total catalyst weight had been maintained constant among all the catalysts, the observed DME conversion would not have been properly indicative of the proportions of the remaining acid sites.

| Catalyst | Total catalyst weight | Inert-exclusive |
|------------|------------------------|-----------------|
| Catalyst | used for reaction (mg) | WHSV (h⁻¹) |
| H-MOR 6.5 | 200 | 3.15 |
| H-MOR 7.7 | 232 | 2.72 |
| H-MOR 8.6 | 254 | 2.48 |
| H-MOR 10.1 | 296 | 2.13 |
| H-MOR 11.2 | 320 | 1.97 |
| H-MOR 13.0 | 368 | 1.71 |
| H-MOR 15.4 | 434 | 1.45 |

Table 5.2. Amounts of dealuminated catalyst used in DME carbonylation and the subsequent WHSV.

Results for the conversion of DME, production of MeOAc, and selectivity towards MeOAc, MeOH, and other species are shown in Figures 5.1, 5.2, and 5.3 respectively. Conversion of DME and selectivities were calculated as detailed in Section 3.3.1. Detailed numerical results are given in Table 5.3. The catalyst lifetime as given is the time taken for the catalyst to deactivate to a 15% post-peak conversion level of DME. H-MOR 6.5 had the shortest lifetime of all catalysts tested at 20.5 h but had the highest peak MeOAc productivity at 6.6 kg_{MeOAc} kg_{Al}⁻¹ h⁻¹. As the catalyst deactivated, the selectivity towards MeOH and other products increased as shown in Figure 5.3. These results are consistent with what has been found by other groups for H-MOR with a Si/Al ratio of approximately 6.5 [89,90,92,212,233,235,236]. However, the catalyst lifetime of H-MOR 6.5 was ~10 h less than the same catalyst (H-MOR) run as part of the Cu-Zn/H-MOR study with results detailed in Table 4.2. The difference between the studies is the catalyst amount. In this study, 0.2 g total were used for H-MOR 6.5 while in the Cu-Zn/H-MOR study, the amount of H-MOR used was 0.3 g. With only 67% of the catalyst used and all other conditions maintained the same, the total reaction runtime was 33% less.



Figure 5.1. Conversion of DME during carbonylation over dealuminated H-MOR catalysts.

Figure 5.2. Productivity of MeOAc by DME carbonylation over dealuminated H-MOR catalysts.

After only a small amount of dealumination to create H-MOR 7.7, the total amount of MeOAc produced increased by ~63% over that of H-MOR 6.5. The total amount of MeOH produced increased similarly, though this is more likely due to the lifetime of the catalyst being 33.8 h as compared to only 20.5 h for H-MOR 6.5. Peak MeOAc productivity was not significantly affected, but the time to reach it has increased as well as the time that the catalyst is noticeably deactivating. The selectivity towards MeOAc on H-MOR 7.7 does not decrease on deactivation to the same extent that it does when using H-MOR 6.5. This is especially apparent when observing the selectivity to MeOH and others on deactivation as shown in Figure 5.3. H-MOR 8.6 performed nearly identically to H-MOR 7.7 and the reader is directed to Table 5.3 for detailed results and Figure 5.1, 5.2, and 5.3 for comparison with the other catalysts.

The decrease in performance of the MOR catalysts began with H-MOR 10.1. Compared to H-MOR 8.6, the total MeOAc produced decreased by approximately 20% while the MeOH produced increased by 5%. The peak conversion of DME has decreased by a large amount between H-MOR 8.6 and H-MOR 10.1 (from 90% to 58%). This is reflected in the MeOAc production results as well, where the peak productivity has decreased from 6.4 $kg_{MeOAc} kg_{Al}^{-1} h^{-1}$ for H-MOR 8.6 to 4.3 $kg_{MeOAc} kg_{Al}^{-1} h^{-1}$ for H-MOR 10.1. The saving grace of the H-MOR 10.1 was that its lifetime was 3.4 h longer as compared to H-MOR 8.6. Also, the deactivation has been considerably retarded and there was no longer a substantial amount of other not identified hydrocarbons produced. The extended period of deactivation is also likely why more MeOH was produced as compared to H-MOR 8.6. With H-MOR 11.2 and H- MOR 13.0, which both had similar performance as shown in Figures 5.1 - 5.3, the total amount of MeOAc produced decreased from H-MOR 10.1 by approximately 17% while the MeOH produced increased. The deactivation period was extended with no other compounds detected. The deactivation behaviour between H-MOR 10.1, 11.2, and 13.0 was very similar in all regards. However, by this point in the dealumination the peak MeOAc productivity had dropped to less than half that of H-MOR 6.5 (Figures 5.1 and 5.2). Further dealumination to H-MOR 15.4 decreased the peak MeOAc productivity and had now decreased the total MeOAc produced to less than half that of H-MOR 6.5 while producing about the same amount of MeOH. H-MOR 15.4 appears to no longer be a suitable catalyst for DME carbonylation, as there are now substantial amounts of MeOH and other compounds produced as is shown in Figure 5.3.

Table 5.3. Total MeOAc and MeOH produced, time before catalyst deactivation, and peak productivity of MeOAc for dealuminated H-MOR catalysts used in DME carbonylation.

| Catalyst | Total MeOAc | Total MeOH Produced | Catalyst | Peak Activity |
|------------|-----------------------------|----------------------------|--------------|------------------------------------|
| Catalyst | $(kg_{MeOAc} kg_{Al}^{-1})$ | $(kg_{MeOH} kg_{AI}^{-1})$ | lifetime (h) | $(kg_{MeOAc} kg_{Al}^{-1} h^{-1})$ |
| H-MOR 6.5 | 80.8 | 7.3 | 20.5 | 6.6 |
| H-MOR 7.7 | 131.6 | 11.1 | 33.8 | 6.4 |
| H-MOR 8.6 | 131.6 | 10.8 | 32.2 | 6.4 |
| H-MOR 10.1 | 105.8 | 11.3 | 35.6 | 4.3 |
| H-MOR 11.2 | 89.5 | 12.2 | 39.8 | 3.3 |
| H-MOR 13.0 | 87.8 | 13.4 | 40.9 | 2.9 |
| H-MOR 15.4 | 40.2 | 7.9 | 37.5 | 1.3 |



Figure 5.3. Selectivity to MeOAc, MeOH, and others in DME carbonylation performed over dealuminated H-MOR catalysts of varying Si/Al ratios.

With the exception of H-MOR 15.4, the selectivity towards MeOAc was improved with increasing dealumination from H-MOR 6.5 to H-MOR 13.0 (Figure 5.3). Even with a minor amount of dealumination to H-MOR 7.7 and 8.6, the selectivity towards MeOAc after substantial deactivation has increased from 40% to 55 - 60%. The amount of other hydrocarbons detected on H-MOR 7.7 and 8.6 has significantly decreased from H-MOR 6.5 while selectivity towards MeOH has decreased slightly as well (though more MeOH was produced due simply to the extended catalyst deactivation). With the decrease in activity between H-MOR 8.6 and H-MOR 10.1 came a significant increase in the selectivity towards MeOAc during catalyst deactivation. While the selectivity towards MeOH over H-MOR 10.1 only decreases slightly from H-MOR 8.6, there are no longer any other not identified hydrocarbons detected upon deactivation. This is also the case for H-MOR 11.2 and H-MOR 13.0. H-MOR 15.4 is no longer usable as a catalyst for DME carbonylation, as reflected in both the selectivity and activity results. The selectivity of this catalyst towards MeOAc is still approximately 70% on deactivation with the selectivity towards MeOH and other hydrocarbons being at similar levels to each other, but this is a significant decrease from the ~85% selectivity towards MeOAc on deactivation with H-MOR 11.2 and 13.0. The overall activity is such that a great amount of H-MOR 15.4 would have to be used to have reasonable overall production, and any of H-MOR 10.1, 11.2, and 13.0 would be preferable to H-MOR 15.4 for use at an industrial level.

When interpreting these results, it is very important to recall that the amount of Al present in the reactor during the reaction is the same between all trials. Thus, the DME carbonylation over H-MOR must be either site specific [212,215–217] or require two sites within a reasonable proximity of each other to facilitate the reaction [90]. Otherwise, the behaviour of all the catalysts should have been very similar between all Si/Al ratios tested. It could also be the case that the dealumination procedure has so greatly affected the acidity of the MOR that the activity levels are more heavily impacted by that than removal of specific Al or increased distance between the Al_f. It could even be that a substantial loss of crystallinity has caused some active DME carbonylation sites to become inaccessible. The catalyst characterizations as detailed below will be directed towards understanding the reasons of the observed effects of dealumination and attempting to ascertain the primary reason for the loss of activity and, ultimately, the reason why only partial dealumination has rendered the catalyst unusable in DME carbonylation.

5.4 Dealuminated H-MOR catalyst characterization

Unfortunately, the behaviours observed in DME carbonylation with dealuminated H-MOR catalysts with Si/Al ratios of 7.7 – 15.4 (and the original ratio of 6.5) are likely not the result of just one characteristic, such as acidity or where the Al is located in the framework. There are probably many contributing factors with increasing dealumination. Using several different characterizations, which include XRD, surface area, pore volume and distribution, ²⁷Al MAS NMR, TEM, DME TPD, NH₃-TPD, Py-TPD, DRIFTS, Py-DRIFTS, and evaluation of cation exchange capacity, the different effects will be separated, and conclusions will be drawn about how dealumination has caused the observed behaviour of the catalysts in reaction.

5.4.1 XRD

X-ray diffraction (XRD) was carried out as described in Section 3.3.13 to determine how the overall crystallinity was affected by the dealumination procedure. While XRD patterns were taken for 5 – 90° 2 θ , only the relevant region between 5 – 50° 2 θ will be presented. There was no data of significant note at 2θ greater than 50°. The non-calcined NH₄-MOR with Si/Al ratio 6.5 was taken as the reference when calculating crystallinity and was assigned a value of 100%. The crystallinity was calculated in two ways. The first way was adopted from O'Donovan et al. [377] and van Laak et al. [184] and consisted of adding the peak intensities due to the (330), (150), (202), (350), and (511) planes and comparing it against that of the reference material. The second way was by comparing the total of the peak areas, as this seemed to be more representative as some amount of peak broadening was observed with increasing dealumination [185]. It was also desired to understand how much crystallinity was lost during calcination. To advance this understanding, XRD profiles were taken of both non-calcined and calcined catalysts. Results are shown for the XRD profiles for all catalysts in Figure 5.4 and values for crystallinity are given in Table 5.4. As expected, calcination produces an immediate loss in crystallinity, even in H-MOR 6.5 which has had no acid treatment. By both methods of calculating crystallinity, the crystallinity decreases from 100% to ~84%. With further dealumination came further decreases in crystallinity, both before and after calcination. However, crystallinity is well-maintained in the H-MOR 6.5, 7.7, and 8.6 samples, with the crystallinity of calcined samples being very similar to that of H-MOR 6.5 for the three catalysts. This result is in agreement with earlier studies that the removal of extraframework AI was favoured over framework AI in mild acid treatments [176,183,286,378,379].

| Catalyst | Crystallinity by pe | ak intensity (%) | Crystallinity by peak area (%) | | |
|------------|---------------------|------------------|--------------------------------|----------|--|
| Catalyst | Non-calcined | Calcined | Non-Calcined | Calcined | |
| H-MOR 6.5 | 100 | 84 | 100 | 84 | |
| H-MOR 7.7 | 97 | 82 | 92 | 82 | |
| H-MOR 8.6 | 96 | 81 | 92 | 83 | |
| H-MOR 10.1 | 77 | 56 | 88 | 69 | |
| H-MOR 11.2 | 75 | 41 | 85 | 66 | |
| H-MOR 13.0 | 77 | 38 | 81 | 58 | |
| H-MOR 15.4 | 64 | 27 | 72 | 48 | |

Table 5.4. Crystallinity of non-calcined and calcined dealuminated H-MORs as measured by XRD.

With H-MOR 10.1, a substantial loss in crystallinity was observed in both methods of calculation implying that at this point in the dealumination framework AI had begun to be removed. This is also the point where a small increase in 20 is observed in both the non-calcined and calcined samples. This is indicative of contraction of the pore structure. The trend in crystallinity loss continues from H-MOR 10.1 to H-MOR 15.4, where, when calculated by crystallinity, the sample only has 26.7% of the original crystallinity the NH₄-MOR 6.5 showed. When calculated by peak areas, 48.1% of the original crystallinity has been maintained on H-MOR 15.4. These substantial decreases in crystallinity are expected in dealumination and are indicative of severe damage to the framework. These types of crystallinity decreases have been observed in other dealumination studies [184,377]. These results do not necessarily indicate that the MOR framework has completely collapsed. Rather, they simply imply that a certain amount of disorder has been introduced into the framework.

It is interesting to note that the (200) peak at 11.34° 20 (shown in Figure 5.4) does not decrease in intensity with dealumination, but rather increases. As indicated by Baerlocher and McCusker [380], the low angle peaks are the ones most strongly influenced by non-framework species. The increase in intensity of the peak may be a sign of an increasing number of terminal Si groups created by the removal of Al atoms from the framework. The increase may also serve as an indication of the creation of mesoporous cavities and other mesopores in the MOR framework.



Figure 5.4. XRD of non-calcined and calcined dealuminated H-MOR catalysts with original and increasing Si/Al ratios.

In terms of which XRD peaks decrease the most with dealumination, the compared intensities of the major peaks are given in Table 5.5. Firstly, the intensity of peak (150) compared to (202) decreases with increasing dealumination, which gives the impression there is a larger change occurring in the k plane (the directions of the planes are shown in Figure 2.11 for MOR). The comparison of (511) and (150) shows an increasing ratio with dealumination, which again indicates a change occurring in the k plane but this is not conclusive given the large difference in the h plane here. However, when comparing (511) and (350), there is again a large increase in the ratio with increasing dealumination. As further evidence to indicate that there is little change in the h plane, the comparison of (511) and (202) gave no real trend and did not show a large difference in ratio with increasing dealumination. When comparing (350) and (330), the ratio of intensities decreases with increasing dealumination. It would thus appear that a large change is occurring in the k plane of MOR with increasing dealumination. It could be the case that the pore contraction is occurring more in that direction compared to the h plane. This could be an indication of selective T3 and T4 removal (see Figure 2.12). With the T1 and T2 locations being held mostly intact by each other, the pores may collapse into the 8-MR and 12-MR channels as T3 and T4 are removed respectively.

| Catalyst | (150)/(202) | (511)/(150) | (511)/(350) | (511)/(202) | (350)/(330) |
|------------|-------------|-------------|-------------|-------------|-------------|
| H-MOR 6.5 | 0.902 | 0.397 | 0.729 | 0.359 | 0.890 |
| H-MOR 7.7 | 0.903 | 0.403 | 0.687 | 0.364 | 0.971 |
| H-MOR 8.6 | 0.930 | 0.445 | 0.735 | 0.414 | 0.919 |
| H-MOR 10.1 | 0.817 | 0.454 | 0.777 | 0.371 | 0.775 |
| H-MOR 11.2 | 0.697 | 0.594 | 0.919 | 0.414 | 0.830 |
| H-MOR 13.0 | 0.690 | 0.559 | 0.976 | 0.385 | 0.633 |
| H-MOR 15.4 | 0.612 | 0.632 | 1.12 | 0.387 | 0.570 |

Table 5.5. Relative intensities of the main XRD peaks of calcined dealuminated H-MOR catalysts.

It must also be noted that the peaks shifted to slightly higher angles during the dealumination. Between H-MOR 6.5 and H-MOR 15.4, the (330) peak shifted from 22.80° 20 to 23.04° 20. This ~0.2° 20 shift was present in the other major peaks as well with increasing dealumination. The (150) peak shifted from 25.84° 20 to 26.06° 20. The (202)

peak shifted from 29.84 to 30.12° 20. The (350) peak shifted from 30.56 to 30.88° 20, and the (511) peak shifted from 32.22° 20 to 32.38° 20. This peak shift is an indication that the unit cell is contracting, as is expected in dealumination by acid leaching [185,377,381]. Interestingly, the peaks shifted in position most between H-MOR 7.7 and 11.2. The peaks did not shift in position as much with increasing dealumination from H-MOR 11.2 to H-MOR 15.4.

5.4.2 ²⁷AI MAS NMR

To give some indication as to the balance of framework AI (Al_f) and extraframework AI (Al_{ef}), ²⁷AI MAS NMR was used as was described in Section 3.3.12. Al_f has a tetrahedral orientation and gives a chemical shift of ~55 ppm when studied via solid state MAS NMR, while Al_{ef} takes on an octahedral orientation and gives a chemical shift of 0 ppm [285– 289,3821. Results from ²⁷AI MAS NMR experiments are shown in Figure 5.5 with calculated ratios of Al_f to Al_{ef} based on peak areas and intensities shown in Table 5.6. The original H-MOR 6.5 has the most Al_{ef} and this immediately decreases with mild acid treatment to create H-MOR 7.7 and H-MOR 8.6 as was suspected from XRD. However, the number of Al_{ef} seems to increase from H-MOR 8.6 with a harsher acid treatment to H-MOR 10.1. It is known that acid treatments can cause an increased amount of Alef species at certain acid concentrations, and the increase of Al_{ef} from H-MOR 8.6 to H-MOR 10.1 was not surprising given the XRD results [185,338,377,383]. Moving one step further to H-MOR 11.2, this sample evidently had the least Al_{ef} of all samples. While one perspective could be that the increasingly harsh acid treatment between H-MOR 10.1 and 11.2 simply means that the additional acid is cleaning up the Al_{ef} created by the treatment to create H-MOR 10.1, this is not in line with the reaction results (Section 5.3). Although Al_{ef} may bind with CO [384,385] and Lewis acid sites may interact with Brønsted acid sites to create superacid sites [146,147], it is assumed that Al_{ef} does not have a significant effect on the reaction rate as indicated by the reaction results in this study and was also postulated by Cheung et al. [90]. The number of Al_{ef} seems to increase again with H-MOR 13.0 and then decrease with H-MOR 15.4. While the creation of Al_{ef} in dealumination is reasonable to assume, the comparison of intensities of the peaks or the entire peak areas as shown in Table 5.6 do not seem to create a realistic proportion of AI_{f} to AI_{ef} . As no attempt was made to calibrate the NMR peak areas for AI content, the NMR results will only be used here as an indication of the relative amounts of Al_{ef}. The cost/benefit ratio of calibrating and running the ²⁷Al MAS NMR in such a way that the amounts of Al could be quantified was too high. Given the

possibility of NMR invisible Al and potential variance in results with water content, even the quantified results could still be heavily scrutinized [285–287].

| Catalyst | Ratio of Al _f to Al _{ef} based on: | | | | |
|------------|--|------------|--|--|--|
| Catalyst | Peak intensity | Peak areas | | | |
| H-MOR 6.5 | 1.5 | 2.1 | | | |
| H-MOR 7.7 | 6.5 | 7.2 | | | |
| H-MOR 8.6 | 7.5 | 9.0 | | | |
| H-MOR 10.1 | 2.1 | 3.4 | | | |
| H-MOR 11.2 | 14.6 | 17.6 | | | |
| H-MOR 13.0 | 2.5 | 2.7 | | | |
| H-MOR 15.4 | 5.1 | 7.3 | | | |

Table 5.6. Calculated ratios of framework Al to extraframework Al based on peak intensity and areas.



Figure 5.5. ²⁷Al MAS NMR profiles for H-MOR with received ratio and dealuminated H-MOR catalysts.

5.4.3 Surface area and pore distribution

Physisorption experiments were carried out utilizing liquid Ar to evaluate properly the alteration of the crystal structure of the MOR before and after various levels of dealumination. It was also deemed necessary to determine how much mesopore volume, however limited, is created. The Ar physisorption characterizations were performed as described in Section 3.3.14. Experiments were carried out with both liquid N₂ and liquid Ar, but when comparing the HK prediction of the micropore distribution, the liquid Ar provided a much improved estimate and allowed the smaller 8-MR channels and 8-MR side pockets to be differentiated from the micropore volume due to the larger 12-MR channels [200,262,269,309]. Langmuir and BET surface areas along with micropore and mesopore data predicted by various methods are given in Table 5.7. The HK prediction of the micropore distribution is shown in Figure 5.6. The mesopore area curves as predicted by the BJH desorption method are shown in Figure 5.7. Finally, the adsorption/desorption isotherms themselves for H-MOR 6.5 and H-MOR 15.4 are shown in Figure 5.8.

Both the Langmuir and BET surface areas were calculated based on the adsorption curves. Between the two, the Langmuir surface area was calculated at very low P/P^0 , approximately where the initially very high adsorption began to decrease as this was assumed to be where a complete monolayer would form. The BET surface area was calculated at higher P/P⁰ as it was desired for that description of the surface area to include the multilayer physisorption behaviour that may be created with increasing mesoporosity. The trend with dealumination seems to fit with what would be expected from the removal of Al atoms from the framework. The monolayer surface area predicted by Langmuir decreases with increasingly intense dealumination treatments, confirming the removal of Al and being in line with what XRD predicted regarding the maintenance of the crystallinity of the framework. Between H-MOR 6.5 and H-MOR 15.4, the Langmuir surface area decreased by 11.8% (52 m²/g). The decrease in Langmuir surface area between H-MOR 6.5 and 7.7 is minimal and consistent with the idea that mostly Al_{ef} has been removed at this level of treatment. There is a larger decrease in Langmuir surface area between H-MOR 7.7 and 8.6 that is likely associated with the removal of some Al_{f} . Curiously, there was no decrease in Langmuir surface area between H-MOR 11.2 and H-MOR 13.0. No explanation is offered for this anomaly. As expected, the BET surface area increases with increasingly harsh dealumination conditions, though the change is not as extensive as with the Langmuir surface area. As additional mesopores are introduced, it can be expected that a higher degree of multilayer adsorption may be taking place. Between H-MOR 6.5 and 15.4, the

BET surface area has increased by 6.3% (28 m²/g). While the overall BET surface area did increase, not every step of dealumination led to an increase over the previous catalyst. For example, between H-MOR 7.7 and 8.6, the BET surface area actually decreased slightly, though the numbers could be considered to be within acceptable error of each other. Rather, a more pronounced difference would be between H-MOR 10.1 and H-MOR 11.2, where the BET surface area decreased from 469.33 m²/g to 462.77 m²/g. Given that the crystallinity of H-MOR 10.1 and H-MOR 11.2 is quite similar, it could be assumed that no additional mesoporosity has been created between the two with the harsher dealumination treatment.

| | Surface a | e area | | -plot micropore data | | HK micr | ropore data | BJH mesopore | |
|------------|-----------|--------|----------------------|----------------------|--------------|----------------------|-------------|----------------------|--------|
| | (m²/g |) | | | | | | dat | a |
| Catalyst | Langmuir | BET | Volume | Micropore | External | Volume | Median | Volume | Area |
| | | | (cm ³ /g) | Area | Surface Area | (cm ³ /g) | Pore Width | (cm ³ /g) | (m²/g) |
| | | | | (m²/g) | (m²/g) | | (Å) | | |
| H-MOR 6.5 | 440 | 448 | 0.1601 | 421 | 19.3 | 0.1633 | 6.81 | 0.00493 | 16.5 |
| H-MOR 7.7 | 437 | 461 | 0.1620 | 409 | 27.9 | 0.1672 | 6.88 | 0.00461 | 23.9 |
| H-MOR 8.6 | 424 | 459 | 0.1607 | 394 | 30.1 | 0.1653 | 6.94 | 0.00448 | 24.5 |
| H-MOR 10.1 | 416 | 469 | 0.1614 | 380 | 35.6 | 0.1668 | 7.01 | 0.00489 | 30.6 |
| H-MOR 11.2 | 403 | 462 | 0.1591 | 369 | 34.1 | 0.1642 | 7.09 | 0.00473 | 28.3 |
| H-MOR 13.0 | 403 | 479 | 0.1635 | 361 | 41.5 | 0.1687 | 7.15 | 0.00491 | 34.9 |
| H-MOR 15.4 | 388 | 476 | 0.1596 | 341 | 46.7 | 0.1669 | 7.19 | 0.00534 | 38.3 |

Table 5.7. Surface area and pore volume as measured by Ar physisorption for dealuminated H-MOR catalysts.

The predictions for micropore volume did not show as clear a trend as the surface areas. By the t-plot method, the micropore volume did not produce a trend and, with some variance, seemed to stay constant with the varying degrees of dealumination. It first increased from H-MOR 6.5 to H-MOR 7.7, which could be interpreted as some micropore volume becoming available with removal of the Al_{ef} species. It then decreased with H-MOR 8.6, though the two values may be within acceptable error of each other. The largest changes occurred between H-MOR 10.1, 11.2, 13.0, and 15.4. From the t-plot micropore volume of 0.1614 cm³/g for H-MOR 10.1, it decreased by 1.4% for H-MOR 11.2. The micropore volume for H-MOR 13.0 increased by 2.8% compared to H-MOR 11.2. Finally, the micropore volume again decreased for H-MOR 15.4 by 2.4% compared to H-MOR 13.0. Interestingly, this follows the trend of Al_{ef} creation and removal predicted by ²⁷Al MAS NMR. From H-MOR 10.1, the amount of Al_{ef} decreased for H-MOR 11.2, then increased for H-MOR 13.0, then again decreased for H-MOR 15.4. This is actually the opposite of what would be anticipated. With AI_{ef} species creation, as in H-MOR 10.1 and 13.0, it would be expected that these Al_{ef} species may block microporous areas and the predicted micropore volume should be lower. Instead, the t-plot micropore volume prediction for those two catalysts is the highest among all catalysts tested. It may then be the case that the t-plot prediction of micropore volume is somewhat unreliable. Also from the t-plot model, it was predicted that the micropore area decreased and external surface area increased with increasing dealumination. This seems to make sense – some micropore area has been destroyed with dealumination, creating mesopore area that is interpreted as external surface area. The HK method also did not produce a trend for micropore volume that is consistent from H-MOR 6.5 to H-MOR 15.4. As shown in Table 5.7, the micropore volume predicted by this method decreases and increases seemingly randomly between treatments. However, the prediction of the median pore width increases at a steady rate from 6.806 Å to 7.193 Å between H-MOR 6.5 and H-MOR 15.4. While this may seem contrary to the pore contraction predicted by XRD, it is to be remembered that this is an average pore width. If the smaller 8-MR pores become inaccessible and it is not possible to see them with the adsorbent, the median pore width would shift to favour the 12-MR. From XRD, it was proposed that T3 and T4 Al_f may be being selectively removed. This could cause deformation to the 8-MR and 12-MR that may have been interpreted by Ar physisorption as an increase in the median pore width. However, to properly assess this, it is necessary to study the pore size distribution.

The pore distribution predicted by the HK method is shown for all catalysts in Figure 5.6. The pore width below 6 Å corresponds to the 8-MR channels and the 8-MR pockets which connect the 8-MR and 12-MR channels in the k direction. Anything above 6 Å pore

width could be attributed to the 12-MR. There are some immediately obvious trends here. Interestingly, the pore diameter of the 12-MR does not seem to have been impacted by the dealumination treatments. The apex of the pore size distribution peak for the 12-MR for H-MOR 6.5 occurs at 6.83 Å. For H-MOR 11.2 and 13.0, the apex occurs at ~6.97 Å. For H-MOR 15.4, the apex occurs at 6.92 Å. Despite little change in the overall pore diameter, the 12-MR channel has obviously been deformed by the dealumination treatments. While the total pore volume contribution from the 12-MR does not seem to change significantly, the curve is broadened with even the mildest dealumination with increased contribution to micropore volume occurring at pore diameters greater than 7.2 Å as compared to H-MOR 6.5. This serves as an indication that the majority of the 12-MR channel is held intact during dealumination while some damage, including possibly Al_f removal, has occurred that does not significantly affect the overall pore volume. The 12-MR channel appears to be merely deformed and misshapen. Interestingly, from XRD it was shown that the crystallinity of H-MOR 7.7 and H-MOR 8.6 were nearly the same as for H-MOR 6.5, yet the pore distribution analysis shows a large amount of deformation to the 12-MR.





The behaviour of the 8-MR in Figure 5.6 is far more inconsistent compared with the 12-MR. For reference, for a H-MOR with Si/Al ratio of 6, the pore size for the 8-MR channel is 3.8 Å, for the 8-MR side pocket is 5.1 Å, and for the 12-MR channel is 6.7 Å [200]. With the original H-MOR 6.5, the peak for the 8-MR channel and side pockets is shown with an

apex at approximately 5.2 Å and contributes less in terms of pore volume as compared to the 12-MR as expected. It is important to mention here that the data obtained for the 8-MR channel and 8-MR pockets of MOR is at the very edge of where the instrument is able to provide results and inconsistent peaks along with poor resolution should be expected. It is unfortunately not possible to separate the contribution of the 8-MR channel and 8-MR side pockets with the present data, and for simplicity this peak at < 6 Å pore width will be referred to collectively as 8-MR. With mild acid treatment, H-MOR 7.7 shows a much sharper and more pronounced peak for the 8-MR. This continues with H-MOR 8.6 where the initial physisorption is high enough that a distinguishable peak is hardly created. This is consistent with the ideas presented earlier that the dealumination treatments for H-MOR 7.7 and H-MOR 8.6 were more cleaning up the Al_{ef} than extensively removing Al_{f} (Al_{ef} may obstruct what would be otherwise accessible micropore volume). Between H-MOR 8.6 and 10.1, the 8-MR has been impacted negatively, with the peak even lower than that of H-MOR 6.5 and a decreased contribution to the micropore volume. With H-MOR 11.2, the 8-MR again appears to have been cleaned up a little, though the physisorption isn't as high as it was for H-MOR 8.6. At H-MOR 13.0 the 8-MR again appears to have been negatively impacted, followed by being cleaned up with increased dealumination to create H-MOR 15.4.

While these behaviours may be seemingly random, another characterization has predicted this exact trend. From the ²⁷Al MAS NMR results, the intensity of the peak at 0 ppm, associated with octahedrally-coordinated Al_{ef}, follows the same trend as the 8-MR peak behaviour predicted by physisorption. Given its smaller pore diameter and known to have nearly half of the Al_f present in MOR [197,200,212], it is not surprising that the 8-MR would be more likely to experience blockage from Al_{ef}. Initially the MOR has much of the Al_{ef} cleaned up, making the 8-MR more accessible and increasing its contribution to pore volume. Between H-MOR 8.6 and 10.1, the number of Al_{ef} increases and the 8-MR has become less accessible. With H-MOR 11.2, the number of Al_{ef} again decreases and the 8-MR becomes more accessible. The matching of the trends continues with H-MOR 13.0 and H-MOR 15.4. While it is imperfect, as the ASAP 2020 is operating very near to its limit, the trends do seem to follow each other and serve to indicate a high degree of alteration and potential damage to the 8-MR with the dealumination treatments.

It has been previously mentioned that dealumination does not lead to substantial increases in the mesopore volume [163,176,182,185,377,378] and the results from the BJH desorption method corroborate this, shown in Table 5.7. In fact, mesopore volume initially decreases from H-MOR 6.5 to H-MOR 8.6. After this point, it begins to increase but the final

mesopore volume for H-MOR 15.4 is not significantly higher than the mesopore volume for H-MOR 6.5. Rather, it is more interesting to discuss the mesopore area as shown in Table 5.7 and Figure 5.7. Aside from H-MOR 11.2, the mesopore area gradually increases with dealumination, with a more than 130% increase between H-MOR 6.5 and H-MOR 15.4. It is likely that very large mesopores are not created as would be expected in desilication; rather, small pockets and mesoporous cavities may have been created in areas where a substantial amount of Al_f was concentrated [186]. Due to the low resolution of the desorption data, it is not possible to determine conclusively what the mesopore diameter may be, though it is likely between 30 and 40 Å. While dealumination is destructive, from the perspective of the original MOR with Si/Al of 6.5, the crystal was already imperfect as shown in Figures 5.7 and 5.8. If the MOR crystal had been perfectly formed, there should not have been as substantial a difference between the adsorption and desorption of Ar, nor should there have been any mesopores. Due to imperfections in the crystal, such as the Al_{ef}, there is some hysteresis present between the adsorption and desorption curves for every catalyst though only the data for H-MOR 6.5 and H-MOR 15.4 is presented (other data are redundant).



Figure 5.7. Mesopore surface area as measured by the BJH desorption method for H-MOR with received ratio and dealuminated H-MOR catalysts.



Figure 5.8. Adsorption and desorption profile for Ar on H-MOR 6.5 and 15.4.

Given the importance of the Ar physisorption data and the amount of information yielded from it, it is worthwhile to briefly summarize what it showed. Purely based on the Langmuir and BET surface areas, it was possible to observe the level of damage caused to the microporous framework and decreasing crystallinity shown by decreasing monolayer adsorption and increasing multilayer adsorption. While it appears that the overall micropore volume did not change much (shown by both the t-plot and HK methods), the pore distribution showed extensive deformation to the 12-MR channel and blockage in the 8-MR channel and side pockets that increased and decreased with the amount of Al_{ef} present. This suggests that Al_f is preferentially removed from the 8-MR and is simply left behind in the channel as Al_{ef} at some levels of dealumination. Pore contraction as predicted by XRD was not observe that the mesoporous surface area had increased by ~130%.

5.4.4 TEM

TEM images were taken of the H-MOR with original Si/Al ratio 6.5 and all dealuminated ratios with images shown in Figure 5.9. Consistent with what has been discussed and shown by surface area and pore distribution analysis, no major defects are seen in the crystals at any ratio as a result of the acid treatment. Only in H-MOR 15.4 are very small notches seen at the edge of the crystal. It is concluded that dealumination does not lead to any substantial increase in mesoporosity.



Figure 5.9. TEM images of the calcined form of a) H-MOR 6.5, b) H-MOR 7.7, c) H-MOR 8.6, d) H-MOR 10.1, e) H-MOR 11.2, f) H-MOR 13.0, and g) H-MOR 15.4.

5.4.5 Acid site titrations with DME and DME TPD

DME adsorption at the reaction temperature of 210°C followed by DME TPD was performed to determine the number of accessible acid sites which are able to activate DME to form methyl groups [82,83,207]. This approach of H⁺ titration with DME has been discussed in detail elsewhere [89,90,314]. For one DME molecule dissociated per two acid sites, the number of the titrated H⁺ per total amount of Al is referred to as sites populated with methyl groups [206–208,314]. DME adsorption and subsequent desorption were carried out as described in Section 3.3.4. Specifically, for this study it was desired to see if the loss in crystallinity and unit cell contraction would cause some of the acid sites to become inaccessible to DME. As the total Al content was not maintained the same in each characterization trial as was the case in the DME carbonylation reactions, two values are calculated for each parameter. The first is the amount per gram of catalyst, while the second is calculated per mole of Al.

Detailed results are presented in Table 5.8 and the DME TPD results are shown in Figure 5.10. As expected, the amount of DME adsorbed per gram of catalyst decreases with decreasing Al content. Comparing H-MOR 6.5 and 15.4, where ~53% of the Al has been lost, the amount of DME adsorbed decreases by 55%. These two numbers are within reasonable error of each other and were expected to be the same. When comparing the amount of DME adsorbed compared with the Al content, no trend was really observed. On H-MOR 6.5 (and others), the amount of DME adsorbed is greater than 0.5 mol_{DME}/mol_{AI}, and can be interpreted as a sign of physisorption occurring along with the reaction of DME to methylate two acid sites. While not completely following the trend of Al_{ef} content predicted by ²⁷AI MAS NMR, the DME adsorption data does seem to reflect it. Compared to the amount of DME adsorbed, there was a very small amount of MeOH produced. The H-MOR 10.1 catalyst showed the highest level of MeOH produced at 11.9% of the DME adsorbed. The H-MOR 13.0 and 15.4 catalysts produced by a wide margin the least MeOH. As determination of the MeOH amounts was quite complicated as described in Section 3.3.4, no conclusions will be drawn regarding its production. The total amount of DME desorbed scaled with AI content as expected. This time, the amount of DME desorbed decreased by 56% between H-MOR 6.5 and H-MOR 15.4. This value is well within error of the amount of Al lost and the decrease in DME adsorption between these two catalysts. When comparing the amount of DME desorbed to the amount of Al present in the sample, no trend was observed, though the values for H-MOR 10.1, 11.2, 13.0, and 15.4 are noticeably lower as compared to those for the catalysts with higher Al content.

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| | Total DME | Adsorbed | Total I | МеОН | Total | DME Desor | rbed | Unaccounted | Acid sites |
|------------|-----------------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|--------|---------------------------------------|------------|
| Catalyst | | | Produ | Produced | | | | | methylated |
| Catalyst | µmol/g _{cat} | mol _{DME} / | µmol/g _{cat} | mol _{DME} / | µmol/g _{cat} | mol _{DME} / | Peak T | mol _{DME} /mol _{Al} | % |
| | | mol _{Al} | | mol _{Al} | | mol _{Al} | (°C) | | |
| H-MOR 6.5 | 1002.3 | 0.550 | 32.3 | 0.018 | 232.1 | 0.127 | 234 | 0.422 | 79.8 |
| H-MOR 7.7 | 941.0 | 0.578 | 47.4 | 0.029 | 214.4 | 0.132 | 234 | 0.447 | 86.4 |
| H-MOR 8.6 | 875.4 | 0.586 | 22.2 | 0.015 | 185.7 | 0.124 | 247 | 0.461 | 90.9 |
| H-MOR 10.1 | 736.7 | 0.576 | 87.7 | 0.069 | 138.9 | 0.109 | 226 | 0.468 | 86.6 |
| H-MOR 11.2 | 598.2 | 0.506 | 22.6 | 0.019 | 128.8 | 0.109 | 234 | 0.397 | 77.5 |
| H-MOR 13.0 | 502.4 | 0.489 | 6.9 | 0.007 | 107.6 | 0.105 | 239 | 0.385 | 76.2 |
| H-MOR 15.4 | 447.1 | 0.513 | 3.4 | 0.004 | 101.7 | 0.117 | 241 | 0.397 | 78.9 |
| | | | | | | | | | |

Table 5.8. Amounts of DME adsorbed, desorbed, and unaccounted for over H-MOR with received ratio and dealuminated H-MORs along with the theoretical number of acid sites methylated and the peak temperature of desorption.

After calculating the number of sites methylated, it is obvious that most of the acid sites within all the MOR samples are converted to a methoxy group. For H-MOR 6.5, approximately 80% of acid sites are methylated, which increases to ~88% for H-MOR 7.7, 8.6, and 10.1. For H-MOR 7.7 and 8.6, this may be attributable to removal of Al_{ef} . The value drops to ~77% for Si/Al ratios of 11.2 – 15.4. While the decrease does seem to indicate some acid sites are lost (or are more difficult to get to) with the crystallinity decrease, this is still clear evidence that the MOR framework has not completely collapsed with the acid treatments and that most of the remaining Al sites are accessible and can be populated with a methyl group and potentially used for DME carbonylation.

The non-dissociated DME molecules were found to desorb as one peak at ~235°C, which is shown in Figure 5.10. However, the peaks asymmetry suggests the involvement of at least two chemisorption active sites at ~225 and ~175°C. It has been theorized by Boronat et al. [215,216] that the most stable methoxy groups are created at the T3-O33 location in the 8-MR channels (shown in Figure 2.12, otherwise referred to as T3-O9). The activation is also feasible in 12-MR's T4-O44, T2-O24 and T1-O11. If the peak at 225°C is arbitrarily assigned to the T3-O33 sites with the most stable methoxy groups while the lower-temperature peaks are assigned to the other potential sites, the relative contribution of the T3 peak decreases with Si/Al increase. This is in line with the suggested preferential removal of the T3 and T4 Al's at the 4-MR with dealumination predicted by XRD and shown by others [386–388].



Figure 5.10. DME concentration during TPD of DME-saturated H-MOR with received ratio and dealuminated H-MORs.

Aside from the potential for the contribution of the several different types of acid sites to the DME-TPD curve, it does not appear that the acidity of the MOR is greatly changed with the changing Si/Al ratio. As detailed in Table 5.8, the peak temperature at which desorption of DME is occurring most rapidly does not change significantly with decreasing Si/Al ratio. With varying Si/Al ratio, the acidity of any zeolite should change considerably [136,137,139,141–144,163,176,182,184,185,376,377]. The acidity of the samples will thus be explored in more detail by NH₃-TPD and Py-TPD.

5.4.6 NH₃-TPD

Adsorption and desorption of NH₃ was carried out as described in Section 3.3.7. As was described earlier, NH₃-TPD is a quite common technique for determining the acidity of any given zeolite. It can be applied universally, as the small size of NH₃ allows it to get nearly everywhere in the zeolite with ease. As far as it applies to the current case, NH₃-TPD was only applied generally. No complicated mathematical treatment or deconvolution was performed on the TPD profiles for the purposes of finding the individual peaks associated with different acid site positions and strengths [321–324]. Quite typically, one requires somewhat specialized equipment in order to guarantee that what is desorbed is truly NH₃ and not water or some other species caused by decomposition of the zeolite framework. This means that reliable NH₃-TPD experiments are usually performed under vacuum so that high temperatures of desorption are not required. As the proper equipment for very detailed analysis of the TCD signals from the TPD was unavailable, the NH₃-TPD results will only be considered in a general sense and only used as an indication of the overall acidity.

Adsorption levels in both the low temperature and high temperature NH₃-TPD regimes are shown in Table 5.9. For the purposes of this set of experiments, the low temperature regime and high temperature regimes were defined as below and above 325°C respectively. This is not necessarily the case in many other studies [322,325,326], but was selected based on the raw TCD profiles shown in Figure 5.11 as it was considered to be the most representative separation point. When processing the results, the increase in the TCD signal past a temperature of 600 - 700 °C was considered to be an artifact and not included in the quantification of the results. To quantify the results, Gaussian-style curves were fit to both the low temperature and high temperature peaks and the areas under those curves were used along with the calibration of the TCD signal for NH₃ content to determine the total amounts of NH₃ desorbed in each region. As there are some assumptions associated with this (especially in the high temperature region), the values were compared with available information in literature to determine their relevance.

| | NH ₃ desorption | | | | | | | |
|------------|---|--------|-----------------------------|-------------|--|--|--|--|
| Catalyst | Low T (<3 | 325°C) | High T (>3 | 25°C) | | | | |
| | mol NH ₃ /mol Al Peak T (°C) | | mol NH ₃ /mol Al | Peak T (°C) | | | | |
| H-MOR 6.5 | 1.55 | 212 | 1.98 | 575 | | | | |
| H-MOR 7.7 | 1.52 | 206 | 1.87 | 571 | | | | |
| H-MOR 8.6 | 1.60 | 201 | 1.96 | 564 | | | | |
| H-MOR 10.1 | 1.48 | 196 | 1.75 | 541 | | | | |
| H-MOR 11.2 | 1.59 | 194 | 1.83 | 535 | | | | |
| H-MOR 13.0 | 1.55 | 191 | 1.79 | 531 | | | | |
| H-MOR 15.4 | 1.56 | 186 | 1.80 | 500 | | | | |

Table 5.9. Acidity evaluation of dealuminated H-MOR catalysts with NH₃.



Figure 5.11. NH_3 -TPD curves obtained with H-MOR with received and dealuminated Si/Al ratios.

It is immediately obvious from Table 5.9 that there is more NH₃ adsorbed than there is Al in the H-MOR catalysts. At the low temperature regime, this may be just physisorbed NH₃ on the framework in, more or less, random locations. When comparing the amounts of NH₃ adsorbed in the low temperature regime, no trend is produced and the amounts are likely within error of each other. This is reasonable, as the lowest amount adsorbed is 1.48 mol NH₃/mol Al while the highest low temperature amount is 1.60 mol NH₃/mol Al. This is only an 8.1% difference as compared to the amount physisorbed for H-MOR 10.1. It is

reasonable to assume that the acceptable error for these experiments is ~10%. In the high temperature regime, the nearly 2 mol NH₃/mol Al adsorbed for H-MOR 6.5 and 8.6 is likely due to the formation of NH₄⁺·nNH₃ associations [330,331]. The NH₃ adsorbed amount for H-MOR 7.7 should be the same as for those two catalysts and the difference is likely due to experimental error. While some error is acceptable, there is a trend in the high temperature regime NH₃ desorption. When dealumination gets to the point of producing Si/Al ratios >10, the amount of NH₃ adsorbed immediately decreases to 1.75 mol NH₃/mol Al from the ~1.97 mol NH₃/mol Al for H-MOR 6.5 and 8.6. The trend of lower NH₃ chemisorption continues for H-MOR 11.2, 13.0, and 15.4. While a potential explanation could be that overall unit cell contraction as shown by XRD may sterically limit the formation of these NH₄⁺·nNH₃ associations, the difference is likely attributable to decreased acidity.

The temperatures of desorption in each regime show that the acidity of the H-MOR is decreasing with increasing Si/Al ratio. For the low temperature regime, the peak desorption temperature drops steadily from 212°C for H-MOR 6.5 to 186°C for H-MOR 15.4 (a 26°C decrease). For the high temperature regime, a much different behaviour is observed. For H-MOR 6.5, 7.7, and 8.6, the peak temperature of desorption for the chemisorbed NH_3 is ~570°C. Between H-MOR 8.6 and 10.1, this peak temperature decreases to 541°C – a 23°C decrease from H-MOR 8.6. This further decreases to 531°C for H-MOR 13.0. It could be argued that H-MOR 10.1, 11.2, and 13.0 all have similar acidity. Finally, for H-MOR 15.4, the peak desorption temperature drops to 500°C. This is a 75°C decrease from the original H-MOR 6.5. This is a substantial decrease, though it was not unexpected as acidity should decrease with decreasing Al content [143,185,376,377]. The acidity decrease is not solely due to the decrease in Al content. It is also due to the decreases in crystallinity. It is no coincidence that the largest decreases in required desorption temperature of chemisorbed NH₃ are in line with the largest decreases in crystallinity as predicted from XRD. With decreasing crystallinity will come decreasing acidity. Recall that this is the reason Al-substituted M41S materials have such low acidity [133,134,136–139,389,390]. Of course, as has been mentioned repeatedly before, the loss of some of the next nearest neighbours will also impact the acidity of a specific site [141,142].

5.4.7 Py-TPD

Along with NH₃-TPD, Py-TPD is another of the most common techniques for evaluation of zeolite acidity, though it may see decreased usage as probing of acid sites via alkane adsorption continues to gain popularity. The issue with Py is its size. It's a rather bulky molecule, and for a long time it was believed that it could only access the 12-MR main

channel of MOR. It is known now that, in addition to being an indication of the acidity in the 12-MR, it can also yield information regarding the 8-MR side pockets of MOR [169,218,219]. Recent information has led some to believe that Py, given enough time and put under the correct conditions, could also reach into the smaller 8-MR channel and chemisorb there as well [332]. The results from Py-TPD and Py-DRIFTS thus become highly dependent upon the conditions of Py adsorption. Typically, for Py to make its way into the 8-MR channels (if it can), adsorption must be performed at an elevated temperature and given considerable time for the diffusion to take place. In the present case, where Py adsorption was conducted at ~60°C and for a period of one hour, it is assumed that the Py adsorbed is more of an indication of the acid sites in the 12-MR, and perhaps not even all of the sites located there. Regardless of What actually happens, there is now coming forth considerable debate regarding the usefulness of Py adsorption and subsequent TPD (along with Py-DRIFTS). It was done here due simply to its common use, and in the future alkane adsorption may be more useful, though this requires considerable study.

The results from pyridine desorption are shown in Table 5.10 and visually in Figure 5.12. The Py desorbed at low temperature $(<300^{\circ}C)$ is assumed to be simply physisorbed Py and is not actually indicative of the acid site strength of MOR [218,334]. It is to be noted that the amount of Py adsorption at low temperature increased by over 6 times relative to the amount of AI in the MOR with increasing dealumination from H-MOR 6.5 to 15.4. This is likely due to the increasing mesoporous surface area as indicated from surface area measurements (shown in Section 5.4.3), which would give Py more opportunity for physisorption as compared to the physisorption on a purely microporous structure. The increasing mesoporosity would also mean Py could more easily get nearer to the Al in the framework, again resulting in increased (and stronger) physisorption. This is implied in the increasing temperature of desorption for the physisorbed Py. For H-MOR 6.5, the physisorbed Py was removed at a peak temperature of 166°C which increased to 188°C for H-MOR 11.2. This cannot be assumed to be a sign of increasing acidity of the dealuminated zeolite, as NH₃-TPD presented in the previous section showed a large decrease in overall acidity from H-MOR 6.5 to H-MOR 11.2. Rather, this increase is likely more indicative of how close physisorbed Py could get to the Al acid site centres. While physisorption levels increased greatly from H-MOR 11.2 to 15.4 (for which the mesoporous area predicted from BJH desorption method increased greatly), the temperature of desorption did not increase, instead decreasing by 3°C. This can be considered to be experimental error. By this point, it may be that the decreasing acidity is catching up with the effect of the increasing proximity of physisorbed Py to framework Al.

| | Low Temperature Desorption (<300°C) | | | High Temperatur | | | |
|------------|--|--------------------------|------|------------------|--------------------|-------------|--|
| | | | | Desorption (>300 | Amount of Py equal | | |
| Catalyst | mol Py/mol Al | Peak T mmol (°C) Py/g | | mol Py/mol Al | Peak T (°C) | (mmol Py/g) | |
| H-MOR 6.5 | 0.04 | 166 | 0.54 | 0.29 | 621 | 1.47 | |
| H-MOR 7.7 | 0.06 | 171 | 0.51 | 0.32 | 632 | 1.47 | |
| H-MOR 8.6 | 0.07 | 177 | 0.47 | 0.32 | 626 | 1.44 | |
| H-MOR 10.1 | 0.12 | 185 | 0.50 | 0.39 | 630 | 1.47 | |
| H-MOR 11.2 | 0.14 | 188 | 0.52 | 0.44 | 642 | 1.44 | |
| H-MOR 13.0 | 0.28 | 186 | 0.52 | 0.51 | 629 | 1.44 | |
| H-MOR 15.4 | 0.25 | 185 | 0.41 | 0.47 | 653 | 1.44 | |

Table 5.10. Acidity evaluation by pyridine for H-MOR with received Si/Al ratio and dealuminated H-MOR catalysts.

The increasing mesoporosity may also be the reason why the amount of chemisorbed Py (the Py desorbed at temperatures >300°C) increased with increasing dealumination relative to the amount of Al, shown in Table 5.10. It must be noted that, compared to the total weight of catalyst, Py chemisorption levels did not change significantly enough to be considered outside the error of the measurements until H-MOR 15.4, where it decreased significantly from the average for the other catalysts of 0.51 mmol/g to 0.41 mmol/g. For most cases, the amount of chemisorbed Py did not seem indicative of the actual amount of acid sites in the 12-MR main channel or the 8-MR side pockets, with a theoretical acid site distribution of T1:T2:T3:T4 of 36:20:43:29 [197–200]. This means more than half of the acid sites should be located in the 12-MR (T2 and T4 are located completely in the 12-MR, while the T1 is shared between the 12-MR and 8-MR channels, see Figure 2.12). The theoretical amount of Py required to fill the volume of the 12-MR was also calculated, shown in Table 5.10 [334]. Again, the level of Py chemisorbed did not exceed 40% of this calculated value. This theoretical amount is based purely on the volume of the 12-MR from pore distribution measurements and in no way reflects or takes into account the acid site concentration in that channel. The low level of Py chemisorption is likely due to the low temperature of Py adsorption, as diffusion is the limiting step of Py chemisorption and not the actual interaction of Py with the acid sites [332,333]. Between H-MOR 6.5 and 13.0, the amount of chemisorbed Py relative to Al amount increases by ~76%. The decrease between H-MOR 13.0 and 15.4 may be within experimental error and no other explanation is offered for it. The increasing level of Py chemisorption relative to the amount of AI in the MOR could be considered as strong evidence that AI is being selectively removed that Py would not have been able to bind to in the first place without a higher temperature or longer adsorption period (which could be evidence of a higher rate of Al removal in the 8-MR as compared to the 12-MR). However, the effect of increasing mesoporosity on removing some of the diffusion limitations for Py in the MOR cannot be discounted. From pore distribution analysis, it was shown that the 12-MOR channel had been significantly deformed with increasing contribution to pore volume occurring at pore widths >7 Å with increasing dealumination. At the conditions of adsorption and based on other sources [169,218,219], the Py adsorbed at the conditions in this study is likely more of an indication of the acid sites in the 12-MR as opposed to the 8-MR, and the data does imply selective removal of framework AI in the 8-MR, though this cannot be stated conclusively.

The effects of the additional mesoporosity may actually be minimal, indicated by the temperature required for desorption of the chemisorbed Py. The peak temperature required for desorption does not change significantly except for H-MOR 11.2 and H-MOR 15.4. With

the addition of mesoporosity, some diffusion limitations should be removed [333], which, based on NH₃-TPD that showed decreasing acidity, would imply that the temperature of desorption should decrease. Especially for H-MOR 15.4, it appears that there are increased diffusional limitations as the desorption temperature increased considerably. This is likely due to the substantial decrease in crystallinity as shown by XRD of this sample. Even though some mesoporosity is introduced into the MOR with dealumination, it is not enough to counter the increased diffusional limitations imposed by the loss of crystallinity and potential framework contraction shown by XRD. It can therefore be considered that the increased level of Py chemisorption relative to Al amount is due to selective removal of Al from places Py would not have been able to chemisorb at under the conditions used in this study.



Figure 5.12. Py-TPD curves obtained on H-MOR with received and dealuminated Si/Al ratios.

5.4.8 Py-DRIFTS

As Py-TPD does not offer any information with regards to whether the Py is chemisorbed on a Brønsted acid site (BAS) or Lewis acid site (LAS) (at least not without complex mathematical treatment of the data), DRIFTS was used to differentiate between the two. Py-DRIFTS with MOR is well understood and the contribution of BAS and LAS can be separated and an approximate ratio developed between the two [218,219,270,335,336]. As mentioned previously in Chapter 4, there are three peaks of interest for Py-TPD. For BAS, these occur at ~1545 cm⁻¹ and ~1590 cm⁻¹. For LAS, the main peaks are ~1590 cm⁻¹
and $\sim 1450 \text{ cm}^{-1}$. As the peak at $\sim 1590 \text{ cm}^{-1}$ is shared between both LAS and BAS, it is not typically used for quantification of results. The results for Py-DRIFTS were not quantified in the Cu-Zn/H-MOR study as the peaks seemed to be too varied in intensity for consistent results. The problem in that study was that each catalyst was run in IR spectroscopy at different times on different days, and as such the proportions of KBr to catalyst may have been varied (unintentionally) or just the sample amount may have been more or less. For Py-DRIFTS in the hierarchical study, all catalysts were run at the same time and the treatment of the samples was kept consistent so as to achieve results that were quantifiable. As compared to known data, in this study the peak for LAS seemed to occur at 1445 cm⁻¹. It is accepted that there may be some variance in peak position with different samples. To determine the approximate ratio of Py-adsorbed BAS and LAS, the molar extinction coefficients 1.67 cm µmol⁻¹ for 1545 cm⁻¹ (BAS) and 2.22 cm µmol⁻¹ (LAS) were used as these seemed to produce a total quantity of chemisorbed Py that was in agreement with the Py-TPD results. The use of molar extinction coefficients has some level of error associated with it as various values have been published for them that seem to be specific to different MOR samples [218,270,336,391]. The calculated ratio of BAS to total acid sites using chemisorbed Py is given in Table 5.11 and the DRIFTS spectrums of each sample are shown in Figure 5.13. While there was admittedly some variance in the data, the overall trend is a decrease in the number of BAS relative to the total number of acid sites. This is especially obvious when looking at the ratio of the areas of the peaks at 1545 cm^{-1} and 1445 cm⁻¹. This implies that BAS are removed at a higher rate as compared to the acidcleaning of LAS, and/or that LAS are created during dealumination by nitric acid and subsequent calcination [392–394]. Given the levels of Py adsorbed based on Py-DRIFTS, it seems that BAS are being removed from the 12-MR and potentially the side-pockets of the MOR, leaving highly accessible LAS, though this conclusion is inconsistent with the ²⁷Al MAS NMR, XRD, and pore distribution results. If the previous results showing selective removal of 8-MR Al_f are taken into consideration, it could be that mesopore creation nearer to the 8-MR has created substantial amounts of Al_{ef}. This is not unreasonable, as the mesopore creation is only caused by removal of Al in the present case and at the larger mesopores it is highly likely that some Al has been left behind as LAS and not completely cleaned away by the acid treatment. The creation of the mesopores closer to the 8-MR would allow greater access for Py. This seems unlikely though, given that the 8-MR channel could only be accessed through the 8-MR side pockets. Additional mesoporosity would have to be created at the side pockets to permit access for Py. In this case, the results from XRD have to be considered that implied removal of T4 Al_f. With the removal of T4 Al_f, that point could

serve as a location for higher concentrations of Al_{ef} and would also subsequently reduce the number of BAS that Py is known to have higher access to. This seems much more reasonable. Therefore, Py-DRIFTS results may be considered as evidence for selective T4 Al_f removal. It should be recalled that Py-DRIFTS results can only be considered to be representative of only a fraction of the MOR. The results cannot be considered applicable to the entirety of the crystals of the H-MOR catalysts and thus do not have to sync completely with ²⁷Al MAS NMR, XRD, or pore distribution results.

Table 5.11. Ratio of BAS to LAS from Py-DRIFTS for H-MOR with received ratio and dealuminated H-MOR catalysts.

| | Py-DRIFTS | | | | | | |
|------------|-------------|-----------|------|--|--|--|--|
| Catalyst | Area Ratios | | | | | | |
| | 1445/1425 | 1545/1445 | | | | | |
| H-MOR 6.5 | 0.83 | 0.77 | 0.37 | | | | |
| H-MOR 7.7 | 0.67 | 0.74 | 0.36 | | | | |
| H-MOR 8.6 | 0.94 | 0.40 | 0.23 | | | | |
| H-MOR 10.1 | 1.90 | 0.29 | 0.18 | | | | |
| H-MOR 11.2 | 1.76 | 0.46 | 0.26 | | | | |
| H-MOR 13.0 | 1.59 | 0.32 | 0.19 | | | | |
| H-MOR 15.4 | 2.69 | 0.39 | 0.22 | | | | |

^aDetermined based on molar extinction coefficients for 1545 cm⁻¹ and 1445 cm⁻¹.

Accompanying the 1445 cm⁻¹ peak was an additional peak (found through deconvolution) at a wavelength of 1420 cm⁻¹, which is shown in Figure 5.13. This peak was not able to be conclusively identified and is not present in most other Py-DRIFTS studies. However, given the broad behaviour of the peak, it may be due to some weakly physisorbed Py which was not removed prior to using the sample for DRIFTS, though this is expected to occur more closely to the chemisorption peak, and, in the case of this study, would likely be around 1435 cm⁻¹ [395]. In this regard, the peak at 1445 cm⁻¹ cannot necessarily be attributed solely to chemisorbed Py, and may include some amount of physisorbed Py. This is a plausible explanation for the lack of correlation between ²⁷Al MAS NMR and Py-DRIFTS, and would also be why the peak was not significantly affected by the changing concentration of Al sites. Per gram of material, the amount of physisorbed Py increased

with increasing dealumination while the amount of chemisorbed Py decreased. From the NIST database, it is also known that the frequency 1433 cm⁻¹ is due to the C-H bond in pyridine itself. The presence of a peak at the frequency of 1420 cm⁻¹ may even be due to another adsorbed species and not necessarily Py. Given the several reasons presented, the peak area due to the 1420 cm⁻¹ frequency peak was not used in the analysis of the results nor was further work conducted in an attempt to identify it.



Figure 5.13. Deconvolution of the Py-DRIFTS results in the range 1400 – 1600 cm⁻¹ for H-MOR with received ratio and dealuminated H-MOR catalysts.

5.4.9 DRIFTS of calcined catalysts

In addition to doing DRIFTS on samples with adsorbed Py, DRIFTS on calcined catalysts, or rather, on the H-MOR form, was also conducted to discern some additional information regarding if certain Al was removed or not. Many groups have attempted to quantify the amounts of Al using information in the 3800 cm⁻¹ to 3500 cm⁻¹ region and work is still ongoing. As was mentioned earlier, what is believed at this time for MOR and similarly for other zeolites is that the BAS for the 12-MR have a peak at \sim 3610 cm⁻¹ and the BAS for the 8-MR have a peak at \sim 3585 cm⁻¹ [212–214,270,347–353]. Terminal silanol groups show up in the IR spectrum at \sim 3745 cm⁻¹ and Al_{ef} is visible at 3650-3660 cm⁻¹ [270,335,347]. These are just approximate ranges for where the peaks should be; they are influenced by the acidity of each different sample. Lukyanov et al. [347] have specifically shown that the wavenumber ranges for the BAS in each channel may be expanded. However, this was with significant mathematical analysis of the IR spectroscopic results that were performed under very controlled circumstances. For a proper IR study of MOR, an in situ cell is necessary so that water can be removed from the zeolite. Adsorbed water will have some influence on the DRIFTS spectra obtained. In the present work, only three Gaussian-style curves were attempted to be fit to each peak and, due to the circumstances under which IR spectroscopy was performed as detailed in Section 3.3.9, some variance in the data from other studies is expected. In no way will the contribution to the overall curve of each of the several different acid sites be attempted to be distinguished and quantified. Only relative area ratios will be considered.

The DRIFTS spectrum for the frequency range 3700 cm⁻¹ to 3500 cm⁻¹ is shown in Figure 5.14 and 5.15. Relative ratios of the peaks of interest are given in Table 5.12. In each deconvolution, a peak was observed at ~3655 cm⁻¹ and was attributed to Al_{ef}. The second deconvoluted peak occurred at ~3630 cm⁻¹. This is not specifically in the known range of 12-MR hydroxyl groups, but given the circumstances of the study and the broadness of the peak, it was assumed that this peak was most representative of the Si-OH-Al groups in the 12-MR. The third peak occurred at ~3575 cm⁻¹ and was attributed to the Si-OH-Al groups in the 8-MR. While it is acknowledged that the frequencies are somewhat different from what is shown in other studies, a reasonable level of error is accepted (both in instrument and in material treatment) and the peaks selected are assumed to be most representative of the locations specified above. What is important is the order of the peaks: the –OH groups for the 12-MR should occur at higher wavenumber than the –OH groups for the 8-MR. Figure 5.14 shows the signals scaled to the same Kubelka-Munk unit at a wavenumber of 3650 cm⁻¹. This was intended to show the change in the ~3575 cm⁻¹ region. The peak in this region decreases with increasing dealumination, indicating that Al is being selectively removed from the 8-MR as opposed to the 12-MR of MOR. This was also evident in the comparison of peak areas shown in Table 5.12 between the 12-MR and 8-MR, which showed an increasing amount of Al in the 12-MR relative to the 8-MR with dealumination. A value is not given in Table 5.12 for H-MOR 15.4 as at this point peak deconvolution failed to find a peak between 3600 and 3550 cm⁻¹ and thus no assignment of 8-MR Al could be conclusively conducted. Even with the error associated with the measurements and analysis, the results strongly indicate selective removal of 8-MR Al over Al in the 12-MR. It should be recalled that while the T3 location in the 8-MR can be considered to be the most probable location for Al_f to be, the total number of Al_f (and consequently hydroxyl groups) in the 12-MR will still be higher.

| | | | C |
|------------|----------------|-------|---|
| Catalyst | Ratio of 12-MR | 1 | C |
| | AI/8-MR AI | Jnit | C |
| H-MOR 6.5 | 1.2 | J yur | c |
| H-MOR 7.7 | 1.5 | a-Mu | C |
| H-MOR 8.6 | 1.9 | lbelk | |
| H-MOR 10.1 | 1.7 | Ϋ́ | Ľ |
| H-MOR 11.2 | 1.8 | | C |
| H-MOR 13.0 | 1.9 | | C |
| H-MOR 15.4 | N/A | | |



Table 5.12. Ratio of the peak areas for 12-MR to 8-MR hydroxyl groups as obtained from DRIFTS analysis for H-MOR catalysts. Figure 5.14. DRIFTS spectrum in the hydroxyl region for calcined H-MOR and dealuminated H-MOR catalysts (scaled to show change in \sim 3575 cm⁻¹ peak).

The deconvoluted peaks from the DRIFTS spectra in the hydroxyl region are shown for H-MOR 6.5 and the dealuminated H-MOR catalysts in Figure 5.15. While the accuracy of the spectra could be called into question (the reasons are unknown for why the wavenumbers are as dissimilar as they are from literature values), the observable trends are quite obvious. Firstly, the comparison of the peak areas for the Al_{ef} (~3655 cm⁻¹) to the nearby 12-MR hydroxyl group's peak (~3635 cm⁻¹) follows the same trend as was predicted by ²⁷AI MAS NMR. H-MOR 6.5 has guite a bit of Al_{ef}, followed by decreases for H-MOR 7.7 and 8.6. For H-MOR 10.1, a larger amount of Al_{ef} was predicted and this is quite obvious in Figure 5.15. The amount of Al_{ef} then decreases and increases again for H-MOR 11.2 and 13.0 respectively, again matching the trend shown in DRIFTS. The DRIFTS for H-MOR 15.4 became quite hard to interpret. It looks like the acidity has changed so much that the peak for the 12-MR hydroxyl groups has shifted to 3653 cm⁻¹ and the peak indicating 8-MR hydroxyl groups has shifted to 3607 cm⁻¹ and there is no Al_{ef} present. Though this is likely the case, this is the extent of the analysis of the DRIFTS spectra for H-MOR 15.4 in the hydroxyl region. The decrease in intensity of the peak for the 8-MR hydroxyl groups at ~3575 cm⁻¹ compared to the intensity of the 12-MR hydroxyl peak is obvious with increasing dealumination, suggesting the preferential removal of the acid sites in the 8-MR channels that many of the other characterizations have been implying. However, it is apparent that some of the acid sites in the 12-MR are being removed as well, especially in the samples with Si/Al ratio >10. In fact, it may be the case that an equivalent number of acid sites are being removed from the 8-MR and 12-MR at these ratios. Given the results from XRD, this seems to imply that Al_f is being removed from the T3 and T4 locations at the same rate while T1 and T2 locations are largely left untouched.



Figure 5.15. DRIFTS spectrum for H-MOR and dealuminated H-MOR catalysts deconvoluted into 3 separate peaks in the hydroxyl region between 3700 and 3500 cm⁻¹.

5.4.10 Cation exchange capacity using Cu²⁺ as metal probe

In one of the first studies of the use of MOR for DME carbonylation, and prior to the work surrounding the identification of the necessarily T3 active site [212,215–217], one theory regarding the strange activity correlation with protonic site concentration was that BAS needed to be within reasonable proximity in order to facilitate the reaction [90]. As a means towards quantifying the distance between Al atoms in the dealuminated materials, the liquid-based ion-exchange of divalent Cu was conducted (used as a metal probe). This was following the conventional idea that a divalent metal would require two Al framework atoms to balance the positive charge and facilitate ion-exchange [167,170-172,396]. It was already known from past works that MOR has about a 50% ion-exchange capacity for divalent metals, though this can be increased with certain treatments [168–171]. It was assumed that with the removal of Al_f that the cation exchange capacity (CEC) of MOR for a divalent metal would decrease relative to Al amount as the distance between Al_f increased. However, as shown in Table 5.13, this was not the case, and the CEC for Cu^{2+} actually increased from 48.0% for a Si/Al ratio of 6.5 to 69.8% for dealuminated MOR with Si/Al 15.4. While the increased CEC may be due to contraction of the unit cell and reduction of the distance between framework Al's, pore distribution analysis did not show an appreciable change in the pore size or micropore volume and Al_f proximity should not be any higher on H-MOR 15.4 as compared to H-MOR 6.5. The CEC also did not appear to be affected by the presence of Al_{ef}.

| Catalyst | Si wt % | Λ wt 0_{6} | Cu wt % | Cation exchange |
|------------------------------|-----------|----------------------|-----------|-----------------|
| Catalyst | 51 WC. 70 | AI WC. 70 | Cu wt. 70 | capacity (%) |
| Cu/NH ₄ -MOR 6.5 | 34.9 | 4.9 | 2.8 | 48.0 |
| Cu/NH ₄ -MOR 7.7 | 35.3 | 4.4 | 2.6 | 51.3 |
| Cu/NH ₄ -MOR 8.6 | 35.6 | 4.0 | 2.5 | 53.4 |
| Cu/NH ₄ -MOR 10.1 | 36.5 | 3.4 | 2.4 | 58.9 |
| Cu/NH ₄ -MOR 11.2 | 36.1 | 3.3 | 2.3 | 59.9 |
| Cu/NH ₄ -MOR 13.0 | 36.7 | 2.9 | 2.1 | 63.5 |
| Cu/NH ₄ -MOR 15.4 | 37.5 | 2.6 | 2.2 | 69.8 |

Table 5.13. Compositions of Cu^{2+} liquid-based ion-exchanged NH₄-MOR catalysts with received and dealuminated ratios.

Given the results from the liquid-based ion-exchange of Cu²⁺, the location of ionexchanged Cu²⁺ required assessment, which is actually still a debated issue as has been mentioned in Chapter 4. Some groups have figured that Cu²⁺ first preferentially ionexchanges into the 8-MR [233,302–304], while further work indicates that ion-exchange in the 12-MR main channels may occur first [301,362]. Still other groups feel that ionexchange will occur preferentially around the 8-MR side pockets [169,254,364]. Despite this work, in this thesis an answer has already been formulated for where Cu²⁺ preferably ion-exchanges on MOR. This conclusion was reached by a combination of modeling and experimental techniques. For detailed information, the reader is directed to Chapter 4 and only a brief summary of the most relevant results will be provided here. For the purposes of the present argument, the IR spectrum between H-MOR and Cu/H-MOR with Si/Al ratio of 6.5 was compared to ascertain the most probable location for Cu^{2+} . Note that these samples had CO chemisorbed onto them prior, though based on the comparison of H-MOR from DRIFTS before CO chemisorption and after, it has minimal effect on the results of H-MOR alone. The large peak for Si-OH-Al in the 3700 cm⁻¹ to 3500 cm⁻¹ region was deconvoluted as described above and is shown in Figure 5.16. The results from H-MOR are quite typical, following the same trend of the three peaks as was described in the previous section. The deconvoluted peaks include 3658 cm⁻¹ for Al_{ef} , 3631 cm⁻¹ for -OH groups in the 12-MR and 3587 cm⁻¹ for the –OH groups in the 8-MR. The ratio between the 12-MR and 8-MR hydroxyl peak areas was 1.57 and is somewhat inconsistent with DRIFTS results in the previous section. However, the characterizations were performed a long time apart and may have been due to equipment operation or sample treatment conditions (or changes in peak deconvolution). The ion-exchange of Cu^{2+} changed the results significantly. Firstly, the peaks were shifted to lower wavelengths for the 12-MR and 8-MR to 3626 cm⁻¹, and 3583 cm⁻¹ respectively. Secondly, the ratio of 12-MR Si-OH-Al to 8-MR Si-OH-Al peak areas decreases to 1.14 - a 27% decrease from H-MOR. This strongly indicates that Cu²⁺ ionexchange occurs preferentially in the 12-MR of NH₄-MOR. With this realization, the Cu²⁺ ion-exchange quantities then make complete sense. If the 8-MR Al_f was being preferentially removed during dealumination and was not involved in Cu²⁺ ion-exchange in the first place, this would cause the perceived CEC of the dealuminated H-MOR to increase. While some error can be expected due to peak deconvolution and the shift of the peak wavelengths, the associated error would not outweigh the change in the ratio of the peak areas. While T4 Al_f may also be removed selectively by the acid leaching, it has been previously concluded in Chapter 4 that the T4 Al_f did not serve as a primary ion-exchange location. It was more likely that the T1 and T2 Al_f's were the primary sites for ion-exchange. The CEC results

then also imply that those T1 and T2 Al_f 's are largely left untouched by the dealumination treatments, at least when compared to the preferential removal of the T3 and T4 Al_f 's.



Figure 5.16. Results from CO-DRIFTS for H-MOR and Cu/H-MOR with Si/Al ratio of 6.5.

Unfortunately, the original intent of the Cu^{2+} probe experiments was not realized. It was desired to understand if Al sites had become significantly further apart from one another, and divalent metal ion-exchange was meant to provide a direct proof of this. Despite this, the evaluation of CEC has provided another experimental evidence for the preferential ion-exchange of Cu^{2+} in the 12-MR, specifically at the T1 and T2 Al_f locations.

5.5 Discussion

The original goal of this work was to identify whether or not an enhancement to stability could be gained from dealumination via nitric acid. Despite the hazards associated with the use of nitric acid, it does not have the same energy requirement as steaming and, under the right circumstances, will remove Al_f completely rather than simply creating Al_{ef} [180,181,286,338,377–379]. However, based on the reaction results, even minor dealumination led to a decrease in activity and after removal of approximately half of the Al in the MOR, the H-MOR was no longer useful for DME carbonylation. As such, investigation was required into why, with half the Al still present in the zeolite as Al_f, the MOR could no longer serve as a catalyst for the reaction.

With the initial discovery of the use of protonated MOR for the carbonylation of DME, Cheung et al. [89,90] developed several theories with regards to how it worked. To obtain a marginal amount of insight, the amount of acid sites was varied by partial ion-exchange with Na⁺. The rate of MeOAc production did not vary linearly with the number of acid sites, which led to the theory that the whole of MOR was not active. It was theorized that either acid sites had to be within a reasonable proximity of each other or that there was a specific site required for the reaction [90,212]. Boronat et al. [215,216] took this idea and modeled the different acid sites of MOR using DFT methods to determine if there was an acid site more inclined towards the formation of MeOAc. Their results agreed with the specific site theory, and they found that the T3 position, specifically the oxygen atom O9 (otherwise labeled as T3-O33 in Figure 2.12), in the smaller 8-MR channel was most inclined towards the creation of an acetoxy group. The acetoxy group has been deemed necessary for the creation of MeOAc. Despite this advancement in knowledge, it was not determined whether sites had to be within a reasonable proximity for carbonylation to occur – only that theoretically the T3-O9 acid site was absolutely necessary.

In the current study, very mild dealumination (from Si/Al ratio of 6.5 to 7.7 and 8.6) did show an enhancement in stability, increasing the catalyst lifetime from 20.5 h to ~33 h. From an industrial perspective, this is quite useful, especially as it did not require high concentrations of HNO₃ or a very high temperature to achieve. The procedures used to create H-MOR 7.7 and 8.6 are relatively safe. With the Si/Al ratio of 7.7 and 8.6, only a very minor loss of activity occurred. There was also an improvement in the selectivity towards MeOAc on deactivation though some amount of unidentified hydrocarbons was still produced. Based on the results of ²⁷Al MAS NMR and DRIFTS, mostly Al_{ef} and only some of the Al_f were removed with these levels of acid treatment. The DRIFTS results indicated that any Al_f that was removed by acid leaching was removed from the 8-MR, though this does not seem to have had a significantly detrimental impact on the activity of the catalyst as a function of the total Al content. From NH₃-TPD, it did not appear that the acidity of the H-MOR was decreased significantly at this level of dealumination either, nor was the ability of the acid sites to be populated with CH_3^+ groups as indicated by DME-TPD. The amount of chemisorbed NH₃ relative to Al content remained reasonably constant with this minor amount of dealumination. XRD did not show a substantial loss in crystallinity at this level though there was some loss in micropore volume and some alteration of the 12-MR structure as indicated by pore distribution analysis.

Despite only a minor level of dealumination between H-MOR 8.6 and 10.1, the behaviour of the catalyst was altered significantly. The peak activity towards MeOAc production decreased by 33% from H-MOR 8.6 with only a ~3 hour increase in effective catalyst lifetime. This meant that, per Al amount, the total MeOAc produced decreased, but was still higher when compared to H-MOR 6.5. Though the activity of the catalyst had

suffered, the selectivity did not, with no detectable unidentified hydrocarbons produced during severe catalyst deactivation. The amount of produced MeOH did not seem to decrease. Many other characterizations showed a significant change between H-MOR 8.6 and 10.1. While the crystallinity of the MOR had been maintained in H-MOR 7.7 and 8.6, the crystallinity of H-MOR 10.1 had decreased from 83% for H-MOR 8.6 to 69% for H-MOR 10.1. This was also the point where it appeared the main peaks in XRD began to shift to higher 20, indicating contraction of the unit cell. While the amount of Al_{ef} had decreased with dealumination to H-MOR 7.7 and 8.6, it increased with 10.1 from what H-MOR 8.6 had shown. While some removal of Al_{ef} did occur from H-MOR 6.5, there was still a substantial amount of it in H-MOR 10.1. The NH₃-TPD showed a substantial decrease in acidity at this level of dealumination, with peak temperature of desorption decreasing from 564°C to 541°C. The amount of NH₃ chemisorbed decreased as well from H-MOR 8.6. DRIFTS indicated that at this point it was likely both 12-MR and 8-MR Al_f being removed. These trends continued to H-MOR 11.2 and 13.0, though H-MOR 11.2 had significantly less Al_{ef} present as indicated by ²⁷Al MAS NMR.

With H-MOR 15.4, it appeared that the dealuminated MOR had reached a level where it was no longer useful as a catalyst for DME carbonylation. As a function of Al content, it produced approximately half the MeOAc that H-MOR 6.5 did before it deactivated, and took \sim 38 h to do it as compared to H-MOR 6.5's lifetime of 20.5 h. The peak MeOAc productivity was only 20% of what H-MOR 6.5 had shown, and, very importantly, the selectivity had completely changed. During the entirety of the reaction with H-MOR 15.4, other not identified hydrocarbons were produced and the selectivity towards MeOAc, at best, was 70%. XRD showed that H-MOR 15.4 had only 48% of crystallinity preserved as compared to non-calcined H-MOR 6.5. Pore distribution analysis showed some alteration to the pore structure, though the general structure of the channels still appeared to be maintained. It was with H-MOR 15.4 where TEM first started to show that visible damage to the edges of the crystals was beginning. A substantial loss in acidity occurred in the dealumination to H-MOR 15.4, decreasing the high temperature desorption curve peak for NH_3 to 500°C, previously at 531°C for H-MOR 13.0. It is noteworthy that the H-MOR 15.4 still appeared to have had no trouble activating DME, with 79% of acid sites populated with a CH_3^+ group. The ability of DME to get to the acid sites and create methyl groups also shows that the loss in crystallinity did not harm the utilization of the DME by the MOR. However, given the amount of time required to achieve the peak MeOAc productivity in reaction, it could be argued that significant diffusion limitations had been introduced. This was evident in Py-TPD, where the required temperature of desorption of Py increased to 653°C from 629°C for H-MOR 13.0. It could also be the case that decreased acidity had slowed the utilization of DME by H-MOR 15.4. From DRIFTS, it appeared that most of the Al in the 8-MR had been removed as peak deconvolution was unable to produce a peak at that frequency range. Fundamentally, from DRIFTS it was apparent that the H-MOR 15.4 had been changed significantly from all other H-MOR catalysts, with all problems with it likely stemming from the significant crystallinity loss. This crystallinity loss would also be responsible for the acidity decrease. Both the acidity decrease and loss of so much of the T3 Al's would be responsible for the substantial change in catalytic behaviour.

When putting all of the data from characterizations together, there is one obvious trend that emerges that all characterizations support. The results from XRD were consistent with what is known about dealumination for MOR [184,185,377,380,381]. Upon closer examination, the crystallinity in the k plane appeared to be damaged the most as opposed to the other planes. The h and k planes run perpendicular to the direction of the 8-MR and 12-MR channels, and as such the shape of the channels must be damaged but not necessarily their pore volume, as they are less damaged in the / plane. This was supported by the pore distribution analysis, which showed that while the shape of the channels was being changed, the overall pore volume actually did not change very much. Although XRD does show contraction of the unit cell and loss of crystallinity, the MOR still appears to be intact. While pore distribution information showed that the 12-MR was deformed, the effect on the 8-MR is far more inconsistent. With minor dealumination to H-MOR 7.7 and 8.6, it appeared the 8-MR was more open and had increased pore volume. This was synonymous with a decrease in Al_{ef} from ²⁷Al MAS NMR. Decreases in pore volume of the 8-MR from the pore distribution analysis were matched by increases in Al_{ef}. This information alone seemed to imply that the Al in the 8-MR was more susceptible to dealumination, though it could also be argued that, given the size of the 8-MR, it was more likely to be blocked by Al_{ef}. Regardless, it does mean Al_f was being significantly affected in the 8-MR by dealumination.

Despite the loss of crystallinity, the ability of the acid sites of MOR to be populated with DME was not harmed, though the optimum level for DME utilization appeared to be H-MOR 8.6 and may have had something to do with the decreased amount of Al_{ef} and still high crystallinity. The loss of Al_f led to a substantial decrease in acidity, shown by NH_3 -TPD. NH_3 is small enough that it would not be affected by diffusional limitations imposed by the crystallinity loss [397]. Between H-MOR 6.5 and H-MOR 15.4, the required temperature of desorption for chemisorbed NH_3 decreased by 75°C, with the biggest decrease being from H-MOR 13.0 and H-MOR 15.4. This was also the point where the required temperature of desorption for Py increased the most, though this was likely guided by diffusional limitations imposed by crystallinity loss and deformation of the 12-MR channel [332,333]. The amount of Py chemisorbed did increase relative to Al content with increasing dealumination, which could be an indication that 12-MR Al and 8-MR side pocket Al are not as strongly affected by dealumination as the 8-MR Al. However, given the increase in mesoporosity of MOR with dealumination, it could also be that Py simply gains access to more Al acid sites. The DRIFTS results, though some error is to be accepted with them, did prominently show the overall trend that Al was being removed from the 8-MR preferentially though some loss of Al in the 12-MR is also shown by the method. At Si/Al ratios >10, it appears that equal amounts of Al are being removed from the 8-MR and 12-MR with dealumination.

One of the more useful characterizations turned out surprisingly to be divalent Cu ion-exchange onto the MOR. By this method, it appeared that the exchange capacity of the MOR was increasing, which, if all Al_f was removed at equal rates, should not have been occurring. As Al_f gets further apart, it is less likely to stabilize divalent metals and ionexchange levels should decrease relative to Al content. However, in the current study they increased, showing that Al_f were still sufficiently near to each other to facilitate ionexchange. While the debate rages on about where Cu^{2+} prefers to ion-exchange on MOR, the DRIFTS evidence for H-MOR and Cu/H-MOR as well as previous modeling by other groups [301], coupled with evidence from DRIFTS of the dealuminated MORs, points to preferred ion-exchange of Cu^{2+} in the 12-MR of MOR. As the level of Cu^{2+} ion-exchange increases with respect to total Al content, it is a strong sign that divalent Cu's preferred ionexchange locations in the 12-MR are not as affected by dealumination by acid leaching as other acid sites are. This means the T1 and T2 framework Al are mostly unaffected by dealumination. It could also be argued that the introduction of mesoporosity and unit cell contraction simply creates new areas where Cu^{2+} ion-exchange could occur, though this is assumed to not be as likely. Mesopores would be created where Al is harmed in some manner, and likely renders them ineffective for ion-exchange. Unit cell contraction, though shown by XRD, was not strongly supported by the pore distribution analysis.

Though not one of the characterizations could stand alone to prove beyond doubt what is occurring during the controlled dealumination process, the overall trend from all characterizations and the reaction results indicate that the Al located in the 8-MR, specifically the T3 location, and at higher Si/Al ratios the Al located at the T4 position in the 12-MR, are being more selectively removed as opposed to the T1 and T2 framework Al's. The strongest indications of this dealumination behaviour came from the reaction results, pore distribution analysis combined with ²⁷Al MAS NMR, XRD, Py-TPD, DRIFTS analysis, and the cation exchange capacity of Cu²⁺. By themselves, each of these characterizations has a flaw in it that could be used to argue against this point but together they provide sufficient evidence of selective Al removal from the 8-MR. As this is where the active site is theorized to be [212,215–217], this also explains why, by a Si/Al ratio of 15.4, the MOR is no longer suitable as a catalyst. Most of the Al in the 8-MR has been removed by that point, shown by DRIFTS analysis. This conclusion of preferred removal of Al in the 8-MR is consistent with what has been found previously by other groups [386–388].

However, this does not explain why the selectivity of the catalyst appears to be improved with Al removal. This point can be explained by utilizing the DRIFTS results for the ratio of the Al in the 12-MR and the 8-MR. This ratio first increases very rapidly, from 1.2 for H-MOR 6.5 to 1.9 for H-MOR 8.6, but after this point it stays reasonably constant. It is likely that the most active sites for DME carbonylation are removed first, which would result in the increased time before peak activity of the catalyst was reached. This would also mean many of the other acid sites are left untouched. The selectivity towards other hydrocarbons is only reduced for H-MOR 7.7 and H-MOR 8.6 and not eliminated entirely. It is with dealumination to H-MOR 10.1 and likely removal of some of the Brønsted acid sites in the 12-MR that the selectivity towards others is eliminated. The selectivity improvement at first could also be related to acidity, which is shown to decrease substantially at H-MOR 10.1. A decreased acid strength would slow the rate of formation of strongly adsorbed larger hydrocarbons (coke), leading to the stability increase observed in reactions [234,260,398]. However, there is something far more subtle here that the acid strength implies that is quite important to realize. Between H-MOR 6.5, 7.7, and 8.6, where it could be argued that there is minimal removal of Al from the 12-MR, the stability of the catalyst actually significantly increases. It was previously suggested that T4 Al's (located in the same 4-MR as the T3 Al) are removed preferentially as well [386-388]. With the decreasing ratio of (T3+T4)/(T1+T2) with increasing Si/Al ratio, the results strongly indicate that not only is the absolute number of T3 Al's important, but also the overall density of the T3 and T4 sites. If the concentration of the T3 and T4 Al's is too high, it may negatively impact the stability of the H-MOR catalyst. It has already been discussed numerous times in this thesis how the number of Al's present in the framework will influence the acidity. With removal of some of the next nearest neighbours to the active sites, the acidity is decreased such that the probability of creating by-products that lead to catalyst deactivation may be minimized. Removal of T4 Al is also beneficial for keeping the 8-MR side pockets open. The T4 AI's make up part of the mouth of the 8-MR side pocket where it connects to

the 12-MR main channels. Coking reactions here would more directly prevent access to the active sites in the 8-MR than coking reactions at other locations. It must also be considered that the T3 Al's are not as innocent as they may appear from modeling. Other reactions may occur here as well that will poison or otherwise block them.

With the data accumulated in this study, the turnover frequency (TOF) of the catalyst was calculated based on results from DRIFTS and ²⁷Al MAS NMR and available literature data [386–388] and is shown as a function of reaction time in Figure 5.17. The first assumption was based on the distribution of Al atoms in the framework, which was taken from Ban et al. [200] as T1:T2:T3:T4 = 36:30:43:29. For H-MOR 7.7 and 8.6, it was assumed that much of the Al removed was Al_{ef}, and only ~40% of Al removed were T3's. Beyond a Si/Al ratio of 8.6, equal amounts of T3 and T4 Al's were assumed to be removed with no removal of T1 or T2 Al's. Only between H-MOR 8.6 and 10.1 was some accommodation made for Al_{ef}, where an additional amount of T3 Al was assumed to be rendered inactive for DME carbonylation. This produces calculated TOFs that are within 20% error of each other and also produces a final number of 8-MR Al that is in agreement with what is shown in DRIFTS for the H-MOR 15.4 (where a peak was not able to be deconvoluted in the 3590 cm⁻¹ to 3570 cm⁻¹ region). It also shows that stability is somewhat more enhanced at H-MOR 15.4, but would require much more of the catalyst to produce reasonable rates relevant for an industrial level of production of MeOAc.



Figure 5.17. Catalyst turnover frequency for H-MOR with received ratio and dealuminated ratios assuming selective T3 framework AI removal in the 8-MR and that this T3 AI is the active site for reaction.

5.6 Conclusions

In this work, the carbonylation of dimethyl ether (DME) was carried out over protonated mordenite samples with varying degrees of dealumination. Although the use of MOR for this reaction has been known for nearly a decade [89,90], the issue of MOR stability has not been completely resolved. The original objective of this work was to study whether or not simple dealumination via nitric acid treatment could provide a degree of enhancement to stability. While some stability enhancement was achieved, it was at the cost of activity relative to total Al content. Characterization began to reveal a consistent trend in terms of which of the two channels in MOR was most impacted by the dealumination procedure. While XRD showed a substantial decrease in crystallinity and NH₃-TPD showed a large loss of acidity with dealumination, this did not inhibit the ability of the MOR to create methyl groups on its acid sites from dimethyl ether. Pore distribution showed a significant amount of deformation to the 12-MR as well as blockage of the 8-MR that coincided with the amount of Al_{ef} determined from ²⁷Al MAS NMR. The results of pyridine TPD proved to be affected mostly by diffusional limitations, though one interpretation of the results was that 12-MR Al and side pocket Al was impacted to a lesser degree with the dealumination compared to the 8-MR framework Al. Pyridine DRIFTS showed that some of the BAS were being removed that it normally had access to, which serves as evidence for the removal of some AI from the 12-MR. DRIFTS results on calcined catalysts showed a decrease in both 12-MR and 8-MR AI, though the loss of 8-MR AI occurred at a higher degree at lower Si/Al ratios. Cation exchange capacity utilizing Cu²⁺ was evaluated and found to increase with dealumination, which served as a strong indication of selective removal of 8-MR AI and another evidence for selective ion-exchange of Cu²⁺ in the 12-MR of MOR. Deformation of the 12-MR was also evidence for removal of Al from there. When putting the results of all the characterizations together, the conclusion is reached that at lower Si/Al ratios, it appears the Al located at the T3 position in the 8-MR is selectively removed while beyond a Si/Al ratio of ~10, T4 Al's in the 12-MR are removed at the same rate as T3 Al. The Al located at the T1 and T2 locations seem to be mostly unaffected by the dealumination and likely serve as the primary points of Cu²⁺ ionexchange. The T3 Al site had been theorized as the Brønsted acid site location in MOR most selective for DME carbonylation [212,215–217]. With its removal, the activity of the MOR as a whole decreased but at low removal amounts stability was considerably increased. However, when considering all of the data and estimating the TOF based strictly on the T3 Al's, the TOF was reasonably constant at all levels of dealumination. Ultimately, while the T3 Al site location is important for the reaction, in terms of stability, having too high an acid

site density at the T3 and T4 locations will also contribute to catalyst instability and deactivation.

This study has provided substantial experimental evidence via removal of Al for the theory that the T3 Al site is quite possibly the only acid site in MOR where DME carbonylation to methyl acetate can selectively occur. This study has also identified that the acid sites in the 12-MR are not solely responsible for the deactivation of MOR. The concentration of acid sites at the T3 and T4 sites also plays a role in the catalyst's stability.

Chapter 6

Bimetallic Fe-Zn on mordenite, other small tests, and paths forward

The difficulty lies not so much in developing new ideas as in escaping from old ones.

--John Maynard Keynes

6.1 The idea of selective site blockage

There are some common themes and results that came forth from both the bimetallic ion-exchange of Cu^{2+} and Zn^{2+} on MOR and the dealumination of MOR studies. These themes are present in previous literature on the use of protonic zeolites in reactions and in available recent publications on the use of ion-exchanged Cu^{2+} on MOR for DME carbonylation. They were simply not obvious due to relatively little variance in conditions and molar fractions of individual species [92,223,232].

From the bimetallic Cu-Zn on MOR study, one startling conclusion came forth: at the pretreatment used and the reaction conditions tested, Cu⁺ didn't actually increase the reaction rate and no substantial evidence was found that it actually helped directly with the reaction. Peak production rates of MeOAc weren't significantly different from H-MOR and the other metal ion-exchanged H-MOR catalysts. While there is some difference, the argument could be made that H-MOR is already deactivating before it can achieve the highest possible MeOAc production rate. Monometallic Cu/H-MOR didn't even perform as

well as H-MOR by itself and didn't quite achieve the same peak MeOAc production rate, though those values seemed to be within reasonable error of each other. It will be acknowledged here that Zhang et al. [232] did find that the calcination temperature of Culoaded H-MOR catalysts greatly affected the activity during reaction. Calcination at 270°C gave very low conversion, but it could be argued that at this temperature adsorbed water had not been removed from the H-MOR. Calcination at 430°C and 500°C gave the best results for DME conversion and MeOAc selectivity while calcination at 600°C decreased DME conversion considerably, though MeOAc selectivity was still reasonable. The authors concluded that the copper nitrate on the surface of the catalyst could be completely decomposed at 430°C and then easily reduced by H_2 . This is unlikely, as Cu(NO₃)₂ dissolves in solution to Cu²⁺ and NO₃⁻ ions. The nitrate ions should have absolutely no attraction to the MOR crystal. What is more likely is that water was not completely removed from the MOR until 430-500°C. By 600°C, the ion-exchanged Cu may have been sintering, which would have contributed to the lower activity observed with that particular catalyst. Reaction data was only presented for 145 minutes of reaction. The levels of Cu ion-exchange were also not reported in the paper. In the present work and in past work by others [89,90,212], the induction period for the catalyst (the period before which peak activity was achieved) didn't occur until after at least four hours of reaction. In the present work, sometimes peak activity wasn't achieved until after 10 hours of the catalyst being at reaction conditions.

Initial studies from BP Chemicals Ltd. [223,225,230] have provided a wealth of information. In the earlier patents, Cu/H-MOR with 55% of possible theoretical ionexchange (approximately the same as used in Chapter 4) was usually used with encouraging reaction results presented. However, in one of the latest works, Cu/H-MOR was not used and only H-MOR was used at similar reaction conditions but with varying amounts of H_2 in the feed. The data presented showed that the H-MOR could last longer than Cu/H-MOR given the proper reaction conditions. Results were not presented for Cu/H-MOR run at the same conditions. The implication from this is that Cu by itself on MOR may not actually do much to stabilize the H-MOR catalyst. From the TPO results of used catalysts in the present work, Cu/H-MOR had much lighter coke deposits on it. This is particularly favourable for less intense regeneration conditions and monometallic Cu/H-MOR has substantial value purely from that perspective. Regeneration did not show a return to the original activity, and activity of regenerated catalysts decreased with each regeneration [223]. From the present work, it was obvious from TEM that Cu had sintered during reaction. This would likely be a reason for the incomplete restoration of catalytic activity after regeneration [234].

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Monometallic Zn/H-MOR was shown to have increased stability and higher selectivity to MeOAc during deactivation as compared to Cu/H-MOR. This likely is due to the site blockage capabilities ion-exchanged Zn²⁺ exhibits on MOR. By this point in time, there is more than enough evidence available to conclude that not all sites on MOR contribute to DME carbonylation to MeOAc [212,215-217]. While Zn^{2+} may block some of the active sites for DME carbonylation, it will more preferably block sites where coking reactions would normally take place as evidenced by reaction results and the stability enhancement. This is confirmed by TPO, though Zn did not seem to prevent the formation of heavier coke as compared to Cu. It could be argued that this may have been due to the length of reaction (Zn/H-MOR was used in reaction for double the length of time of Cu/H-MOR). Other roles ion-exchanged Zn²⁺ may play are a little more subtle and open to interpretation. Ionexchanged divalent metals may lead to significant deformation of a zeolite framework. In the present case, ion-exchanged Zn^{2+} may lead to either increased or decreased framework deformation which would have some influence on the strength other ion-exchange locations. However, characterizations showed that Zn²⁺ did not substantially change the acidity of the MOR (NH₃-TPD) but did substantially decrease the amount of non-dissociated DME adsorbed. On the best bimetallic catalyst, 1Cu-4Zn/H-MOR, it was found that Zn^{2+} stabilized the Cu in its monovalent state and prevented it from sintering. Both metals would have stayed at their ion-exchange locations in this scenario. It is not to be concluded here that Cu^+ did not help with reaction, but it will only be mentioned again that there was not substantial evidence that it did. When a bimetallic $Cu-Zn/Al_2O_3$ catalyst with an equimolar ratio of Cu:Zn was tested, there was no activity for DME carbonylation.

The hierarchical study provided some valuable insight. This was only possible because dealumination was performed at differing conditions to achieve only small amounts of dealumination. With removal of approximately half the Al in the MOR (Si/Al ratio of 15.4 from 6.5), the catalyst was already ineffective for DME carbonylation. The two primary reasons for this are not unrelated. The Al's located at the T3 location (the selective DME carbonylation site) had been preferentially removed but what was also important was that the acidity of the MOR had decreased substantially. The acid strength may have been reduced to a point where the H-MOR was no longer usable for reaction. However, small decreases in the acid site strength and density had actually made the H-MOR more stable.

With the knowledge that selective site blockage and reduction/modification of the acid site strength was the likely key to providing enhanced stability, a limited set of experiments were carried out using another metal combination that did not consist of

metals normally used for carbonylation reactions.

6.2 Bimetallic solid-state ion-exchange of Fe-Zn onto mordenite

In one of the earlier patents from BP Chemicals Ltd., they suggested the ionexchange of one or more of copper, silver, gold, nickel, iridium, rhodium, platinum, palladium or cobalt [223]. Noticeably, Zn was left off of the list. Iron was also not mentioned. This is for good reason: iron is not a carbonylation catalyst. It has become well-known by this point that Fe-based catalysts are often used in Fischer-Tropsch type syntheses for the production of lower olefins (C2's to C4's) [41,399–402]. A variety of supports have been used and bimetallic combinations of Fe and Mn have been proposed for improved stability and activity. In terms of being used in ion-exchange on MOR, Fe has found limited uses. Early papers on ion-exchanged Fe on MOR have shown that it was useful for the decomposition of N₂O and production of N₂ [403–405]. Similarly, Fe on MOR has also been used for the selective catalytic reduction of NO by ethylene and the selective catalytic oxidation of NH₃ to N₂ [406,407].

Quite relevant to the current focus, Zhou et al. [408] synthesized MOR with Fe³⁺ isomorphously substituted into the framework via a template-free hydrothermal method. Synthesized catalysts were ion-exchanged with NH₄NO₃ and subsequently calcined to give the protonic form of the FeMOR. Catalysts were calcined at 400°C and then used for DME carbonylation at 200°C with a 5% DME/35% CO/60% H_2 mixture. A reaction pressure of 3.0 MPa was used. High Fe content (\sim 3 wt%) in the MOR framework negatively affected the crystallinity. However, at an Fe content of 1.62 wt% the crystallinity of the sample was still quite high. The isomorphous substitution unfortunately did not make the MOR any more stable, even with 60% H₂ in the feed. After 10-12 hours of reaction, the catalysts were already mostly deactivated. Lower Fe content seemed to give the best result for DME conversion but selectivity to MeOAc decreased considerably with deactivation of the catalyst. The FeHMOR with Fe content of 1.62 wt% seemed to give the best balance of DME conversion and selectivity to MeOAc with deactivation (in part due to its high crystallinity). Higher isomorphous substitution of Fe (\sim 3 wt%) continued to give better selectivity to MeOAc during deactivation but gave the lowest conversion of DME (~40% peak DME conversion compared to ~80% for 1.62 wt% Fe). TPO also showed that heavy coke was formed on the catalysts, requiring temperatures in excess of 500°C to remove. While the isomorphous substitution of Fe into MOR didn't appear to make the catalyst much better in terms of avoiding deactivation, the present theory of site blockage will be employed to see if it may apply.

6.2.1 Synthesis of Fe-Zn on MOR catalysts

Note: This was a preliminary study, and very little work was done on the bimetallic Fe^{2+} - Zn^{2+} on MOR catalysts. As such, synthesis and other procedures were not optimized.

Due to time limitations, oxidative solid-state ion-exchange was used in place of liquid-based ion-exchange to make some of the MOR catalysts with ion-exchanged Fe²⁺ and Zn^{2+} [93,167,173,409]. It was also figured that the liquid-based ion-exchange of Fe³⁺ might not produce high loadings of the metal. Higher loadings were desired for increased site blockage. As such, Fe²⁺ was used and, due to the relative cost of this material, solidstate ion-exchange was determined to be a more effective means by which to conduct the ion-exchange. In a typical synthesis, the dried NH₄-MOR (Si/Al = 6.5, purchased as Na-MOR from *Zeolyst*, CBV-10A) was ground together with FeCl₂·4H₂O (purity ≥99.0%, Sigma-Aldrich) and/or $ZnCl_2$ (purity \geq 98.0%, Sigma-Aldrich) until the mixture appeared completely homogeneous. The amounts used of each metal precursor were directly proportional to the preferred amount of ion-exchange and the final desired ratio of Fe:Zn. This dry mixture was then transferred to a 1/2" packed bed reactor. The reactor was first half-filled with glass beads and then a bed of quartz wool was put in for the powder to rest on. The loaded reactor was then transferred to a Thermo Scientific Lindberg Blue M tube furnace and mounted in place. A flow of ultra-dry air (Praxair) was started through the sample and the furnace heated to 600°C. It will be commented here that a temperature of 600°C is likely not necessary. Zinc chloride will melt at 293°C and iron chloride tetrahydrate will melt at 105°C. Temperatures of approximately 300-400°C as listed in some sources would be entirely reasonable [93,167,173,409]. While temperatures of 600°C may cause some damage to occur to the H-MOR, it should still be stable at that point. The mixture was maintained at this temperature and under a flow of dry air for a period of six hours. This amount of time is likely not required and can be shortened.

After the oxidative solid-state ion-exchange, the reactor tube was removed from the furnace and the synthesized catalyst recovered. Catalysts containing Fe²⁺ and/or Zn²⁺ were typically synthesized the same day they were to be used for the reaction. The compositions of the synthesized catalysts are shown in Table 6.1 and a TEM image of the 3Fe(II)-1Zn/H-MOR is shown in Figure 6.1. Part of the concern with solid-state ion-exchange was whether or not larger metal clusters would form at the surface of the crystal. This would mean the procedure used did not result in ion-exchange and would have been more similar to conventional impregnation. From TEM, it does not appear that any large metal clusters have formed during the solid-state ion-exchange and the metals that are visible are highly

dispersed. This is very similar to the 1Cu-4Zn/H-MOR catalyst depicted in Chapter 4.



Figure 6.1. TEM image of as-synthesized 3Fe(II)-1Zn/H-MOR prepared by solid-state ionexchange.

| Catalyst | Al wt.% | Si wt.% | Cu wt.% | Fe wt.% | Zn wt.% | Fe/Zn Ratio | Total ion-exchange |
|-------------------|---------|---------|---------|---------|---------|-------------|--------------------|
| | | | | | | (molar) | (mol%) |
| H-MOR | 5.09 | 35.66 | - | - | - | - | - |
| Cu/H-MOR | 4.72 | 33.26 | 3.21 | - | - | - | 57.8 |
| Zn/H-MOR | 4.82 | 33.66 | - | - | 3.05 | - | 52.2 |
| 1Cu-4Zn/H-MOR | 4.76 | 33.13 | 0.57 | - | 2.47 | - | 53.1 |
| Fe(II)/H-MOR | 4.71 | 32.88 | - | 3.53 | - | - | 72.5 |
| 3Fe(II)-1Zn/H-MOR | 4.67 | 33.05 | - | 2.98 | 1.21 | 2.8 | 83.5 |
| 1Fe(II)-1Zn/H-MOR | 4.68 | 33.01 | - | 1.90 | 2.40 | 0.93 | 81.8 |

Table 6.1. Compositions of ion-exchanged H-MOR catalysts containing one or more of Cu, Fe, and Zn.

6.2.2 Carbonylation of DME with ion-exchanged Fe²⁺ on H-MOR

DME carbonylation was performed and reaction results processed as described in Section 3.3.1. As the catalyst was exposed to the lab atmosphere for a brief moment, the calcination procedure was again carried out to guarantee all water had been removed. Reduction was also still conducted at 325°C as was done previously for the bimetallic Cu-Zn/H-MOR study.

The results are shown in Figure 6.2 for DME conversion, Figure 6.3 for MeOAc production, and Figure 6.4 for the selectivity comparison of H-MOR, Cu/H-MOR, and Zn/H-MOR with the monometallic Fe(II)/H-MOR. Detailed results are listed in Table 6.2. As shown, the solid-state ion-exchanged Fe(II)/H-MOR did much better in DME carbonylation when compared to both monometallic Cu/H-MOR and Zn/H-MOR at the conditions tested. Peak conversion of DME over Fe(II)/H-MOR was ~10% higher than for Cu/H-MOR or Zn/H-MOR. The peak MeOAc productivity was also $\sim 10\%$ higher. It also appears that no additional methanol was produced. Based on GC analysis, no methane was produced over Fe(II)/H-MOR either. The total amount of MeOAc produced over Fe(II)/H-MOR was nearly double Zn/H-MOR, which is due in part to its 37% longer lifetime. Despite the high amount of ion-exchange, it doesn't appear that the activity of Fe(II)/H-MOR was hurt in any way by site blockage (when compared to the activity of H-MOR). This implies that the Fe^{2+} is not blocking any important active carbonylation sites. When compared to the best bimetallic Cu-Zn/H-MOR catalyst, 1Cu-4Zn/H-MOR, the Fe(II)/H-MOR is not better. While the peak productivities of the two catalysts are very nearly the same, the 1Cu-4Zn/H-MOR lifetime was 37% longer. As a consequence of the longer lifetime, the 1Cu-4Zn/H-MOR catalyst produced 25% more MeOAc before deactivation compared to Fe(II)/H-MOR. In terms of selectivity, the Fe(II)/H-MOR maintained a higher selectivity to MeOAc with deactivation than either of Cu/H-MOR or Zn/H-MOR. There were no unidentified hydrocarbons detected. If one had to select a monometallic ion-exchanged H-MOR, Fe²⁺ would be preferable to either of Cu²⁺ or Zn²⁺ if solid-state ion-exchange was possible (and perhaps even if it was not). The synthesis of a monometallic ion-exchanged zeolite catalyst is much simpler as no optimization has to be performed of the ratio between two or more ion-exchanged metals.

| Catalyst | Total MeOAc | Total MeOH | Catalyst | Peak Activity |
|-------------------|--|-----------------------------|----------|------------------------------------|
| | (kg _{MeOAc} kg _{cat} ⁻¹) | $(kg_{MeOH} kg_{cat}^{-1})$ | lifetime | $(g_{MeOAc} kg_{cat}^{-1} h^{-1})$ |
| | | | (h) | |
| H-MOR | 3.57 | 0.28 | 30 | 213.3 |
| Cu/H-MOR | 2.51 | 0.26 | 23 | 205.9 |
| Zn/H-MOR | 6.00 | 0.46 | 46 | 217.2 |
| 1Cu-4Zn/H-MOR | 14.24 | 0.47 | 86 | 240.1 |
| Fe(II)/H-MOR | 11.40 | 0.39 | 63 | 237.4 |
| 3Fe(II)-1Zn/H-MOR | 13.89 | 0.52 | 97 | 244.8 |
| 1Fe(II)-1Zn/H-MOR | 7.46 | 0.42 | 66 | 189.1 |
| | | | | |

Table 6.2. Total MeOAc and MeOH produced, time before catalyst deactivation, and peak productivity of MeOAc for H-MOR catalysts containing one or more of Cu⁺, Zn²⁺, or Fe²⁺.



Figure 6.2. Comparison of the conversion of DME over H-MOR, liquid ion-exchanged Cu/H-MOR, Zn/H-MOR, 1Cu-4Zn/H-MOR,

Figure 6.3. Comparison of the productivity of MeOAc over H-MOR, liquid ion-exchanged Cu/H-MOR, Zn/H-MOR, 1Cu-4Zn/H-MOR, and solid-state ion-exchanged Fe(II)/H-MOR. and solid-state ion-exchanged Fe(II)/H-MOR.



Figure 6.4. Selectivity to MeOAc, MeOH, and others in DME carbonylation performed over H-MOR, liquid ion-exchanged Cu/H-MOR, Zn/H-MOR, 1Cu-4Zn/H-MOR, and solid-state ion-exchanged Fe(II)/H-MOR.

The graphical results for the comparison of Fe(II)/H-MOR with two bimetallic Fe(II)-Zn/H-MOR catalysts are shown in Figure 6.5 for DME conversion, Figure 6.6 for MeOAc productivity, and Figure 6.7 for comparison of the selectivities. Adding some Zn did show an improvement over monometallic Fe(II)/H-MOR. The 3Fe(II)-1Zn/H-MOR catalyst (composition given in Table 6.1) lasted 50% longer compared to Fe(II)/H-MOR and made 18% more MeOAc (using the data shown in Table 6.2). The peak productivity of MeOAc was also a bit higher, but likely cannot be considered to be outside the error of the experiments. The 3Fe(II)-1Zn/H-MOR also seemed to make more total MeOH, though the level of MeOH produced is still very low given the length of time of the reaction. The level of MeOH produced was not substantially different from 1Cu-4Zn/H-MOR. The 3Fe(II)-1Zn/H-MOR had the same very high selectivity to MeOAc for the entirety of the reaction as Fe(II)/H-MOR did. The performance of the 1Fe(II)-1Zn/H-MOR was an entirely different story. By this lower ratio of Fe/Zn, it appears that many of the active sites of the catalyst have actually been blocked with one of the ion-exchanged metals as the peak DME conversion was 20% lower compared to the other Fe^{2+} ion-exchanged catalysts. The MeOAc peak productivity was suitably 20% lower as well. 1Fe(II)-1Zn/H-MOR lasted about as long in reaction as Fe(II)/H-MOR. Selectivity towards MeOAc when using 1Fe(II)-1Zn/H-MOR was very high during the entirety of reaction. Based on these results, for the bimetallic $Fe^{2+}-Zn^{2+}$ ion-exchange over MOR, it appears having only a slight amount of Zn is beneficial. No other Fe:Zn ratios were tested at these conditions. It is the belief of the author that 3Fe(II)-1Zn/H-MOR may not be the best combination and molar ratios of Fe:Zn of 4-5 should be tested. However, as it stands now, 3Fe(II)-1Zn/H-MOR and 1Cu-4Zn/H-MOR behave incredibly similarly during DME carbonylation at the conditions tested.





Figure 6.6. Comparison of the productivity of MeOAc over solid-state ion-exchanged H-MOR catalysts containing Fe^{2+} and/or Zn^{2+} .



Figure 6.7. Selectivity to MeOAc, MeOH, and others in DME carbonylation performed over solid-state ion-exchanged H-MOR catalysts containing Fe²⁺ and/or Zn²⁺.

The results from the DME carbonylation tests with the solid-state ion-exchanged Fe^{2+} and Zn^{2+} on H-MOR catalysts have proven the initial theory of site blockage at these reaction conditions. Even at a very high loading of metal, the reaction still proceeded at rates very similar to the bimetallic Cu-Zn/H-MOR catalysts with lower metal loadings. Iron is not typically known as a carbonylation catalyst and it is not expected that it would serve to activate CO any better in any of its oxidation states as compared to Cu⁺. The purpose of Fe^{2+} is then very similar to that of Zn^{2+} . It is there to block acid sites that would normally contribute to coking reactions and to somewhat impact the acidity of the T3-O9 active sites in the 8-MR. It is to be remembered for these cases of ion-exchange that no Al has been removed from the framework – the ion-exchanged metals have just replaced the H⁺ or other cations at the locations of negative framework charge. Instead of an acid site, the ion-exchanged metal is occupying the location. It is also confirmed that it is not a specific amount of Zn^{2+} that is important for the stabilization of MOR, as with Fe^{2+} very little Zn^{2+} was needed before it actually became detrimental to the performance of the catalyst.

6.2.3 Why is Fe(II) so good, even by itself?

Unfortunately there was not enough time to do a proper study on the solid-state ionexchanged Fe²⁺ on MOR catalysts. The possibility exists that it could even be better with a lower temperature used for the ion-exchange and calcination processes, this being somewhat similar to the study by Zhang et al. [232] that found that the calcination temperature of Cu/H-MOR made considerable difference in its catalytic performance. There is much work left to be done and optimization performed with these catalysts.

As a tiny hint, TPR was done as detailed in Section 3.3.2 of Fe(II)/H-MOR and 3Fe(II)-1Zn/H-MOR. The results are shown in Figure 6.8. Pre-reduction of the Fe(II)/H-MOR catalyst at 325°C likely does reduce some of the Fe²⁺, though it is not conclusively known at what oxidation state the Fe was in at this point. The primary reduction peak doesn't happen until much later, at >600°C. There are smaller peaks at lower temperatures, indicating that perhaps there are Fe clusters or that Fe is just at different ion-exchange locations in the zeolite. The introduction of Zn greatly changes the TPR profile. For 3Fe(II)-1Zn/H-MOR, the first reduction peak does not occur until >400°C, so for this particular catalyst the pre-reduction at 325°C probably did not affect the catalyst performance much compared to if no pre-reduction had been conducted. It again looks like there is another reduction peak at >550°C, but the TPR was not run past 600°C for this catalyst. This first reduction peak for 3Fe(II)-1Zn/H-MOR, 415°C vs. 385°C.



Figure 6.8. Initial TPR experiments for Fe(II)/H-MOR and 3Fe(II)-1Zn/H-MOR.

It is certainly beginning to look like the secret to stabilizing the ion-exchanged H-MOR for DME carbonylation at the conditions tested is, to a greater or less degree, just getting the ion-exchanged metals to stay at their respective ion-exchange locations. Cu by itself sinters and appears to be highly mobile. It takes a large amount of Zn before Cu will stay where it is ion-exchanged in its monovalent state. In the case of Fe(II)-Zn/H-MOR, only a very small amount of Zn is needed to stabilize the Fe²⁺ and increase the temperature required for reduction. Further study would be needed to see if Fe sinters on monometallic Fe(II)/H-MOR. Increasing levels of Zn past 3Fe(II)-1Zn/H-MOR likely just excessively blocks active sites, resulting in the substantially reduced performance of the catalyst. This can be fixed by simply changing the loadings of the metal, which is very simple to do using solid-state ion-exchange procedures. Again, there was not enough time to test these theories and the bimetallic Fe(II)-Zn/H-MOR catalysts require further investigation.

6.3 Combine stability improvements – ion-exchange on dealuminated MOR

In the present work, ion-exchange on MOR using monometallic Fe^{2+} or Zn^{2+} ionexchange or the bimetallic combinations $Cu^+ - Zn^{2+}$ and $Fe^{2+} - Zn^{2+}$ provided much more of a stability enhancement than dealumination. Arguably, this could be because the active sites for DME carbonylation on MOR were not protected against dealumination as in other studies [229,235]. However, in the studies that have been published in literature, selective dealumination of the AI located in the 12-MR only provided marginal improvements in the stability of the H-MOR catalyst. Given the complicated and extensive procedures by which selective dealumination must be carried out, the stability enhancement offered does not appear to be worth the trouble. The unselective dealumination by acid leaching carried out in this work did still show some enhancement to the stability of the MOR though it came at the cost of activity. In attempting to balance stability enhancement and activity loss, only a small amount of dealumination of H-MOR 6.5 to H-MOR 8.6 was necessary. The catalyst H-MOR 8.6 also offered some improvement to selectivity, though a small amount of unidentified hydrocarbons were still produced on deactivation. It must be acknowledged here that the biggest problem with MOR is not the activity as MOR is very cheap compared to other catalysts (especially those based on precious metals). If stability could be achieved at the cost of activity, this may be a reasonable price to pay. The thought then occurred: could ion-exchanging a divalent metal onto a dealuminated H-MOR provide even higher stability? Or, at the very least, could the stability be enhanced to the point where it would be worth the trouble of purchasing the H-MOR with Si/Al ratio of 6.5, controlling the

dealumination so that a Si/Al ratio of 8-9 was achieved (which is not necessarily easy), and finally doing a controlled ion-exchange of a divalent metal? If the catalyst could be made inherently stable, it would certainly be worth the intricate synthesis procedure.

To this end, a monometallic Fe(II)/H-MOR was prepared with a Si/Al ratio of 8.6. The Na-MOR with Si/Al ratio of 8.6 was produced by the procedures described in Section 5.2.1 and had a composition shown in Table 5.1. The Na-MOR 8.6 was then converted to NH₄-MOR 8.6 via ion-exchange using NH₄NO₃ as described in that same section. Ion-exchange of Fe²⁺ was then conducted via liquid-based ion-exchange using a 0.2 M solution of FeCl₂. 50 mL of solution was used for every gram of NH₄-MOR 8.6. The slurry mixture was heated to ~70°C, covered and stirred for a period 3 hours. After this time, the slurry was vacuum filtrated and the powder recovered. The recovered powder was dried overnight in a 60°C oven. The liquid ion-exchange was repeated 3 additional times to get the maximum loading of Fe²⁺ possible. The final loading of metal achieved was 2.66 wt.%, which worked out to 65% of the possible theoretical ion-exchange level.

The produced $Fe(II)/NH_4$ -MOR was calcined and reduced and then run in DME carbonylation as described in Section 3.3.1. Results are shown in Figure 6.9 for DME conversion, Figure 6.10 for productivity of MeOAc, and Figure 6.11 for the selectivity during reaction. H-MOR 8.6 as part of the hierarchical study detailed in Chapter 5 managed to make a total of 5.3 kg_{MeOAc} kg_{cat}⁻¹ and 0.44 kg_{MeOH} kg_{cat}⁻¹ before deactivation. The Fe(II)/H-MOR 8.6 managed a total of 9.8 $kg_{MeOAc} kg_{cat}^{-1}$ and 0.46 $kg_{MeOH} kg_{cat}^{-1}$. The H-MOR 8.6 lasted 32 h before near complete deactivation while the Fe(II)/H-MOR 8.6 had not yet completely deactivated by 96 h when the test was terminated (deactivation being defined as when conversion of DME decreased to <15%. At 96 hours the conversion of DME was still ~26% over Fe(II)/H-MOR 8.6). The test with Fe(II)/H-MOR 8.6 could likely have continued for at least another 24 h. Ion-exchange on a partially dealuminated H-MOR thus potentially makes the best combination for stability improvement, though it did come at the cost of activity. The peak productivity to MeOAc was only ~140 g_{MeOAc} kg_{cat}⁻¹ h⁻¹, while for H-MOR 8.6 it was ~258 g_{MeOAc} kg_{cat}⁻¹ h⁻¹. This serves to explain why, despite lasting so long, the Fe(II)/H-MOR 8.6 did not make more than double the total MeOAc. Unlike 1Cu-4Zn/H-MOR, Fe(II)/H-MOR, or 3Fe(II)-1Zn/H-MOR, a relatively stable level of MeOAc production was never achieved over Fe(II)/H-MOR 8.6 as shown in Figure 6.10. Rather, the deactivation was just extremely hindered and the induction period before peak productivity was achieved was very long (~30 h). The selectivity was quite high towards MeOAc during most of the reaction, the only exception being during the induction period where substantial levels of

MeOH were produced. Even at 96 hours, the selectivity towards MeOAc was ~95% - much higher than for any other catalyst that managed to last that long.



Figure 6.9. Conversion of DME over a liquidbased ion-exchanged Fe(II)/H-MOR with Si/Al ratio of 8.6. Figure 6.10. Productivity towards MeOAc over a liquid-based ion-exchanged Fe(II)/H-MOR with Si/Al ratio of 8.6.



Figure 6.11. Selectivity towards MeOAc, MeOH, and other unidentified hydrocarbon species over a liquid-based ion-exchanged Fe(II)/H-MOR with Si/Al ratio of 8.6.

It was also desired to see the effect of a little Zn²⁺ with the Fe²⁺ on H-MOR 8.6. Using solid-state ion-exchange, a bimetallic 3Fe(II)-1Zn/H-MOR with Si/Al ratio of 8.6 was created as described in Section 6.2.1. The final loadings of Fe(II) and Zn were 2.0 and 0.8 wt.% respectively, with a total ion-exchange level of 61%. The results for DME conversion, MeOAc productivity, and selectivity are shown in Figures 6.12, 6.13, and 6.14 respectively. As shown, the peak conversion and productivity towards MeOAc are decreased substantially from the previously discussed Fe(II)/H-MOR 8.6 despite both being run at the same reaction conditions. A peak DME conversion of only 37% was achieved and the peak MeOAc productivity was 79 $g_{MeOAc} kg_{cat}^{-1} h^{-1}$. The 3Fe(II)-1Zn/H-MOR 8.6 also only lasted 57 hours before deactivation, which pales in comparison to the incomplete deactivation of Fe(II)/H-MOR 8.6 at 96 hours. As such, the total amount of MeOAc produced before deactivation was 3.52 kg_{MeOAc} kg_{cat}⁻¹. The peak selectivity to MeOAc did not exceed 90%, though the selectivity was quite constant during the entirety of reaction. The problem with this catalyst is likely excessive active site blockage, or perhaps even pore blockage caused by the solid-state ion-exchange. In this situation it may even be the case that the bimetallic Fe²⁺-Zn²⁺ combination offers no benefit at all. On the bimetallic Fe(II)-Zn/H-MOR catalysts with Si/Al = 6.5, only a small amount of Zn²⁺ was needed to provide any benefit. The amount of Zn²⁺ required in the bimetallic combinations may decrease with increasing Si/Al ratio.





Figure 6.13. Productivity towards MeOAc over a solid-state ion-exchanged 3Fe(II)-1Zn/H-MOR with Si/Al ratio of 8.6.



Figure 6.14. Selectivity towards MeOAc, MeOH, and other unidentified hydrocarbon species over a solid-state ion-exchanged 3Fe(II)-1Zn/H-MOR with Si/Al ratio of 8.6.
A couple of good points have been raised by the work of ion-exchange on partially dealuminated H-MOR, at least with regards to the ion-exchange of Fe^{2+} . Different Si/Al ratios are likely going to require different ion-exchange levels to optimize the performance. In this work, even with the bimetallic Cu-Zn/H-MOR, the level of ion-exchange was not necessarily optimized. Ratios of Cu/Zn beyond 0.25 were also not tested. Especially with the use of Fe^{2+} in ion-exchange, it may be that too much is a bad thing. Also, while 3Fe(II)-1Zn/H-MOR was the best ratio for H-MOR with Si/Al ratio of 6.5, that same ratio performed very poorly for a partially dealuminated H-MOR with Si/Al ratio of 8.6. The likely reason for this is that active sites were blocked by the Zn^{2+} or even potentially the Fe^{2+} . This would require further investigation. All of this brings forth a much dreaded idea. With different Si/Al ratios, the levels of ion-exchange will have to be optimized for each one. If a bimetallic combination of metals is to be used, the ratio of the two metals will have to be optimized for every desired Si/Al ratio. This is why the monometallic ion-exchange of Fe²⁺ onto H-MOR is such an attractive option. Regardless of the Si/Al ratio, the stability enhancement it offered while maintaining higher activity levels was quite impressive. It also brings forth another realization: liquid-based ion-exchange may be a better option than solid-state ion-exchange. Solid-state ion-exchange is easier and, from some perspectives (not energy), more efficient (no wasted metal). The advantage that liquid-based ionexchange offers with divalent metals is that the level of ion-exchange is limited based on the positions available. With solid-state ion-exchange, one can exceed that level (whether or not actual ion-exchange takes place or some sort of impregnation begins to occur at higher metal loadings is not known at this time) and potentially harm activity while offering no extra benefit to stability.

6.4 Random tests and future work

There have already been a few points where it has been mentioned that there is still considerable work left to do. The remainder of this chapter will serve to summarize those ideas as well as present those last remaining "random" tests that have only just barely scratched the surface of some work that needs to be done before this catalyst is successfully industrialized. This is not to say that a few viable options for industrial catalysts have not been offered here. The monometallic Fe(II)/H-MOR and bimetallics 1Cu-4Zn/H-MOR and 3Fe(II)-1Zn/H-MOR with Si/Al ratios of 6.5 would all be excellent catalysts for industrialization. Unfortunately, the harsh realization must occur that zeolites are highly susceptible to coking and deactivation in most of the reactions they are used for. This is not

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the say that it can't be done; it is just unlikely. For example, though the data were not presented to show it, Liu et al. did claim that blocking some of the acid sites and channels of H-MOR with Py allowed it to be used in reaction for greater than 250 hours with minimal deactivation [236]. Site blockage was also shown to be important in Chapter 4 (and in the current chapter). In the dealumination work presented in Chapter 5, it seemed that the number of Al in the T3 and T4 locations also had some influence on the stability. Having too much Al in these locations may be a bad thing, which is unfortunate given that the T3 is the active carbonylation site and the most likely location for Al to be in the framework in MOR.

Given these facts, some comments and hints will be given here that will help to improve the H-MOR catalyst. The possibility does exist of developing a catalyst which can last very long periods between regeneration treatments.

6.4.1 The obvious: optimize reaction conditions

Beginning with the obvious, the reaction conditions were not varied, much less optimized, for any of the catalysts used in this study. A higher pressure test was done with the 3Fe(II)-1Zn/H-MOR 8.6 that was described in Section 6.3 with all results shown in Figure 6.15. Other conditions were changed as well. The catalyst amount was decreased by half to 0.15 g. Calcination and reduction were maintained the same as described in Section 3.3.1. The flow rate was kept at 15 mL/min STP with the same gas mixture as used in all previous work. The new inert-exclusive WHSV for this particular reaction was 4.1 h^{-1} . This reaction was started at 210°C and a pressure of 30 bar. The higher pressure was chosen as considerable evidence presented by other groups has shown that the reaction is likely first order to CO [90]. However, the initial reaction rate was very low with only \sim 30% conversion achieved. Pressure was then increased to 40 bar, which only made DME conversion and MeOAc production worse. It was then determined that the problem was adsorption. The higher pressure was ensuring that the formed products could not desorb. At this point, temperature was first increased to 250°C. This led to a very large increase in DME conversion but MeOAc production was still visibly low. Temperature was eventually increased to 260°C at which point there was enough evidence from the raw mass spectrometer profile that the reaction was occurring (sometimes it was difficult to see from the raw mass spectrometer profile that the reaction was occurring, especially when dealing with the catalyst induction period). The final reaction conditions were a temperature of 260°C and 40 bar pressure with 15 mL/min STP flow rate and 0.15 g of catalyst. Selectivity to MeOAc was very high at ~95% for the majority of the time of reaction with a total of 13.3 kg_{MeOAc} kg_{cat}⁻¹ and 0.59 kg_{MeOH} kg_{cat}⁻¹ produced.



Figure 6.15. Reaction results for DME conversion, MeOAc productivity, and selectivity with variations in temperature and pressure for 3Fe(II)-1Zn/H-MOR 8.6.

There are several implications from this reaction. With increasing pressure of reaction, it appears that temperature must be increased simultaneously for the reaction to occur due to chemisorption/physisorption. This probably justifies the reaction conditions of 70 bar total pressure and 300°C that BP Chemicals Ltd. has used for many of their catalytic tests [223,225,230]. If it is desired that the H_2 present in the reaction stream be actively cleaning the catalyst, a temperature of at least 300°C would likely be required. It should also be noted that half the catalyst amount compared to most of the catalytic tests

presented previously in this thesis was used and yet nearly 100% conversion of DME was achieved. The inert-exclusive WHSV of 2.1 h^{-1} is likely too low, and catalyst amount should be decreased and flow rate increased. Using 0.3 g of catalyst may actually have been detrimental, as over-reaction of products would lead to coking.

Despite this, to properly optimize the reaction conditions, one would have to start at the beginning: the CO:DME ratio. The selection of the CO:DME ratio used in this study was mostly arbitrary. There was an equipment limitation which prevented using >2.5 mol% DME in the feed (otherwise MeOAc condensation could occur in the lines of the Autochem). The reaction being first order, it was then desired to have as much CO as would be permitted. An initial reaction mixture of 93% CO/2% DME/5% He was used in order to imitate a potential commercial gas feed. However, with this feed, a reaction pressure of 10 bar was used that produced behaviour very similar results to the 20 bar pressure used for the 50.0% CO/2.4% DME/2.9% $H_2/44.7\%$ He. This confirms the first order assumption for CO: cut the CO partial pressure in half, have to double the total pressure to achieve the same rates. At the conditions tested, it is in the opinion of this author that the little bit of H_2 present in the feed did not actually participate in any reactions as nothing was observed to indicate otherwise. In the end, the CO:DME ratio will be dictated by what is possible at the industrial level. From modeling, it was suggested that the CO:DME ratio must be >1. A reaction test should be carried out where the DME amount can be varied once the catalyst has achieved a stable level of production. There should be a DME amount at which point it becomes obvious it is in excess of what the catalyst is capable of converting to MeOAc. At that point a proper relationship can be developed between the amount of catalyst to be used and DME fraction in the feed.

Some very initial tests (the results of which will not be shown) were done with lower temperatures (starting at 160°C). At a temperature of 160°C, it did not appear that the reaction was proceeding forward from the raw mass spectrometer profile and temperature had to be increased. At the reaction pressure used, there was a noticeable jump in activity between 200°C and 210°C. This may suggest that there is some diffusion limitation occurring at the lower temperatures for the reactants/products. As a reminder, the tests for external and internal mass transfer limitations were conducted at the reaction conditions and none were found. It could also be that the pressure of reaction was too high for the lower temperature to overcome the strength of adsorption as was observed with the previous test using 3Fe(II)-1Zn/H-MOR 8.6. A proper test should be carried out where a lower temperature is used and pressure should be slowly ramped to see when the reaction

starts to occur. Again, this is difficult when a catalyst has an induction period, and should be done only after the induction period is known to be over. A lower temperature may also help to reduce the rate of coke formation and prolong the lifetime of the catalyst. A proper factorial design of the reaction conditions may not have to be done, given that temperature and pressure must be increased together and, given the lower cost of energy by using a lower reaction temperature and the possible lower coke formation rate, the lowest temperature possible is desired.

The inert He gas present in the reaction mixtures used in this study was only intended for use as the standard for the calibration of the mass spectrometer and subsequent processing of the results. At an industrial level, it is not necessary to use the inert gas. If an inert gas is to be used, it should be N_2 just for the lower costs. Argon may also be a suitable option, given that it will have less interaction with the zeolite itself compared to the N_2 .

6.4.2 The inevitable regeneration of the catalyst

Now, while the possibility may be considered slim, it is in the opinion of the author that there may be a set of reaction conditions and a particular catalyst that will result in high process stability and the achievement of steady-state. However, even in this case, it is unlikely that the catalyst will never require regeneration. Procedures must be put in place for the inevitable regeneration of the DME carbonylation catalyst.

BP Chemicals Ltd. patented a process for the regeneration of a carbonylation catalyst using H₂ [224] that was used here to show that the catalyst could be regenerated in the same way. The liquid ion-exchanged catalyst 1.3Cu-1Zn/H-MOR (Si/Al = 6.5) with a Cu and Zn loading of 1.8 wt.% and 1.4 wt.% respectively (~55% of theoretical ion-exchange) was run in DME carbonylation using 0.15 g of the catalyst (WHSV of 4.1 h⁻¹), 20 bar total pressure, and a temperature of 220°C. After DME conversion had decreased to <20% and selectivity towards MeOAc had begun to decrease, the flow of reaction gas was stopped and pure H₂ was flowed to the catalyst. The pressure of H₂ was kept at 20 bar. The temperature was slowly increased at 1.6°C/min to 400°C where the catalyst was left for a period of 10 hours. After this period of regeneration, the reactor was depressurized and H₂ flow stopped. The catalyst was kept under a 10% H₂/Ar flow and increased to 550°C (when this test was done, it was believed that full reduction of Cu²⁺ was best). It was left at these conditions for 1 hour after which flow was switched to Ar and the reactor cooled to 220°C. The reaction was then again started with the same conditions as above. The results for DME conversion, MeOAc production, and selectivity are shown in Figures 6.16, 6.17, and 6.18 respectively. The results actually look very similar to the regeneration results presented in the patents by BP Chemicals Ltd. [223,224] in that the original conversion level and MeOAc productivity are not completely restored. The results do show that H₂ by itself could be used to remove a large portion of the formed coke. It may be likely that all of the formed coke is removed and the unrestored original activity is due to another issue. The selectivity towards MeOAc after regeneration was quite high (>95%) and was maintained at a very high level while the catalyst further deactivated.



Figure 6.16. Conversion of DME over liquid ion-exchanged 1.3Cu-1Zn/H-MOR with regeneration by H₂ at high pressure and temperature.

Figure 6.17. Productivity towards over liquid ion-exchanged 1.3Cu-1Zn/H-MOR with regeneration by H₂ at high pressure and temperature.



Figure 6.18. Selectivity towards MeOAc, MeOH, and other unidentified hydrocarbons over liquid ion-exchanged 1.3Cu-1Zn/H-MOR with regeneration by H₂ at high pressure and temperature.

The problem with this particular regeneration procedure is that, under pure H_2 at that pressure and temperature, the Cu⁺ is most likely completely reduced to Cu and may then potentially sinter. This would explain the activity decrease of the regenerated catalyst. It's been stated repeatedly in this thesis that the secret to the bimetallic Cu-Zn/H-MOR catalysts is that the Cu needs to stay at its ion-exchange locations in its monovalent state. It cannot be allowed to completely reduce and it cannot be allowed to sinter. With this regeneration procedure, the Cu will sinter and the true activity will not be restored unless the Cu is returned to the ion-exchange sites.

Very little work has been done to show the regeneration of the catalysts, but some important points can be made about it. To maintain the best performance of the Cu-Zn/H-MOR catalysts, an oxidizing gas should be used to remove the formed heavier carbonaceous species in the MOR framework and regenerate the catalyst. An oxidizing gas would prevent reduction of Cu⁺ and prevent excessive sintering during the regeneration procedure. However, it is acknowledged here that there is some benefit to using H₂. What it means is that a syngas mixture of CO and H₂ could be used to regenerate the catalyst. Syngas may be present in an industrial DME carbonylation process as it may be used to synthesize the DME. There is no requirement to bring in additional gases, just extra piping. It may be possible that the regeneration procedure could be optimized in terms of when it is performed and at what conditions so as to avoid the complete reduction of any Cu species, but this would need to be studied in greater detail and cannot be commented on at this time. Otherwise, for the present catalysts it would be preferable to use an oxidizing gas such as O₂. The conditions of regeneration using O₂ would also need to be studied in greater detail.

6.4.3 Optimization of MOR Si/Al ratio

While the dealumination study detailed in Chapter 5 was valuable for showing many things, it cannot be considered to be an optimization of the Si/Al ratio of MOR for the reaction. The original Na-MOR 6.5 was purchased as its Si/Al ratio was similar to that used for many other studies by different groups, and also that it was only one of two ratios available from *Zeolyst*. The dealumination study showed that a decrease in acid site density could be quite beneficial to the performance of the catalyst and the slowing of the deactivation. The problem with doing a dealumination treatment to decrease the acid site density is that it removes the active sites preferentially, and by the time only half the Al is removed the catalyst is already deactivated. Instead, some version of synthesized MOR (whether it be H-MOR, Na-MOR, or NH₄-MOR) should be purchased with a higher Si/Al ratio

(>15) and tested in reaction to see if it is any more stable comparatively. Unfortunately, if the MOR cannot be purchased at a higher Si/Al ratio, it will have to be synthesized. This is unfortunate purely from the perspective that it will take quite a while to properly optimize the Si/Al ratio. The synthesis of MOR by this time is well understood, and one would just need to have access to proper autoclaves, a furnace, and the raw materials. A MOR with added mesoporosity could even be synthesized directly without having to go through the desilication or dealumination treatments [91,288,410–412].

6.4.4 Optimization of Cu-Zn or Fe-Zn bimetallic ratio

If a MOR with a different Si/Al ratio is used, this means that the ratio of Cu-Zn or Fe-Zn will have to be re-optimized. Figuring out the proper bimetallic ratio is not too difficult, though. The procedures for testing this have already been described in this thesis; they would just have to be conducted again. A simple liquid-based ion-exchange using a metal nitrate (or even the metal chloride) could be done with the divalent metal to determine what a feasible ion-exchange level is. Solid-state ion-exchange could be used to exceed this level but trying for high levels of ion-exchange with this method may result in impregnation of the metals on the surface of the zeolite crystal. As the metals themselves were determined to be there just for selective acid site poisoning of the MOR, trying for higher levels of ion-exchange may actually be detrimental to catalyst performance (see 3Fe(II)-1Zn/H-MOR 8.6 presented in Section 6.3). As higher Si/Al ratios are tested, it may be better to just do a simple Fe^{2+} liquid-based ion-exchange. If bimetallic ion-exchange of either $Cu^{2+}-Zn^{2+}$ or Fe²⁺-Zn²⁺ is to be used, the level of Zn required should decrease with increasing Si/Al ratio (increase the ratio of Cu:Zn or Fe:Zn). This is why monometallic Fe²⁺ ion-exchange may be so desirable at higher Si/Al ratios. The Fe(II)/H-MOR was so stable to begin with that at higher Si/Al ratios the addition of Zn^{2+} may be unnecessary.

It may be the case that as the Si/Al ratio gets higher and framework Al's are spaced further apart, divalent transition metal ion-exchange may become too difficult and metal loadings will become too low to make a substantial difference in the stability of H-MOR.

6.4.5 Additional modeling of ion-exchange locations

In Chapter 4, modeling of the preferable locations for Cu²⁺ and Zn²⁺ ion-exchange was conducted. The accuracy of these models was validated with experimental observations and the models were shown to actually be quite pertinent. It was also shown that HF theory was suitable as opposed to DFT theory, which most everyone uses these

days given its better prediction of energy. With the modeling, it took considerable time and effort just to build the MOR framework in the modeling software. Combined with the ongoing experimental work on bimetallic Cu-Zn/H-MOR, the dealumination of MOR, and the unfortunately very limited work on solid-state ion-exchanged Fe(II)-Zn/H-MOR, this did not leave a large amount of time to work on models. Modeling the ion-exchange locations was done because it was the simplest way to utilize the built models with a minimal time requirement. Now that the models are built in Gaussian, considerably more work can be done with them. The modeling of ion-exchange locations is especially simple and reasonably accurate and could even be used to determine whether or not other metals would be suitable for ion-exchange. With the ion-exchange of Fe²⁺, it is suspected that it will ion-exchange in the 8-MR but perhaps not to as great an extent as Zn²⁺. Also, due to time limitations the author did not have enough time to properly determine how to obtain reasonable energy predictions from the models. Some initial DFT models were run to try and obtain preferential ion-exchange locations by minimization of energy, but the results were poor and didn't appear to be comparable among the different ion-exchange locations.

It was also mentioned earlier that the next nearest neighbours to the Al locations will have considerable influence on the acid strength of any given acid site [136,141–143]. This should no doubt have some influence on the ion-exchange behaviour of the zeolite. This was not modeled as part of the present work due to the sheer number of possibilities. It would also require considerable computational power and memory to run the models with a proper basis set and the modeling resources available were already being pushed to their limit. In the future, this would make for an excellent project for another student if the proper computational resources became available.

Many models were also run in trying to understand how the DME would interact with an active site to produce MeOH and an adsorbed methyl group. Additional models were run simulating the interaction of MeOH with another active site to produce H₂O and the second adsorbed –CH₃ group. It was believed at the time that these model results could shed some light on the interesting DME adsorption/desorption results presented as part of the bimetallic Cu-Zn/MOR study in Chapter 4. None of these models converged successfully and, due to time limitations, it was not determined why. This would again be another excellent project for another student. The author was relying mostly on Gaussian to optimize the models successfully and find transition states. This may have simply been asking too much of the software, and more manual work may be required to determine the mechanisms by which DME interacts with the zeolite acid sites.

6.4.6 Solid-state ion-exchange optimization

This was mentioned earlier, but when working with solid-state ion-exchange the author selected conditions that were guaranteed to provide a successful ion-exchange. In reality, 600°C is probably pretty excessive and should not be required for a successful ion-exchange to occur.

Especially with solid-state ion-exchange, it becomes very easy to change the levels of ion-exchange and the ratios of any bimetallic metal combinations. Another advantage to solid-state ion-exchange is that bimetallic ion-exchange of monovalent metals and divalent metals can be done simultaneously very easily. This is not to say that simultaneous ionexchange of monovalent and divalent metals couldn't be conducted in the liquid-phase. It absolutely can, but the monovalent ion-exchange may proceed far more quickly than the divalent and the competitive ion-exchange behaviour would actually be quite interesting. It could either be a good or a bad thing. Monovalent metals are also far more likely to ionexchange at the T3 location and block the active site. This is the basis of BP Chemicals Ltd. patent regarding selective dealumination of the 12-MR of MOR [229]. Monovalent metal ion-exchange at the T3 location may not be a bad thing so long as not all the acid sites are blocked. If only a portion of them are, and this is combined with the ion-exchange of other metals, it may make for a highly stable catalyst. This obviously brings up the idea of trimetallic ion-exchange. Addition of Na⁺ or Ag⁺ to the metal combination of Cu²⁺-Zn²⁺ or Fe²⁺-Zn²⁺ on MOR may (emphasis on "may") produce a highly stable catalyst, albeit at the cost of some activity. This would require considerable testing and variation of ratios to get the best possible combination, and would make a good project for another Ph.D. student.

6.4.7 Isomorphous substitution of other metals into the MOR framework

Quite possibly the only method by which the MOR could be made inherently stable without ion-exchange of metals would be to substitute other metals aside from Al into the framework. Isomorphous substitution of Fe^{3+} into the MOR framework actually did not help the stability much, though it did certainly enhance selectivity [408]. This is again a very complicated topic and much work would have to be done here to find the proper metal and the amount of substitution that would be best. As MOR containing other metals aside from Al in the framework cannot be purchased directly (to the best of the author's knowledge), they would have to be synthesized. What would be very interesting to study would be the ion-exchange of the $Cu^{2+}-Zn^{2+}$ and $Fe^{2+}-Zn^{2+}$ bimetallic combinations onto these isomorphously substituted MOR's, though enhancement of catalyst stability may not be

guaranteed. There is potential for modeling work in this area, and it may be better to start there before proceeding to do this work experimentally.

6.4.8 Other zeolites or zeotypes

Cheung et al. [89] tested a number of zeolites but limited themselves to what was commercially available. Aside from their work, there has been comparatively little done with finding out what other zeolites work. Liu et al. [237] did test an H-ZSM-35 catalyst and showed that it was much more stable for DME carbonylation than H-MOR. ZSM-35 has both a 10-MR and an 8-MR in its framework with dimensions 4.2 x 5.4 Å and 3.5 x 4.8 Å respectively. The successful use of ZSM-35 is in line with the idea that the reaction occurs only in 8-MR channels or pockets. In the present work, it was attempted to synthesize SAPO-40, which has a 12-MR with dimensions 6.7 x 6.9 Å and an 8-MR with dimensions 3.7 \times 3.7 Å. Despite following the directions of a well-referenced paper and using all the same materials [413], none of the several attempts to synthesize this material were successful. The reasons for this are unknown at this time. However, even if SAPO-40 worked, its synthesis involves the use of tetrapropylammonium hydroxide (TPAOH). This is a particularly dangerous (and also expensive) chemical whose use for producing an industrially relevant level of SAPO-40 would be discouraged. Unless SAPO-40 was completely stable in the reaction and required no regeneration, its complicated and harsh synthesis would strongly discourage its use. Commercially available SAPO-34 and SAPO-41 were tested for DME carbonylation with no success.

No other zeolites or zeotypes will be recommended here. It is simply acknowledged that MOR is not the only solution and there is still work to be done here. The best place to start would be with any zeolite or zeotypes containing an 8-MR.

6.5 Summary of the future work

To conclude this section, there is a great amount of work left to be done with these catalysts before industrial implementation can become a reality. Firstly, the Si/Al ratio of the MOR used was never optimized. At the beginning of this project, 1 kg of Na-MOR with Si/Al ratio of 6.5 was purchased and it was the only MOR used for the entirety of the study. No other Si/Al ratios were tested and it is highly probable that the Si/Al ratio of 6.5 is not the optimum. Higher ratios may be more stable, though there is no guarantee of this. It is also apparent that the ratio of Cu:Zn would again have to be optimized for the different ratios with the idea being that higher Si/Al ratios would require less Zn. In short, the Si/Al

ratio should be optimized first, and then metal ion-exchange should again be optimized, including both level of ion-exchange and the ratio of the two metals in any bimetallic combinations. While all the work shown in Chapter 4 does not need to be repeated, a series of reaction trials will have to be carried out to find the best option. The bimetallic Cu-Zn/H-MOR work shown in Chapter 4 clearly illustrates how important the ratio of the two ionexchanged metals is. Even from the few tests that were conducted, it was also obvious that the reaction conditions need optimization. It may indeed be possible to run the reaction at a lower temperature than 210°C, but the pressure will also need to be optimized for this. Increases/decreases in temperature will have to be associated with corresponding increases/decreases in pressure.

There are several reasons why this work was not done as part of this thesis. The biggest reason is that the starting H-MOR was just not stable enough. It didn't last long enough in reaction to allow for proper optimization of conditions. It must also be considered that the catalyst has an induction period. For H-MOR, when the observed induction period was complete the catalyst was already likely subject to the effects of deactivation. There is quite possibly a set of reaction conditions that will help to improve stability. Now that three catalysts have been identified (1Cu-4Zn/H-MOR, Fe(II)/H-MOR, and 3Fe(II)-1Zn/H-MOR) that have enhanced stability, the proper optimization of reaction conditions could be conducted. In addition to alterations to the temperature and pressure of reaction, the catalyst bed length should be decreased so as to prevent the continued reaction of formed products. Overreaction of the products formed may be contributing to coking, and both reactants and products should have a lower residence time.

There are other options for the catalysts, but these may be getting needlessly complicated. The entire idea behind this project was to develop a more stable catalyst that could be synthesized easily and applied at an industrial level. It may be true that other zeolites and zeotypes could be more stable than MOR, but these would require synthesis and testing in a laboratory. If one was identified, it may be possible to contract an external company to make larger batches. There are other changes that could be made to MOR to potentially enhance stability. Other metals could be isomorphously substituted into positions in the framework during synthesis, but this again would require several different MORs to be synthesized and tested. Quite possibly the easiest means by which possible additional stability could be created is by adding another monovalent metal to the bimetallic $Cu^{2+}-Zn^{2+}$ and $Fe^{2+}-Zn^{2+}$ combinations. One way in which this could be done is by solid-state ion-exchange, in which the monovalent metal could be considered to be occupying the

positions that the divalent metals did not. The creation of these trimetallic catalysts could also be done by liquid-based ion-exchange. A first very controlled and partial ion-exchange could be done with the monovalent metal followed by ion-exchange of the divalent metals. This would remove some of the T3 acid sites from reaction, which could be beneficial. The question would be if the monovalent metals would stay at their ion-exchange locations during reaction. This would have to be determined. Coming up with the proper trimetallic combination over the MOR would be quite difficult to do and could potentially be the subject of future research.

There is also much more modeling work that could possibly be done. Now that the models for ion-exchange locations are built, the effects of the next nearest neighbours on the acid site strength could also be investigated at the theoretical level. The mechanism of DME activation over a zeolite could also be studied in more detail.

Chapter 7

Conclusions and Final Thoughts

Now this is not the end. It is not even the beginning of the end. But it is, perhaps, the end of the beginning.

--Sir Winston Churchill

7.1 General conclusions

There is increasing attention being given to renewable and sustainable development in the world today. The impact of our actions on future generations is at the forefront of many people's minds. With that mindset came the principles of green chemistry, and the idea that we should let nothing go to waste. Historically, municipal, industrial, and construction waste often ended up in a landfill and nothing more was done with it. Recently, considerable research has been conducted into utilizing these waste materials as feedstocks for second-generation biofuels. If there is a way to use every last little bit of this waste, it will be through gasification or pyrolysis to form mixtures of CO and H_2 (syngas). Gasification and pyrolysis are not new processes, but only in recent years has more attention been given to them. It is well-known now how to convert these syngas mixtures to valuable products, such as methanol and dimethyl ether. While these two products are valuable by themselves as biofuels, they can also be used as base chemicals for the production of other potentially valuable chemicals. Dimethyl ether, for example, can be converted to methyl acetate via carbonylation. Methyl acetate can be further converted to acetic acid or ethanol. Current methods for producing acetic acid use Rh or Ir-based homogeneous catalysts, which require an iodide co-catalyst. The use of the iodide cocatalyst means harsh halides are present in the process, which necessitates proper materials of construction to deal with. The use of homogeneous catalysts also means that the product must be separated from the catalyst. This involves the use of potentially expensive separation processes.

Dimethyl ether carbonylation first began attracting considerable attention approximately 10 years ago, when Iglesia's group out of Berkeley [89,90], in collaboration with BP Chemicals Ltd., found that the zeolite mordenite (MOR) in its acidic form could be used as a catalyst. Initial tests showed that the catalyst had good selectivity but was unstable. Typically, only 15-20 hours of reaction (at the reaction conditions tested) were possible before the catalyst had to be regenerated. It was later theorized that, of the four possible acid sites in MOR, only the acid site in the 8-membered ring (MR) channel was actually active for DME carbonylation. The others only contributed to coking reactions and subsequent catalyst deactivation [212,215–217]. BP Chemicals Ltd. went on to develop process conditions in which the catalyst could be active for longer periods, though this involved using considerable amounts of H_2 in the feed and more intense reaction conditions [223,230].

The goal of the current study was to find a means by which the MOR catalyst could be stabilized in a simple manner, and without the use of excessive amounts of H_2 in the feed. There are only a handful of ways this could be done. Zeolites have excellent ionexchange capabilities that are easily scalable to an industrial level of catalyst production. Ion-exchange is also one of the easiest ways a zeolite can be modified for catalysis. One of the other methods that may be used to enhance stability is dealumination. Some dealumination procedures can be quite complicated, and only a comparatively straightforward method of dealumination was used here.

7.2 Bimetallic Cu-Zn/H-MOR by liquid-based ion-exchange

Copper-exchanged mordenite had already been used for DME carbonylation by BP Chemicals Ltd. and others, but it was still unstable and didn't considerably prolong the life of the MOR catalyst [92,223,232,233]. This is likely due to excessive sintering of Cu during the reaction. In fact, when comparing the performance of Cu/H-MOR and H-MOR, the H-MOR actually did better. This is because Cu would proceed to migrate and sinter during reaction and block access to the channels of MOR, rendering them useless. The issue then became how to make sure the Cu did not sinter and stayed where it was ion-exchanged. Commercial methanol synthesis catalysts use Zn to promote the Cu and reduce sintering (these catalysts use Al_2O_3 as a support), and it was wondered here if Zn could do the same. At low levels of Zn^{2+} addition, it did not suitably stop Cu^{2+}/Cu^{+} from sintering, though the deactivation of the MOR catalyst was slowed. However, when the Cu:Zn ratio reached 0.25, the catalyst was incredibly stable, with nearly four times the lifetime and six times the methyl acetate produced by monometallic Cu/H-MOR. Only at that high level of Zn^{2+} content did the Cu become stabilized in its monovalent state. The excessive amount of Zn^{2+} also prevented sintering of Cu^+ during the reaction. Quite interestingly, it was determined that Cu^+ , at least with the catalyst pretreatment and reaction conditions, did not actually assist in the reaction. ZnO, being used normally as a base catalyst, also did nothing to increase reaction rate. Instead, at the conditions tested, it was determined that the metals were simply there to block certain acid sites that, without the metals there, would have been used for coking reactions. From the combination of experimental and theoretical evidence, it was also apparent that Cu²⁺ did not prefer to ion-exchange in the 8-MR. It appeared that Zn^{2+} actually preferred to ion-exchange in the 8-MR channels or the 8-MR side pockets of the mordenite, though ion-exchange in the 12-MR was still possible. Together, the two metals would compete for ion-exchange locations. At low Cu²⁺ levels, it would prefer ion-exchange in the 12-MR using framework AI that was shared between the 8-MR and 12-MR channels. As the Cu²⁺ compensated for the negative framework charge in that location, it removed the 8-MR channel as a possible ion-exchange location for Zn²⁺. The Zn^{2+} was then forced to ion-exchange at other locations in the 12-MR instead of in the 8-MR channels. In the 12-MR, the Zn^{2+} was able to do more for slowing the rate of coke formation than Cu^{2+}/Cu^+ was able to.

7.3 Dealumination of mordenite reveals acid site density issue

The original intent of studying the progressively increasing dealumination of MOR was to see if the stability could be enhanced. Only a very simple nitric acid treatment was used, as this had the greatest chance for industrial implementation if dealumination proved worthwhile. Minor dealumination of the received MOR (Si/Al = 6.5) did result in some stability enhancement while maintaining reasonably high activity levels. Further dealumination resulted in substantial activity losses and, with a little over half of the Al removed from the framework, the catalyst was deactivated. At these points, not much stability enhancement was offered to compensate for the activity loss. There were several reasons for the complete loss of activity. The main reason was that the dealumination treatment was preferentially removing the most active and selective site for DME carbonylation. Not unrelated to this, the dealumination was also substantially decreasing

the acid strength of the zeolite. This was partly due to high crystallinity losses. However, the initial stages of dealumination had revealed some very important information. A decrease in the acid site density, or rather, a decrease in the number of framework Al's located in the smallest 4-MR segments of the framework, actually created the minor stability increase. The 4-MR is where the most active site for DME carbonylation is located. This revealed the very important discovery that it was not just the acid sites in the 12-MR that were causing deactivation. Even the acid sites in the 8-MR that were deemed selective to formation of methyl acetate contributed somehow to the deactivation of the catalyst. Regardless, as part of this work, it was experimentally validated that the acid sites in the 8-MR were the only ones suitable for carbonylation of dimethyl ether to methyl acetate. It was also shown experimentally that Cu²⁺ preferred ion-exchange in the 12-MR.

7.4 Applying what was learned: Fe(II)/H-MOR

With the realization that Cu^{2+}/Cu^+ and Zn^{2+} were doing little more than to block active sites on MOR, it was wondered if other metals could serve the same purpose. By the solid-state ion-exchange of Fe²⁺ onto MOR, this theory was tested and shown to be true. Among the monometallic Cu/H-MOR, Zn/H-MOR, and Fe(II)/H-MOR, the Fe(II)/H-MOR proved to be the best in terms of stability and activity. Combining the Fe²⁺ with a little bit of Zn²⁺ made it even better, though this bimetallic Fe(II)-Zn/H-MOR catalyst behaved quite similarly to the best bimetallic Cu-Zn/H-MOR.

Some small experiments with ion-exchanged partially dealuminated H-MOR catalysts revealed that combining the two procedures did have potential for even greater stability enhancement, though this was not investigated to a great extent.

7.5 What's left?

There is still considerable work left to be done. With the discovery of some much more stable catalysts based on MOR, the proper optimization of reaction conditions can now take place. Due to adsorption, increases and decreases in temperature will have to be accompanied by corresponding increases and decreases in pressure. The CO:DME ratio also needs optimization, though lower amounts of DME in the feed would be preferable. The Si/Al ratio of the MOR itself needs optimization, and not by dealumination. Several MOR samples should be synthesized with different Si/Al ratios and tested for DME carbonylation. Only after this is done should ion-exchange be attempted again. At this point, the Cu:Zn or Fe:Zn ratios would again need to be optimized. This re-optimization should proceed quite

quickly, as the synthesis procedures and means of testing have all been detailed in this thesis. Catalyst regeneration also needs to be properly studied.

7.6 Final thoughts

Acidic MOR alone is not suitable as an industrial catalyst for DME carbonylation. As a result of the work that was conducted and presented in this thesis, there are three costeffective catalysts that have been identified as potential industrial catalysts for this process: 1Cu-4Zn/H-MOR, Fe(II)/H-MOR, and 3Fe(II)-1Zn/H-MOR. This does not mean that the catalysts are ready for industrial implementation. Rather, as a result of this work, catalysts that have enough stability to survive optimization of reaction conditions have been identified. What is also important are the implications of this work for other zeolitecatalyzed processes. It is generally widely accepted that zeolites are unstable for any given reaction they are used in. Bimetallic ion-exchange can quite successfully be used to add considerable stability. While it is not necessarily the easiest research to conduct (involves considerable trial and error), the benefits can be, quite simply, amazing. It has also been shown that having a transition metal ion-exchanged onto a zeolite does not necessarily mean that it will participate in a reaction. The transition metal may just occupy space and block acid sites. While this blockage may result in a decrease in the activity of the zeolite, the potential increase in stability and decreased costs of regeneration are plenty attractive enough to accept that slight activity decrease.

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