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One-step Oxidation of Propylene to Acrylic Acid

by

Sachindra Sood ©

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree
of Master of Science

Department of Chemical Engineering

Edmonton, Alberta
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(Signed)____________________

Permanent Address:

C/o. Mr. S.L.Sood
GM, Kunustoria Area
P.O. Tapasi
Dist. Burdwan, West Bengal
India.

15th August, 1995

University of Alberta

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *One-step Oxidation of Propylene to Acrylic Acid* submitted by *Sachindra Sood* in partial fulfillment of the requirements for the degree of *Master of Science*.

KT Chuang

Dr. K.T. Chuang (Supervisor)

S.E. Wanke

Dr. S.E. Wanke

Dr. N. Egiebor

Date: 14th August, 1995

This thesis is dedicated to

Brahmachari Sant Chaitanya

Abstract

This thesis is primarily concerned with the development of a catalytic process for the single step oxidation of propylene to acrylic acid. The process employs palladium catalyst impregnated on polymeric **hydrophobic** supports. These catalysts display promising reactivity and selectivity towards the desired product. The hydrophobicity of these catalysts plays an important role in the marked improvement of their activity over similar catalysts supported on conventional supports. In the course of process development, the controlling effect of various parameters like metal loading, catalyst composition, feed composition, pressure and temperature are also studied, with a view to optimize operating conditions for the process. However, these catalysts failed to stand up to the test of long term stability, deactivating under the conditions of use. This loss in activity is believed to have been caused by a product contaminant, possibly a polymer of acrylic acid.

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Above all, I would like to express my sincerest gratitude to my parents for their unconditional love and support throughout my life regardless of what endeavor I was involved in.

Contents

List of Tables

List of Figures

Chapter 1

Introduction

Acrylic acid (propenoic acid; CH_2=CH-COOH) belongs to the organic group of α, β–unsaturated carboxylic acids. It can be viewed as a derivative of ethylene in which one of the hydrogen atoms have been replaced by a carboxyl group. The carbon-carbon double bond and the carbon-oxygen double bond are separated by just one carbon-carbon single bond; that is the double bonds are in *conjugation*, and hence the designation α,β-compound. Because of this conjugation, acrylic acid and its derivatives display the properties of both the carboxyl group and the unsaturated group and undergo reactions of both functional groups under specific conditions.

Acrylic acid was first prepared in 1847 by air oxidation of acrolein. But it was not until the period of World War II, when Reppe discovered its synthesis from acetylene and CO, in the presence of Ni compounds, that it gained importance in the chemical industry (Hancock, 1973). Interestingly after the use of several other routes in manufacturing, it is the original method involving oxidation of acrolein, derived from the recently developed catalytic oxidation of propylene, which is currently the most favored industrial process for the manufacture of acrylic acid.

Acrylic acid is used primarily as a starting material in the synthesis of emulsion and solution polymers. Acrylic emulsion polymers were first used as coatings for leather in the early 1930s and have found wide utility as coatings, finishes and binders of leather, textiles and paper; as exterior and interior coatings in home and industry; and as adhesives, laminates, elastomers, plasticizers, and floor polishes. Past success and future potential stems from their inherent stability, durability, pigment binding characteristics and copolymerization versatility. Solution polymers of acrylate frequently with minor levels of other monomers, are employed in the preparation of industrial coatings. Polymers of acrylic acid can be used as superadsorbents in disposable diapers as well as in the formulation of superior, reduced-phosphate-level detergents. The polymeric products can be made to vary widely in physical properties through controlled variation in the ratios of the monomers employed in their preparation, by cross linking and control of molecular weight. They share common qualities of high resistance to chemical and environmental attacks, excellent clarity, and attractive strength properties.

The estimated worldwide consumption of acrylic acid is about 1.8×10^9 kg/ yr. The rate of consumption of acrylates grew between 10 and 20% annually during the 1970's. Although growth in the ester market has dropped considerably, new applications for polymers of acrylic acid in the superadsorbent and detergent fields surged in the late 1980's. Current annual growth is in the range 3~5%, and is expected to remain in the same range till the turn of the century (Kirk and Othmer, 1992).

Although acrylic acid can be prepared from a variety of starting materials, it is the route involving synthesis from propylene that occupies the most prominent position in the industry today. Until the late 1960s, the Reppe process and its several modified forms, using acetylene chemistry held centrestage in the manufacture of acrylic acid, when the propylene oxidation method started to emerge as a viable alternative route. By the late 1970s the cost and availability of acetylene made it an unattractive raw material for acrylate manufacture as compared to propylene. As a consequence all commercial units based on acetylene were phased out and almost 95% of the world acrylic acid capacity is now based on propylene as a raw material. The cost and availability of propylene are expected to remain attractive and new acrylate capacity should continue to be propylene based in the foreseeable future.

The current technology proceeds via two separate gas phase oxidation stages, wherein propylene is converted to acrolein in the first stage, followed by oxidation of acrolein to acrylic acid in the second stage. The oxidation stages are followed by an absorption step yielding aqueous acrylic acid.

$$CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO + H_2O \cdots\cdots\cdots (1)$$

$$CH_2{=}CHCHO + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CHCOOH \cdots\cdots\cdots (2)$$

The catalysts used for these reactions are based on bismuth molybdate for the first stage and molybdenum oxides for the second stage. Single reaction step processes are possible and have been studied. However, high selectivity is possible by optimizing catalyst composition and reaction conditions for each of the steps (1) and (2). This results in a more efficient utilization of raw material, which explains the adoption of the two-stage process in preference to the single-stage process in commercial ventures.

However, a survey of literature available on the subject shows that, typically peak temperatures of 330-430°C in the first stage, and 280-360°C in the second stage are required to achieve satisfactory conversion rates. Generally, the elevated temperatures tend to shorten catalyst life and decrease selectivity towards the desired product(s). Also the severe conditions result in higher costs on equipment and safety measures. These factors justify the motivation to simplify the process.

Palladium holds an important position in olefenic oxidation. It had long been known that olefenic hydrocarbons could be oxidized to give vinylic products like acetaldehyde, acetone, and vinyl acetate using solutions of palladium complexes. These reactions are one of the most synthetically useful and industrially important class of reactions, and include the ingenious Wacker reaction used for manufacturing acetaldehyde from ethylene. But it has been reported that under mild conditions, olefins can give *allylic* products rather than *vinylic* products over supported palladium catalysts (David *et al.*, 1971; Lyons, 1988). Thus the use of palladium catalysts in this manner gives new and potentially useful routes to a wide spectrum of chemical oxygenates from olefenic precursors. A catalytic application of this type of reaction is the oxidation of propylene to acrylic acid. But a survey of related literature shows that the topic has received only limited attention. And previous attempts to synthesize acrylic acid by this mechanism have been characterized by low selectivities and poor reaction rates.

The main objective of this investigation is to examine the use of palladium catalyst supported over hydrophobic support for the selective oxidation of propylene to acrylic acid. The efficacy of the use of hydrophobic supports in reactions where water is involved has been recognized (Chauvin *et al.*, 1977; Lieto *et al.*, 1983) and used widely (Fu *et al.*, 1989; Kawakami *et al.*, 1988). Hydrophobicity of these supports prevents the catalyst from being wetted by aqueous solution, and facilitates the transportation of reactants to the catalyst surface.

The suitability of hydrophobic catalyst for use in the liquid-phase (water) oxidation of propylene will be the focus of this thesis. Selection of the best support from various competing contenders, based on catalyst activity, selectivity to the desired product and stability will be a major task of the present work. It is not the intent of this study to investigate the mechanism of propylene oxidation. Nevertheless, the behavior of the candidate catalysts will be studied and existing knowledge will be used to interpret and predict the catalyst behavior under the operating conditions.

Chapter 2

Literature Review

This chapter aims to present a brief review of the various routes that have been used to synthesize acrylic acid. In doing so it takes a historical perspective of the industrially important processes, as also the methods which never saw the light of the day, industrially. The prime objective is to however survey the work that has been done pertinent to the present field of investigation, that is the palladium catalyzed aqueous phase oxidation of propylene to acrylic acid.

2.1 Manufacture of acrylic acid

For a route to be commercially attractive the raw material costs and utilization must be low, plant investment and operating costs not excessive and waste disposal charges should be minimal. First, a brief review of routes that were commercially implemented, but are no longer in use is presented. Next, other possible routes of syntheses which could be commercially implemented, provided the difficulties associated with them could be overcome, are outlined. And finally, the most important route of manufacture using propylene as a raw material is described in some detail. Various methods of manufacture of acrylates are summarized in Figure 2.1, showing their dependence on specific raw materials.

2.1.1 Commercial routes of the past

(a) Acetylene based routes. Walter Reppe, the father of modern acetylene chemistry, discovered the reaction of nickel carbonyl with acetylene and water or alcohols to give acrylic acid or esters. This discovery led to several processes that have been in commercial use. Whichever way the reaction is carried out, the overall result is simply:

$$CH \equiv CH + CO + H_2O \xrightarrow{Ni} CH_2 = CHCOOH$$

The original Reppe process requires a stoichiometric ratio of nickel carbonyl to acetylene. This is called the stoichiometric process because the nickel carbonyl is a reagent and not a catalyst, but is later regenerated from the nickel chloride formed in the process. There are other modifications of the Reppe process. The Rohm and Haas modified or semi-catalytic process provides 60-80% of the carbon monoxide from a separate carbon monoxide feed and the remainder from nickel carbonyl (Kirk and Othmer, 1992). The stoichiometric and the catalytic reactions occur simultaneously, but the catalytic reaction dominates. This process gives acrylate esters directly. Another modification of the Reppe process was developed by BASF at Ludwigshafen in 1956. In this process, acetylene, carbon monoxide, water, and a nickel catalyst react at about 200° C and 13.9MPa (2016 psi). The catalyst used in this process is a mixture of nickel bromide with a cupric bromide promoter. But due to the attractive economics and improved product purity from the propylene route, the acetylene based plants have mostly been shut down, or are in the process of being phased out.

(b) Acrylonitrile Route. This process, based on the hydrolysis of acrylonitrile is essentially a propylene route since acrylonitrile is produced by the catalytic vapor-phase ammoxidation of propylene.

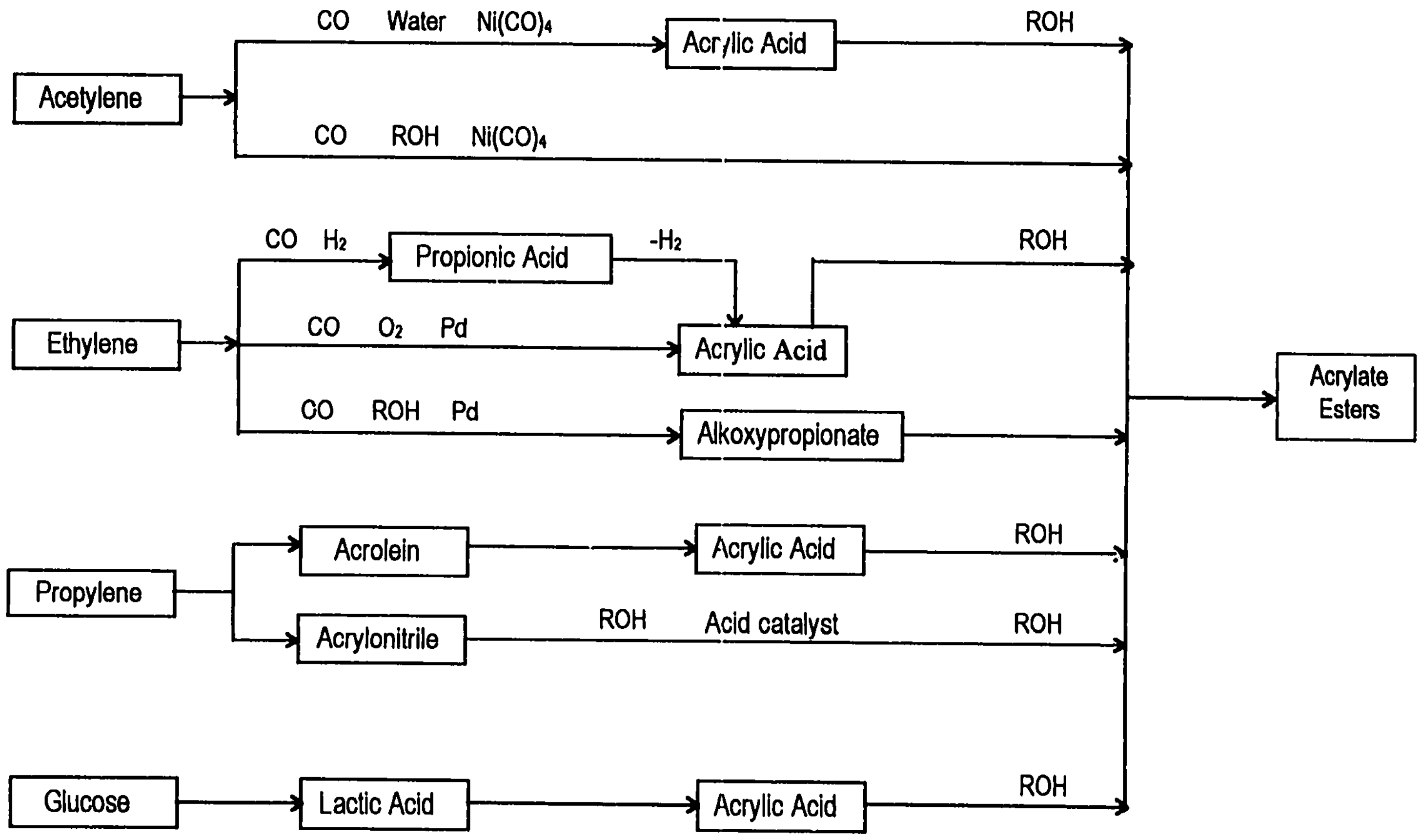


Figure 2.1 Acrylate manufacturing technologies

$$CH_2 = CHCH_3 + NH_3 + \frac{1}{2} O_2 \longrightarrow CH_2 = CHCN + 3\,H_2O$$

But the yield of acrylonitrile based on propylene is lower than the yield of acrylic acid based on the direct oxidation of propylene to acrylic acid. Hence for the large volume manufacture of acrylates, the acrylonitrile route is not attractive since additional processing steps are involved and the ultimate yield of acrylate is much lower. In addition this route is unattractive because of large amounts of sulfuric acid-ammonium sulfate wastes.

(c) Ketene process. The ketene process based on acetic acid or acetone as the raw material was developed by B.F. Goodrich and Celanese. Ketene obtained by the pyrolysis of acetic acid or acetone, reacts with formaldehyde, in the presence of $AlCl_3$ to give 2-propiolactone which in turn reacts with alcohols to give acrylic acid ester. It is no longer used commercially because the intermediate β-propiolactane is suspected to be a carcinogen. In addition it could not compete with propylene oxidation process.

(d) Ethylene Cyanohydrin Process. This process, the first for the manufacture of acrylic acid and esters, has been replaced by more economical ones. During World War I, the need for ethylene as an important raw material for the synthesis of aliphatic chemicals led to the development of this process, in both Germany, in 1927, and the United States, in 1931. In the early versions, ethylene cyanohydrin was obtained from ethylene chlorohydrin and sodium cyanide. In the later versions, ethylene oxide (obtained from the direct catalytic oxidation of ethylene) reacted with hydrogen cyanide in the presence of a base catalyst to give ethylene cyanohydrin. This was hydrolyzed and converted to acrylic acid and by-product ammonium acid sulfate by treatment with about 85% sulfuric acid. The process is of historical interest only, it was replaced by the more economical Reppe process using the acetylene process, in 1954.

2.1.2 Other Syntheses.

Acrylic acid and other unsaturated compounds can also be made by a number of classical elimination reactions, some of which are described below.

Vapor-Phase Condensations of Acetic Acid or Esters with Formaldehyde. Addition of a methylol group to the α-carbon of acetic acid or esters, followed by dehydration, gives the acrylates. The process is technically feasible, but high recovery of unconverted raw materials is required for the route to be practical. Its development depends on the improvement of catalysts and separation methods and on the availability of low cost acetic acid and formaldehyde. Both these raw materials are dependent on ample supply of low cost methanol.

Although the rapid cost increases and shortages of petroleum-based feedstocks forecast a decade ago have yet to materialize, shift to natural gas or coal may become necessary in the new century. Under such conditions, it is possible that acrylate manufacture via condensation of formaldehyde with acetic acid might become attractive. A coal gasification complex readily provides all of the necessary intermediates for manufacture of acrylates.

Oxidative Carbonylation of Ethylene-Elimination of Alcohol from β-Alkoxypropionates. The procedure is based on the palladium catalyzed carbonylation of ethylene in the liquid phase at temperatures of 50-200°C. Esters are formed when alcohols are included. During the reaction, the palladium catalyst is reduced. It is reoxidized by a co-catalyst system such as cupric chloride and oxygen. The products are acrylic acid in a carboxylic acid-anhydride mixture or acrylic esters in an alcoholic solvent. Reaction products also include a significant amount of 3-acryloxypropionic acid and 3-alkoxypropionates, which can be converted thermally to the corresponding acrylates.

Although yields are excellent, the reaction medium is extremely corrosive, so high cost materials of construction are necessary. In addition, the high cost of catalyst and potential toxicity of mercury require that the inorganic materials be recovered quantitatively from any waste stream. Hence, high capital investment, together with continued favorable costs for propylene, have prevented commercialization of this route.

Dehydrogenation of propionates. Oxidative dehydrogenation of propionates to acrylates employing vapor-phase reactions at high temperatures (400-700°C) and short contact times is possible. But this route to acrylates is not presently of commercial interest because of the combination of low selectivity, high raw material costs, and purification difficulties.

2.1.3 Manufacture of acrylic acid from propylene.

As mentioned earlier the propylene oxidation route constitutes nearly 95% of the production of acrylic acid. This route is attractive because of the availability of highly active and selective catalysts and the relatively low cost of propylene. The propylene process was brought on stream by Shell Chemical Corp. for the first time in 1959-1960. Interestingly, the discoveries of effective solid catalysts for the vapor phase oxidation of acrolein to acrylic acid were incidental to the studies of catalysts intended for the oxidation of propylene to acrolein. Widespread interest was aroused, and many laboratories began working towards the development of new and effective catalysts. A formidable number of patents have been claimed on the process and a plethora of catalysts exist for both single stage and two stage conversion of propylene to acrylic acid.

The propylene process has many variations. The first process involves the conversion of propylene to acrolein, separation of acrolein and unreacted propylene, and then conversion of acrolein to acrylic acid in the second catalytic oxidation step. A second alternative differs from the first in that the propylene-acrolein separation step is omitted and the mixture of propylene-acrolein is catalytically oxidized to acrylic acid. And yet another alternative is the direct catalytic oxidation of propylene to acrylic acid in a single phase and single reactor. Each of these variations have concomitant catalysts selective to acrolein, acrolein and acrylic acid in equal amounts, and to acrylic acid respectively.

Early catalysts for acrolein synthesis were based on cuprous oxide and other heavy metal oxides deposited on inert silica or alumina supports. Later, catalysts more selective for the oxidation of propylene to acrolein and acrolein to acrylic acid were prepared from bismuth, cobalt, iron, nickel, tin salts, and molybdic phosphoric, and molybdic silicic acids. Preferred second stage catalysts generally are complex oxides of molybdenum and vanadium.

However, higher selectivity is possible by optimizing the catalyst composition and reaction conditions for each of the steps in the two-stage oxidation process. Highly active and selective catalysts maximizing the yields of propylene to acrolein in the first step and then the conversion of acrolein to acrylic acid in the second step, result in a more efficient utilization of raw material. Due to this reason the two-stage oxidation process finds favor over the single-stage process in most commercial facilities.

Figure 2.2 depicts the oxidation process flow sheet for the two-step process, showing the equipment and typical operating conditions. Vaporized propylene, is mixed with steam and air and fed to the first stage reactor. The feed composition is typically 5-7% propylene, 10-30% steam, and the remainder air (or a mixture of air and absorber off-gas). The preheated gases react exothermally over the first-stage catalyst with peak temperature in the range of 330-430°C, depending on the conditions and catalyst selectivity. The effluent from the first reactor which is an acrolein-rich gaseous mixture is then passed to the second-stage reactor, for the selective conversion of acrolein to acrylic acid. Here the temperature ranges from 280 to 360°C, again depending on the conditions.

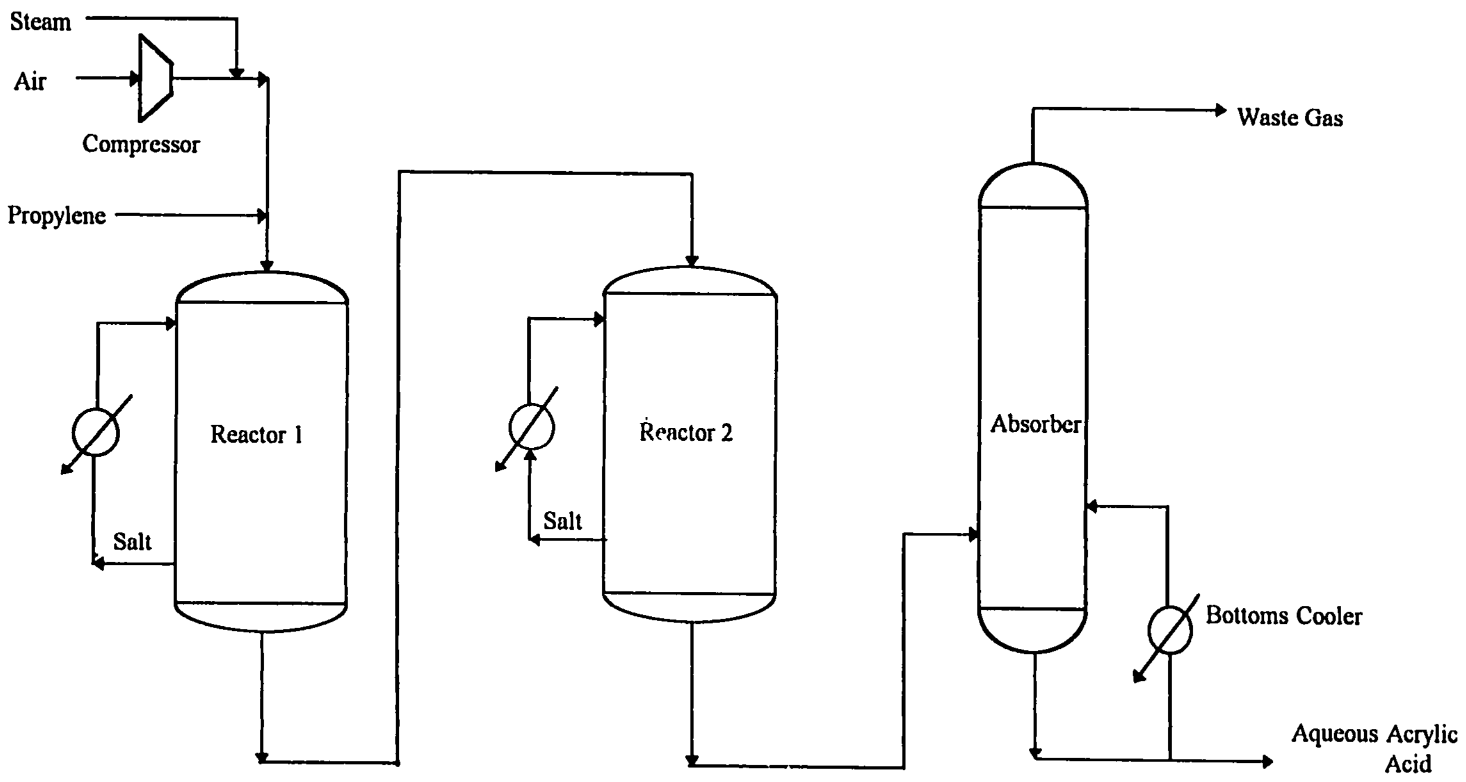


Figure 2.2 Two-stage propylene oxidation process

The reactors in both the stages are of the fixed-bed shell-and-tube type (about 3-5 m long and 2.5 cm in diameter) with a molten salt coolant on the shell side and packed catalyst on the tube side. The heat of reaction in both the stages can be recovered as steam in external waste-heat boilers.

The gaseous reactor effluent from the second-stage oxidation is fed to the bottom of the aqueous absorber and cooled from about 250°C to less than 80°C by contact with aqueous acrylic acid. The gases pass through the absorber to complete the recovery of the product. The absorber off-gas is sent to a flare or a furnace to convert all residual organic material to waste gas. Some of the absorber off-gas may be recycled to the first stage reactor feed to allow the achievement of optimum oxygen to propylene ratio at reduced steam levels. The aqueous effluent from the absorber is 30-60% acrylic acid in about 75-86% yield based on propylene (Kirk and Othmer, 1992), depending on the catalysts, conditions, and age of the catalysts employed.

The effluent from the absorber is sent to the separations section for the recovery of acrylic acid. The acrylic acid is extracted from the mixture with a solvent such as butyl acetate, xylene, di-isobutyl ketone, chosen for their high selectivity for acrylic acid and low solubility for water and by-products. The extraction is performed either in a tower or a centrifugal extractor. The extract is vacuum distilled in the solvent recovery column, which is operated at low bottom temperatures to minimize the formation of polymer and dimer, and is designed to produce acrylic acid-free overheads for recycle as the extraction solvent. A small aqueous phase in the overheads is mixed with the raffinate from the extraction step. This aqueous material is stripped before disposal both to recover extraction solvent values and minimize waste organic disposal loads. The bottoms from the solvent recovery column are fed to the foreruns column where acetic acid, some acrylic acid, water, and solvent are taken overhead. The overhead mixture is recycled to the extraction column. The bottoms from the foreruns column are then fed to the products column, where acrylic acid is taken as overhead. The glacial acrylic acid produced in this stage is of the process typically is at least 98-99% pure.

2.2 Liquid phase oxidation of propylene

The process for the production of acrylic acid by the two-stage catalytic vapor phase oxidation of propylene has been known to the art since long. Although an efficient process yielding high conversions of propylene, there are certain drawbacks associated with it. Principal among these drawbacks is the use of high temperatures in both the oxidation stages. These elevated temperatures tend to shorten the life of the catalyst and decrease the catalyst's selectivity towards the desired product. Furthermore, high temperatures risk the polymerization of acrylic acid into unwanted polymers and dimers, a major reason for acrylic acid losses in the process. Also catalyst preparation requires careful attention to ensure high selectivities to the target compound in each of the oxidation stages. These shortcomings have brought about the need for a simplification of the process, to circumvent the more rigorous conditions and equipment costs involved in the present two-stage vapor phase process.

One such process which achieves the above mentioned objectives is the liquid phase oxidation of propylene over supported noble metal catalysts. This process is significant in its conversion of propylene to acrylic acid in just one step and conditions which are much milder than those being used for the current route. It effectively combines the two oxidation stages and the aqueous absorption stage into a single step, if carried out in a slurry or a trickle bed reactor. Also the temperatures required to accomplish the desired reaction are reported to be in the range of 60-150°C. But literature relating to this novel procedure for the one-step oxidation of propylene to acrylic acid was found to be scarce. In the sections that follow, a summary of the past work that has been reported pertinent to this field of investigation has been collated.

2.2.1 Liquid phase oxidation of acrolein

It is interesting to note that in earlier quests to oxidize propylene to acrylic acid, the acrolein potentially available from propylene oxidation was further oxidized in the liquid phase. Although considerable art on the process is available, the route cannot compete with the vapor-phase technology. Several liquid phase processes were developed, but were never implemented commercially due to the complicated mechanisms or expensive catalysts involved.

2.2.2 Liquid phase oxidation of propylene to acrylic acid over Ni or Mn Catalyst.

The direct liquid phase oxidation of propylene to acrylic acid has been first described in US Patent 3,271,447 (Naylor and Del, 1966), using a catalyst comprising of a salt of a metal of the group consisting of manganese or nickel and in the essential absence of added water. The preferred temperature range is from 125°C to 250°C, and the pressure from 5 to 100 atmospheres. An alkanoic acid such as propionic acid is preferred as a solvent for acrylic acid. The reaction should essentially be conducted in the absence of added water, although small amounts of water are inevitably formed, as in any oxidation reaction involving a hydrocarbon. The reactor walls have a pronounced effect on the course of the reaction. However, the reported conversion rates are in the range of 2-23% under differing conditions. Any further investigation into this route was not uncovered in the literature searched. Apart from these earlier forays into the liquid phase route, however little has been reported on the liquid phase oxidation methodology. The same reaction that was described above can be effected with palladium as the catalyst, offering significant improvements in the conversions of propylene to acrylic acid. It would be worthwhile to discuss the role of palladium in olefinic oxidation before going on to describe the efforts made by other researchers to accomplish the oxidation of propylene by molecular oxygen in the aqueous phase.

2.3 Role of palladium in olefinic oxidation

Palladium holds an important position in olefinic oxidation. Modern palladium chemistry developed very rapidly after an ingenious Wacker process had been developed in 1958. In the Wacker process, acetaldehyde is produced on an industrial scale from ethylene using Pd Cl_2 and Cu Cl_2 as catalysts. The essence of the great success of the Wacker process is the invention of an ingenious catalytic cycle, in which the reduced Pd^0 is reoxidised in situ to Pd^{2+} by Cu Cl_2, and CuCl is easily oxidized to $CuCl_2$. In addition to the Wacker type oxidation of olefins, many reactions involving Pd compounds have been discovered in the last 20 years.

One of the most synthetically useful and industrially important classes of catalytic oxidations reactions involves nucleophilic attack on palladium-olefin π-complexes to give vinylic oxidation products, and the reduced palladium species can be deoxidized in situ by a number of oxidants including Cu^{2+} (Jiro Tsuji, 1977). In this manner, vinylic oxidation products or their stable isomers, including acetaldehyde, acetone and vinyl acetate are manufactured by a series of related catalytic reactions.

However, other productive pathways are available to coordinated olefins, which produce allylic products instead of vinylic products. It has been reported that synthesis of acrylic acid from propylene over supported palladium catalysts (David *et al.*, 1971) can be achieved under mild conditions in the presence of water. The development of this chemistry for the production of a large and important family of allylic oxidation products including α,β–unsaturated alcohols, esters, ketones, and carboxylic acids is possible; yet until recently, only limited application of these reactions has taken place. Another instance in which palladium catalysts, either supported or in solution, can be used to advantage is in the selective oxidation of the aromatic ring. It is interesting to note that palladium catalyzed oxidation of ethylene to acetaldehyde (the Wacker reaction) was first carried out over a supported palladium catalyst, but is now carried homogeneously in solution.

Palladium is a unique element in many respects. Starting with its electronic structure, it is the only transition metal with a d^{10} atomic ground state configuration. It is the first of the platinum group metals and has the least density and the lowest melting point among these metals. Pd compounds are convenient reagents since they are usually stable and easy to handle. Toxicity is also not a serious problem. On the other hand Pd is an expensive metal with a high atomic weight.

2.4 Liquid phase oxidation of propylene using palladium catalyst

The oxidation of propylene to acrylic acid in one step employing a palladium catalyst is first reported in US Patent 3,624,147 (David and Estienne, 1971). This invention claimed the process for preparing acrylic acid which comprises oxidizing propylene with molecular oxygen in the presence of water and a noble metal of Group 10 of the Periodic Table, at a temperature of about 50°C, and pressures exceeding 5 bars gauge. Suitable noble metals included platinum, ruthenium, rhodium, and particularly ***palladium***. The metal loading was varied between 0.01 and 10% by weight based on the reaction medium, and was used either in a finely divided state or deposited on a carrier such as alumina, silica gel, aluminum oxide or aluminum silicate, pumice, active charcoal or bentonite. The temperature was varied between 70°C and 120°C, and the pressure was kept higher than 5 bars, preferably in the range 20-150 bars. The process was however characterized by yields of 60% or less based on the amount of propylene converted. Acrolein was also reported to be formed in yields of about 10%. Moreover, substantial amount of CO_2 were reported as undesired products, and the reaction rates were low. Similar reactions under mild conditions attempted by Seiyama *et al.* (1972) reported low conversions with turnover numbers < 1. The reactions were carried out at 60°C and 1atm.

A different approach using a similar catalyst is reported in EPO published application 145 467 A3 (Lyons, 1985). In this process, the palladium catalyst is first activated by preliminary high temperature contact with an olefin, e.g. propylene. Gaseous oxygen and propylene are then passed through the catalyst bed along with a liquid aqueous phase media which removes the acrylic acid as it is being formed, carrying it downwards for recovery. The catalyst is effective in promoting the reaction at temperatures as low as 25°C, with high selectivities. Moreover the undesired by-product, CO_2, is virtually eliminated.

Even higher selectivities are claimed for this process in EPO published application 145 468 (Suld and Lyons, 1985) where certain surfactants are used in combination with a co-surfactant such as n- or t- butyl alcohol. Similar improvement is claimed in EPO published application 145 469 (Lyons, 1985) when a free radical inhibitor such as butylated hydroxy-toluene is added to the reactants.

Yet another approach to the problem is shown in U.S. Patent 3,792,086 (Frank and Murib, 1974) where palladium is combined with phosphoric acid. This catalyst is claimed to constitute a significant advance in the art in that high selectivity is achieved, but the catalyst efficiency deteriorates rapidly due to tar formation that coats the catalyst thus impeding efficient contact with the reactants. U.S. Patent No. 3,947,495 (Murib *et al.*, 1976) claims to overcome this problem by adding a sulfur modifier. The addition of sulfur (in any one of its several forms) apparently inhibits tar formation thus improving both reaction rates and catalyst stability.

U.S. Patent No. 4,499,301 (Murib, 1985) reveals still another approach to the problem, whereby a solid acid consisting of mixed metal oxides is substituted for phosphoric acid in the catalyst. The catalytically effective metal can be one of a group of noble metals including palladium, gold, and silver, with preferred composition containing palladium and gold. High selectivities are claimed for this process.

Improved selectivity to acrylic acid, enhanced catalytic activity and a better yield of acrylic acid is reported in U.S. Patent 4,435,598 (Hinnenkamp, 1984), by the use of hydroquinone in the oxidation of propylene over palladium supported on powdered catalyst. A preferred range of the hydroquinone used is about 0.1% to 1.0%. It is presumed that hydroquinone inhibits polymerization of acrylic acid, thereby increasing yield.

But, the most comprehensive study insofar on this subject has been presented by Lyons *et al.* (1988). According to the study allylic products can be synthesized in the presence of palladium either in homogeneous solution and over heterogeneous supported catalysts. The author reports that an effective catalyst for propylene oxidation is 10% palladium on carbon. The reaction was carried out as a semi-batch process using a oxygen to propylene ratio of 1.5 in the presence of a radical inhibitor, butylated hydroxytoluene (BHT), which suppresses radical oxidation or polymerization of the reaction product, under a variety of reaction conditions. High selectivities of about 90% were achievable and turnover numbers in the excess of 4 moles acrylic acid per gram atom of palladium per hour were reported. But these turnover numbers are not high enough to initiate practical applications. The study also speculates on the mechanism of the reactions, which is described below in Section 2.5.

2.5 Chemistry of the process of propylene oxidation

It is well known that nucleophilic attack on a Pd(II) π-allyl complex gives an intermediate which can lead to a vinylic oxidation product or its stable isomer. If carried out in the presence of a suitable oxidant which is regenerable in air, this results in catalytic Wacker-oxidation of olefins. In these cases it is established that carbon-hydrogen bond activation (β-hydrogen elimination) takes place after nucleophilic attack. But allylic oxidation products have been shown to arise via some palladium catalyzed oxidation of α-olefins. In these cases it is proposed that results can be rationalized by a mechanism involving allylic C-H bond cleavage to produce a palladium π-allyl intermediate which undergoes nucleophilic attack to produce an allylic oxidation product. Thus if nucleophilic attack on coordinated α-olefin occurs before C-H bond activation, vinylic oxidation products are formed, but if nucleophilic attack occurs after allylic C-H bond activation occurs, allylic oxidation products are produced.

In case of heterogeneous supported catalyst the reaction sites seem to be the activated, coordinatively unsaturated palladium (0) centers. Supported palladium catalysts which can be maintained in a low oxidation state appear to oxidatively add α-olefins to produce π-allyl surface species and give allylic oxidation products. Addition of strong oxidants, or use of forcing conditions - all of which could cause activation of surface Pd(0) to Pd(II) or higher- promote formation of vinylic oxidation products. The presence of halide ions, for example promotes Wacker chemistry to the virtual exclusion of allylic oxidation. This suggests that the active catalyst for allylic oxidations may be low oxidation state palladium.

The proposed scheme for the conversion of propylene to acrylic acid can be viewed diagramatically in Figure 2.3. The first step in the oxidative cycle constitutes the addition of olefin to the low oxidation state metal centers to form surface π-allyl intermediates.
Next, nucleophilic attack at the π-allyl ligand gives rise to allylic oxidation products, and reduced palladium species. When HY is water, acrylic acid is produced in high yields. Presumably in this case, allyl alcohol is the initial product which is rapidly converted to acrylic acid on the surface of the catalyst.

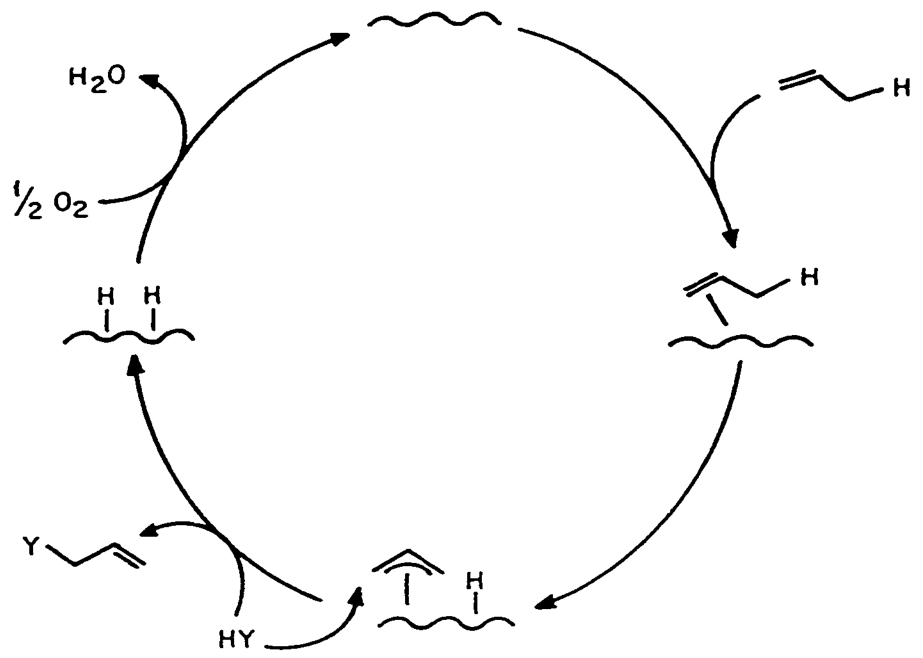


Figure 2.3 Chemistry of the liquid phase oxidation process

Chapter 3

Catalyst preparation and characterization

In this chapter, the various supported metal catalysts used for the direct oxidation of propylene in the liquid phase are profiled. First the basis for the selection of catalyst support material for carrying out this three phase reaction is explained, and its usefulness in an aqueous environment is elucidated. Also the procedure adopted in the preparation of the catalysts and the characterization techniques used are outlined.

3.1 Selection of the support.

If as it usually happens, the catalytic agent is to be on a support, it becomes necessary to select an optimum support material from among the possible contenders according to the criterion of stability, inertness, cost and whether the use is governed by patent laws. For catalytic reactions, the rate is generally proportional to the surface area of the catalyst accessible to the reactants. To maximize the surface area of a metal catalyst it is a common practice to disperse a metal on a high surface area support. The supports used must have a high surface area, which means they are porous with very small pore diameters. When the metal supported catalyst is exposed to a liquid it becomes wet due to capillary effects. A conventional metal catalyst supported on hydrophilic supports such as Al_2O_3, SiO_2, etc., loses its activity when exposed to water (Sherwood, 1981; Jones *et al.*, 1990). The same problem seems to beleaguer previous efforts made in experiments related to our field of investigation. Although some of these prior art processes exhibit high selectivity, reaction rates are generally too low to be of any practical consideration. These rates are several orders of magnitude lower than those reported for the vapor phase reactions. What happens theoretically is attempted to be explained in the following paragraph.

The reason for the low catalyst activity can be attributed to the fact that the reactions are limited by the mass transfer of the reactants to the surface of the catalyst. Clearly, when the catalyst Pd/C is exposed to liquid water, it becomes wet due to the capillary effect, and therefore the gaseous reactants must dissolve in the liquid in order to reach the Pd surfaces. Since propylene and oxygen are sparsely soluble in aqueous solutions, the rate determining step is the mass transfer of reactants to the reaction sites. This limitation cannot be changed by increasing the reaction temperature. Increasing the pressure results in higher gas solubility, but the pressure is limited by liquefaction of propylene. It appears that the process improvement can only be achieved by the redesign of the catalyst to overcome the mass transfer limitation. It is postulated that when conventional catalyst is exposed to aqueous solutions, capillary condensation takes place until it reaches thermodynamic equilibrium dictated by the Kelvin equation (Golodets, 1983) :

$$\ln (P / P_0) = - 2 V \tau \cos\theta / (r R T) \text{..............................} (1)$$

where r = radius of the capillary

V = molar volume of the liquid

τ = Surface tension

θ = contact angle

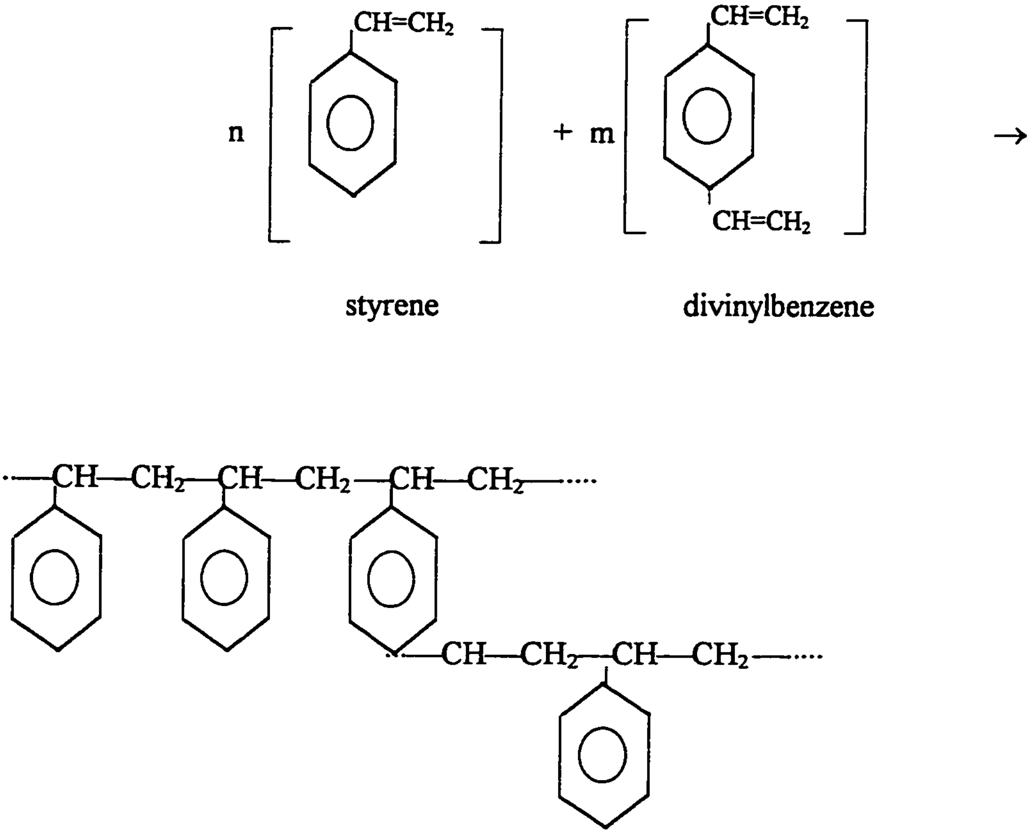
T = temperature

R = gas constant

Equation [1] suggests that for values of the contact angle less than 90°, liquid condenses in the capillary at a pressure P less than the saturation pressure P_o at a temperature T. For conventional catalyst supports, the materials are hydrophilic and the contact angle with an aqueous solution would be close to zero. Thus the whole catalyst is wet when exposed to the liquid. The combination of low solubility and low liquid-phase diffusion coefficients of the reactants results in low activity for catalysts supported on conventional supports.

The equation also implies that increasing contact angle reduces the chances of the pores being wetted by the surrounding liquid. If a hydrophobic material is selected as a catalyst support, its pores will remain dry and accessible to the reactant gases. It has been reported (Katz, 1953) that water does not adsorb appreciably on platinum group metals. If these metals were supported on a hydrophobic material, the presence of water would not affect the performance of the catalyst. For example, the isotopic exchange between H_2 and water proceeds rapidly over Pt supported over hydrophobic materials, but the reaction is almost inactive on alumina. The hydrophobic nature of the support gives higher activity than the conventional metal oxide catalyst due to prevention of excessive multilayer adsorption of water vapor (Iida *et al.*, 1977). With hydrophilic supports such as activated carbon fiber (ACF) and alumina, water vapor becomes adsorbed in multilayers with increasing relative humidity, and the Kelvin equation suggests that condensation takes place at a relative humidity of 0.45 for ACF (Kawakami *et al.*, 1988).

Polymeric supports happen to be fine catalyst supports. They have been recognized widely (Chauvin *et al.*, 1977; Leito *et al.*, 1983) and offer several advantages over conventional supports. They are reported (Leito *et al.*, 1983) to be catalytically inert, easily functionalized and can be prepared with a wide range of physical properties. The only disadvantage they seem to possess is their relatively poor thermal stability at high temperatures. But this drawback is not a concern in the present study. Furthermore among the polymer supports investigated in literature, poly-styrene-divinylbenzene (SDB) has been reported to offer the advantages of a high purity catalyst support. SDB is a copolymer of styrene and a closely related bifunctional monomer, divinylbenzene:



styrene

divinylbenzene

poly-styrene-divinylbenzene

Styrene-divylbenzene copolymer (SDB) is an inert, high surface area material suitable for supporting noble metal catalysts, possessing a number of desirable properties such as rigidity, porosity, and hydrophobicity. Because SDB is hydrophobic, the resulting catalysts are free from capillary condensation and remain active in the presence of water. SDBs have been used extensively for a number of reactions. They have been successfully implemented in the reduction of NO_x with H_2 (Fu *et al.*, 1989), CO oxidation in humid air (Yaparpalvi *et al.*, 1991), the removal of hydrogen and oxygen from explosive mixtures (Ledjef *et al.*, 1987), etc.

For the purposes of this study, the SDBs were obtained from various sources- principally AECL (Atomic Energy of Canada Ltd.), Millipore Corp., Hayes Separation Incorporated, and the Polymers Laboratory of the Department of Chemical Engineering at the University of Alberta. The characteristics of these supports are listed in Table 3.1.

Table 3.1: Various supports

Support	Surface area, m^2/g	Mesh size
Porapak-Q	**637**	**50-80**
Porapak-P	**306**	**80-100**
HayeSep-Q	**637**	**20-40**
HayeSep-D	-	**20-50, 80-100**
AECL	**427**	**20-35**
Polymers Lab.	**80**	**18**

Additionally, another support, TS-720, which is a silica based hydrophobic support was obtained from Cabot Corp. This support was prepared by treating high purity fumed silica (99.8% SiO_2) with an organosilicon compound. But low activity was displayed by the catalyst and the support underwent transformation. Hence the use of this support was terminated after the initial run. A possible explanation for this low activity could be a very poor dispersion of palladium on the catalyst, or the incomplete reduction of palladium precursor salts to metallic palladium.

3.2 Catalyst preparation

Although previous researchers (David and Estienne, 1971; Chuang and Fu, 1993) have reported that the liquid phase oxidation of propylene could be carried out over any noble metal belonging to group 10, the superiority of palladium over other metals is well documented. The activities of the metals decrease in the sequence Pd > Pt >> Ru ≈ Rh (Seiyama *et al.*, 1972). In fact, many later researchers (Hinnenkamp *et al.*, 1984; Lyons, 1988) concentrated only on palladium. As a result, most of the work conducted as part of this study concentrates on palladium as a catalyst. Results from this laboratory using platinum as a catalyst produced carbon dioxide in prodigious amounts. Although, small amounts of other noble metals like iridium, ruthenium and platinum were added to palladium to observe any favorable effects of such combinations.

3.2.1 Pd/SDB

The Pd/SDB catalysts were prepared by the impregnation of SDB with an ethanolic solution of the precursor salt, $PdCl_2$ in this case. The precursor solution was prepared by dissolving a known amount of $PdCl_2$, calculated on the basis of percentage metal loading required, in a mixture of hydrochloric acid and water. Typically, it took 30-40 minutes for the $PdCl_2$ to homogenize into the solution. Ethanol was then added to this solution in order to facilitate the wetting of SDB. An accurately weighed quantity of the support was wetted in the prepared solution. Wetting ensures that the solution is introduced into the pores of the support and distributed there, by the effect of capillary forces. The mixture was then mounted in a rotary evaporator under infra-red lamp and left to dry overnight, typically for a period of 12 hours. This action causes the precursor to crystallize in the pores of the support. The coated support was reduced at a temperature of 523 K by a hydrogen gas stream. For this purpose it was packed in a glass U-tube and placed inside a furnace. The tube was initially flushed with nitrogen for some time before the hydrogen stream was switched on. The temperature was increased in incremental steps and maintained at the reduction temperature for 12 h. Finally, the heat was turned off and the catalyst was allowed to cool to room temperature at a natural rate. The temperature control was accomplished by a premonitored Omega programmable controller.

It should be mentioned that, primarily $PdCl_2$ was used as the precursor salt for making the catalyst. However, two different samples were prepared with $Pd(NO_3)_2$ as the starting metal complex, but the catalysts derived from $Pd(NO_3)_2$ displayed poor activity, justifying abandonment of this route of synthesis.

A sample calculation for preparing 5 g of 10% Pd on SDB is demonstrated. Five grams of 10% catalyst would imply 0.5 g Pd and 4.5 g of the support. Therefore 0.5x176/106 g of $PdCl_2$, i.e. 0.8333 g of $PdCl_2$ was dissolved in 4 ml HCl + 16 ml H_2O (HPLC grade). Then 80 ml of ethanol was added to this solution. 4.5 g of SDB was impregnated with this Pd solution. The various catalysts that were prepared are outlined in Table 3.2.

3.2.2 Pd-Pt/SDB, Pd-Ir/SDB, Pd-Ru/SDB

An approach similar to what has been described above was used for all the metal combinations listed above, with some minor variations. For impregnation of platinum along with palladium, the support was wetted in an ethanolic solution containing a given amount of chloroplatinic acid, H_2PtCl_6, and $PdCl_2$. For iridium impregnation, $IrCl_3$ was dissolved first in a 0.2 wt.% NaOH solution, and then mixed with the solution of $PdCl_2$ obtained via the procedure described above. Similarly for ruthenium the precursor salt was $RuCl_3$. The remaining steps, namely drying and reduction were essentially the same. These catalysts are listed in Table3.3.

Table 3.2: Characteristics of Pd/SDB catalysts.

cat #	support	% metal loading	BET surface area, m^2/g	metal dispersion, %
1	**AECL[a]**	**1**	**436**	**36.0**
2	**AECL**	**5**	**427**	**27.0**
3	**AECL**	**10**	**427**	**24.5**
4	**NHL[b]**	**10**	**80**	-
5	**P-Q[c]**	**5**	**634**	-
6	**P-Q**	**10**	**634**	**29.9**
7	**P-P[d]**	**10**	**306**	-
8	**HS-D[e]**	**10**	-	-
9	**HS-Q[f]**	**5**	**637**	**31.8**
10	**HS-Q**	**10**	**637**	**28.4**
11	**HS-Q**	**15**	**637**	**26.2**

a- SDB from Atomic Energy of Canada Ltd.
b- SDB from the polymers group
c- Porapak-Q
d- Porapak-P
e- HayeSep-D
f- HayeSep-Q

Table 3.3 Pd-Pt/SDB, Pd-Ir/SDB, Pd-Ru/SDB catalysts

cat #	support	Pd%	Pt%	Ir%	Ru%
1	**HS-2**	**10**	**0.1**	-	-
2	**AECL**	**2**	**0.4**	-	-
3	**AECL**	**10**	**2**	**2**	-
4	**AECL**	**10**	-	**2**	-
5	**HS-Q**	**10**	-	**0.2**	-
6	**AECL**	**6**	-	-	**2**
7	**HS-Q**	**10**	-	-	**0.2**

The BET surface area of the catalysts was measured using Omnisorp 360. The metal dispersion was calculated by utilizing the particle size from X-ray diffraction data. Scherrer's formula relates average crystal size to the width of the X-ray lines:

$$t = \frac{0.9\lambda}{\beta_{1/2}\cos\theta}$$

where

t= crystallite size

λ= X-ray wavelength

$\beta_{½}$ = width of the diffraction peak at half intensity.

θ, the angle of diffraction can be obtained from Bragg's law:

$$n\lambda = 2d\sin\theta$$

The metal dispersion is a ratio of the number of metal atoms at the surface, N_s to the total number of metal atoms, N_t.

$$D = \frac{N_s}{N_t}$$

$$N_s = (N_{ads})(\alpha)(N_0)$$

where

N_{ads} = moles of adsorbate per gram of catalyst

α = adsorption stoichiometry

N_0 = Avogadro's number

$$\text{and } N_t = (x/M_a)\, N_0$$

where

x = weight of metal on the support, grams

M_a = molecular weight of metal

The ideal way to calculate dispersion is to obtain N_{ads} data and use it in the formulae above. But in the absence of such data, an approximate calculation of dispersion can be made by obtaining particle size from X-ray diffraction studies.

N_s and N_t can be alternatively defined as

$$Ns = \frac{A_p}{A_a}$$

where

A_p = Area of particle surface = πd_p^2

$$A_a = \text{Area of atom} = \left(\frac{A_{100} + A_{110} + A_{111}}{3}\right)$$

Similarly,

$$N_t = \frac{V_p}{V_a}$$

where

$$V_p = \text{Volume of particle} = \pi d_p^2/6$$

and

$$V_a = \text{Volume of atom} = \frac{M_a}{N_0} \times \frac{1}{\rho_{Pd}}$$

Dispersion can now be related to the particle size d_p by the equation:

$$D = \frac{M_a}{\rho_{Pd} A_a N_0} \times \frac{6}{d_p}$$

By substituting values for M_a, ρ_{Pd}, A_a, N_0 for, the equation for palladium reduces to:

$$D = \frac{1.0717}{d_p}$$

From X-ray line broadening data, if t, crystal size is assumed to be equivalent to particle size d_p, then dispersion for palladium can be represented by:

$$D = \frac{1.0717}{t}$$

where t is expressed in nanometers.

Chapter 4

Experimental setup and procedure

This chapter describes the experimental program adopted to test the propylene oxidation efficiencies of catalysts prepared, as outlined in section 3.7. The equipment used to carry out the experimental runs is described first, followed by an account on the experimental techniques used to carry out the reaction. A review of the analytical techniques used to get product assays is presented at the end of the chapter.

4.1 Experimental Setup

All oxidation experiments were carried out in a stirred tank reactor supplied by Parr Instrument Co. The reactor having an internal diameter of 6.32 cm and a total volume of 300 mL was made of 316 stainless steel. A four-bladed disc turbine impeller of diameter 20 mm was used for agitation. The impeller was driven by a variable speed motor, so that the rate of agitation could be adjusted. The inlet and outlet lines to the reactor consisted of 6.35 mm ID high strength Teflon tubing. The feed gas to the reactor consisted of a mixture of high purity propylene and oxygen, drawn from compressed gas reservoirs. Propylene gas which was supplied by Matheson Gas, while high purity, extra-dry oxygen was obtained from Praxair Canada Inc. The rate of flow of the gases was monitored by mass flow controllers (Unit Instrumentation Co.) attached to the lines connecting the reservoirs to the reactor. These two gases were mixed at a feed manifold before being introduced into the reactor. The constancy in the flow rates of the gases was checked by observing the digital panels on the mass flow controllers. Usually some time elapsed before the flow rates stabilized, after the gas flow into the reactor had been started. Fluctuations if any, were only instantaneous, and the normal values were established within a short period of time. There was provision for nitrogen being introduced into the entire assembly through another line, also connected at the manifold. Nitrogen was used primarily to purge the entire system, or for the purposes of dilution of propylene composition in the feed. The feed blend of the two gases was introduced directly into the liquid phase through a tube extending to the bottom of the reactor.

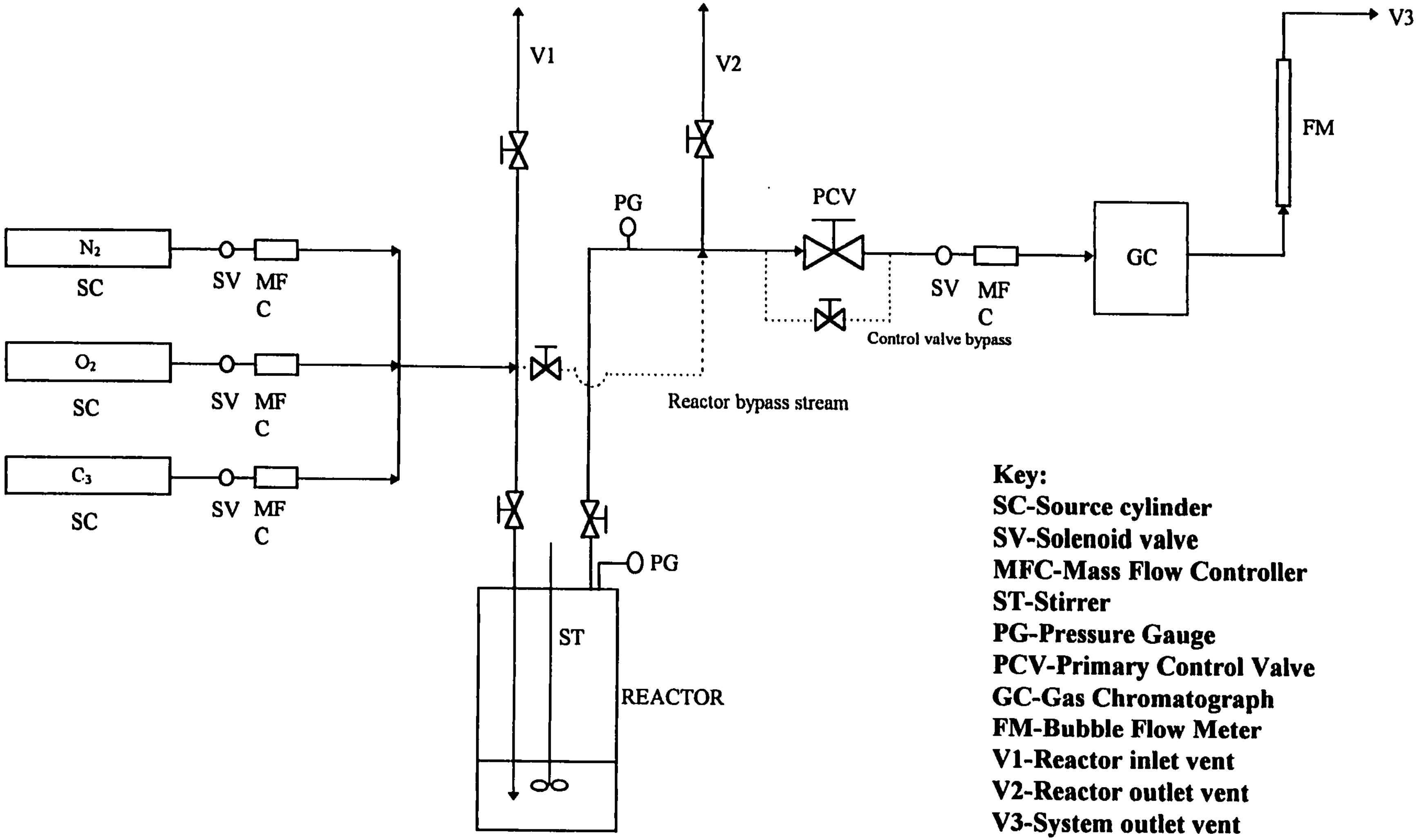
The reactor outlet gas was routed through a HP 5170 gas chromatograph equipped with a 8 ft packed column (Porapak-R) operating at 80°C, enabling the periodic sampling of the exit flow composition. The trend in the variation of the exit gas flow rate could be instantaneously viewed by means of a strip chart recorder which was connected to a mass flow controller attached to the exit line. The reading of the recorder corresponded with the percentage opening of the valve of the mass flow controller. This way a check could be maintained on any anomalous change in the exit gas flow rate. This was useful in detecting any leaks in the reactor, as the control valve would immediately shut, as soon as the pressure in the reactor went down due to a leak, thereby shutting out the gas flow, which was instantaneously recorded by the mass flow controller and hence the strip chart recorder. This feature was also important in rejecting aberrant data which was recorded on a few occasions when the flow rate would rise abnormally for a short period of time. After leaving the gas chromatograph, the exit gases were passed through a bubble flow meter to measure the flow rate of the exit stream, before being vented out of the test system completely.

The temperature during the reaction was maintained at the desired value with an external heater/feedback controller (Parr 4841). A thermocouple extending into the liquid phase of the reactor measured the reaction temperature, feeding this information to a controller which regulated the functioning of the heater. The temperature inside the reactor was maintained with an accuracy of ± 1°C. The total pressure in the system was regulated by a back-pressure controller. Again the concept of the controlling action was similar to that of the control of the temperature. A pressure sensor reading off the reactor pressure, fed this information to a Shimaden PID controller, which in turn controlled the opening and closing of a pneumatic valve, attached down the reactor exit line. The total pressure of the reaction system took some time to stabilize to a constant value, wherefore it stayed within a precision limit of ± 0.3 psi. Deviations beyond these were rare, and usually meant that there was either a leak in the system, or that there was some physical blockage in the assembly. A schematic diagram of the entire flow reactor system is shown in Figure 4.1.

4.2 Experimental procedure

During preliminary screening experiments, the catalysts outlined in Chapter 3 were primarily examined for their activity in converting propylene to the desired product. This procedure essentially consisted of measuring reactor outlet flow rate as well as the propylene, oxygen and carbon dioxide composition in this stream, at different intervals of time. These concentrations combined with the a priori knowledge of the reactor feed conditions were used to evaluate performance characteristics such as propylene conversion, oxygen conversion and acrylic acid selectivity, criteria which were useful and sufficient in identifying the quality of the catalysts. The main purpose of the initial runs was to identify a few candidate catalysts which would meet the requirements of the present study. Upon identification of potential catalyst(s), subsequent experimental runs were conducted to find the effects of variation in catalyst composition and operating parameters such as feed composition, the temperature of the reaction, the total pressure of the system and the flow rates of the gases.

In a typical run, the reactor was initially charged with the appropriate amount of catalyst and 100 mL of water. The catalyst initially floats on the surface due to its hydrophobicity, but on stirring the system behaves like a slurry reactor. After closing the valves to vents V1 and V2, and opening the reactor inlet and outlet valves, the feed gas mixture of



Key:
SC-Source cylinder
SV-Solenoid valve
MFC-Mass Flow Controller
ST-Stirrer
PG-Pressure Gauge
PCV-Primary Control Valve
GC-Gas Chromatograph
FM-Bubble Flow Meter
V1-Reactor inlet vent
V2-Reactor outlet vent
V3-System outlet vent

Figure 4.1 Schematic diagram of the reactor flow system

propylene and oxygen was introduced into the reactor. When the pressure reached 70 psi (482.6 kPa), the heater and the stirrer were switched on. The temperature rose gradually till the desired value was reached. The main pressure control valve remained closed, allowing the pressure in the reactor to build up till the pressure reached a value close to the preferred pressure, whereby the control valve would open. The first set of readings was taken when the pressure remained steady at the desired value for a certain period of time (usually one hour after the initiation of the reaction). This essentially consisted of routing a sample of the exit gases through the GC column to record the outlet gas composition and measuring the outlet flow rate by timing the bubble flow meter. Three such readings of the flow rate were taken and averaged to minimize experimental error. The procedure of taking the readings was repeated at suitable intervals of time, the recordings usually spaced one hour apart. To shut down the experiment, the inlet and outlet valves to the reactor were first closed, the heater and the stirrer were turned off, and the valves on the gas cylinders were turned off. Any gas remaining in the line connecting the reservoirs to the reactor was released by opening vent V1. The reactor was cooled immediately to room temperature by immersing the reactor in cold water. The reactor outlet vent was next opened to let out the gas trapped between the reactor outlet and the pressure control valve. Slowly the reactor outlet valve was opened to release the pressure inside the reactor, caution being exercised in doing so, lest the pressure inside the reactor would force the liquid out into the outlet stream. At no time was the reactor inlet valve ever opened during shutdown, as it would have been easier for the liquid to be forced out due to pressure or the volatility of the liquid at a high temperature, since the inlet tubing dipped right into the liquid phase. The reactor assembly was then dissembled and the liquid product filtered to reclaim the catalyst for the next run. A portion of the liquid sample was collected and stored for analysis. The catalyst was washed several times with water and dried overnight for reuse.

In all the experiments the semi-batch mode of operation was employed. The gas flow through the reactor was continuous, as the unreacted gases and the gaseous products were withdrawn from the reactor constantly. Although the inlet flow rate and composition were maintained constant at all times, the outlet flow rate and composition varied with time. The exit flow rate increased with decreasing activity of the catalyst, as the amount of unreacted gases increased. The reactor was operated in batch mode with respect to the desired product, acrylic acid, as it accumulated in the reactor, dissolving into the water. Water seems to play an important role as a reactant and as a convenient medium for acrylic acid to dissolve into. It was reported by Lyons *et al.*, that when water was kept as a medium, the product was acrylic acid. However, if it was replaced by acetic acid, the major product was allyl acetate. Additionally water offers the advantage of being a good solvent for acrylic acid, keeping in perspective the ease with which separation could be achieved later on to obtain a purer product.

4.3 Analysis of the liquid samples.

The analysis of the samples collected after each experimental run was carried out with the help of High Performance Liquid Chromatography (Waters Scientific Ltd.). The HPLC unit consisted of the following components: U6K injector, M6000A liquid chromatography pump, packed column (C18, a carbon based packing) of dimensions 250mm × 4.6 mm, M440 absorbance detector and the Waters data module 440. The liquid chromatograph is similar in concept to the gas chromatograph, except that the carrier is a liquid. The choice of the carrier is critical to the analysis of the products, the liquid being specific to the spectrum of products being analyzed. The recommended carrier for the analysis of a mixture of acrylic acid and polyacrylic acids is a combination of 74 parts of water, 1 part of phosphoric acid and 25 parts of acetonitrile by volume. Each of the constituent members of this carrier liquid were required to be HPLC grade, obtained from Fisher Scientific. After mixing the liquids in the required ratio in a one-liter measuring cylinder, the mixture was vacuum filtered using a filtering unit supplied by Millipore. The flow rate of the carrier liquid through the detector column was set at 60 mL/s, and the operating pressure was kept at 1000 psi (6894.8 kPa). At the startup of the LC unit it was essential that there were no air bubbles in the line connecting the carrier reservoir to the pump, so as to prevent any priming inside the pump. This was done by withdrawing a small amount of the carrier from a port with a syringe, and visually observing if there were any bubbles in the line, the liquid being withdrawn till the line was free of any bubbles. As the HPLC is a rather sensitive instrument, a small quantity of the liquid sample (10 μL) was enough to give integrable peaks. The absorbance peaks were integrated using a Waters Data Module, a chromatographic data reduction instrument that provides quantitative information on the components of a chromatography separation. Of the several parameters which control peak detection, peak separation and peak integration, the three most important ones were the peak width, the noise rejection and the area rejection parameters. These parameters have to be customized to the particular liquid sample being analyzed to ensure proper peak separation and integration. After the complete analysis, the data module provided a printout of the various compounds detected, along with their retention times and the areas under the respective peaks. The area under the peaks served as a measure of the concentration of the compounds, when the area was read against the concentration from a concentration-versus-area calibration curve. This curve was obtained by plotting the areas obtained for known compositions of the components desired to be detected. In finding the calibration curve it was important that the known compositions lie in the range of the concentration to be expected in the sample being analyzed.

4.4 Mass balance and product distribution

The veracity of the results obtained by the HPLC analysis was established by comparing with the theoretically expected amount of acrylic acid. This theoretical calculation is demonstrated below:

Grams of acrylic acid produced at the end of the reaction = (Inlet propylene flow rate in mols/s) x (Average propylene conversion) x (Average acrylic acid selectivity) x (Time for the reaction in seconds) x (Molecular weight of acrylic acid).

A typical analysis for the product had acrylic acid in the range of 3-7 % by weight. Other products present in measurable quantities were acetic acid and acrolein. Acetic acid concentration usually varied from 0.2 - 0.5%, while the concentration of acrolein was usually under 0.1 %. In practically all the cases, the acrylic acid concentration was within ± 10% of the theoretically calculated amount.

4.5 Definitions of the performance parameters used to compare the catalysts

$$\text{Propylene conversion} = \frac{\text{propylene in(mL/s)-propylene out(mL/s)}}{\text{propylene in(mL/s)}}$$

$$\text{Carbon dioxide selectivity} = \frac{\text{(mols of carbon dioxide produced)} \times 100}{3 \times \text{(mols of propylene reacted)}}$$

$$\text{Acrylic acid selectivity} = 100\text{-}CO_2 \text{ selectivity}$$

$$\text{Acrylic acid yield} = \text{grams of acrylic acid produced/ gram of catalyst/hour}$$

Chapter 5

Results and Discussion

The experimental results obtained using various catalysts outlined in Chapter 3 are presented in the following sections along with a discussion of the key findings. The primary task was to identify the support which would achieve maximum yield of propylene to acrylic acid. Also the experimental conditions, such as pressure, temperature, feed composition and factors like metal loading and catalyst composition were varied over a wide range. The purpose of these experiments was to evaluate suitable operating conditions for the reaction, so as to maximize the efficiency of the yield of propylene to acrylic acid. The effect of these operating parameters on the performance of the catalysts are also presented with an attempt to explain the kinetic behavior.

5.1 Catalyst Screening

Each catalyst prepared in this investigation was screened for its ability to convert propylene to the desired product. The objective of this preliminary screening was to identify which support amongst the various supports listed in Chapter 3 would emerge as most suitable. Similar test conditions were used to evaluate the performance of each catalyst. In a typical experiment, the conditions such as the flow rate, pressure and temperature were adjusted to the desired value and a performance parameter such as the outlet propylene concentration with respect to a fixed inlet flow rate and composition was obtained. The flow rate through the reactor was maintained at 0.833 mL/s, the pressure at

120 psi (827.4 kPa), the temperature at 103°C, and the feed composition was kept at 60% propylene. The acrylic acid yield per gram of palladium per hour has been used as the yardstick to compare the activities displayed by the catalysts, specifically the supports, as all other factors have been kept the same. The yields and the acrylic acid selectivites are listed in Table 5.1. The yields achieved by the catalysts range from 9.0 to 14.37 grams acrylic acid per gram of catalyst per hour, Porapak-Q and HayeSep-Q emerging as the best supports. The activities displayed by these catalysts are in agreement with the surface areas of the individual catalysts. Both HayeSep-Q and Porapak-Q possess high surface areas (637 and 634 m^2/g respectively) allowing better dispersion (28.4 and 29.9 respectively) of the noble metal on them. However, the performance of the SDB provided by the Polymers Lab. cannot be dismissed as unsatisfactory in light of the low surface area characterizing the support. In comparison with other supports, the SDB supplied by the Polymers Lab. has a surface area of 80 m^2/g, but displays a yield of 9.0. The reason for this unusually high activity lies possibly in its low surface area, which effectively relates to larger pore size. A carrier with large pores reduces the diffusional resistance to the reactants and the products, in and out of the pores to reach the catalytic centers. This reasoning seems more plausible when one considers the fact that some product fouls the catalyst, and causes physical blockage of the pores. This topic has been discussed in length in a later section. In view of this phenomenon, low surface area and hence large pore diameter, actually offers an advantage in the case of the Polymers Lab. support (SDB-NHL). The selectivity exhibited by the catalysts examined in this study are quite high and compare favorably with the catalysts used in the past by other researchers. A review of the performance of past catalysts is presented in the next section to provide a basis for comparison.

5.2 Comparison with results from literature

It would be worthwhile to compare the performance of these catalysts to the catalysts used in the past by other researchers. This is to confirm the superiority of hydrophobic

Table 5.1 Effect of various supports on the activity of the catalysts

Support	Acrylic Acid Selectivity (%)	Yield
Porapak-Q	90.60	14.35
HayeSep-Q	93.84	14.37
HayeSep-D	91.46	11.82
SDB-AECL	88.00	11.64
Polymers Group	89.80	9.00

Table 5.2 Comparison with results from past studies

Catalyst	Temp. (°C)	Press. (kPa)	C_3 conv. (%)	Selectivity (%)	Yield (g/gPd-h)	Reference
Pd Black	55	-	-	98	0.96	J.Cat 24, 173 (1972)
Pd+Cu/Alumina	155	-	-	72.5	0.85	US Pat. 4,107,204
10% Pd/C	65	790	-	93.2	3.36	E. Pat. 145,469
5% Pd/ C	100	2450	-	67.1	11.1	US Pat. 4,435,598
10% Pd/C	80	690	-	-	2.65	Cat. Today, 3 (1988)
Mo_{12} V_3 $Cu_{0.5}$ Ge O	-	-	99.6	96.1	-	US Pat. 4,051,180

supports over conventional supports. Table 5.2 lists the yields and selectivities exhibited by some catalysts used in the literature, together with specifications of the conditions used, wherever the information is provided. The results show that the use of hydrophobic support effects a significant improvement in the performance of the noble metal catalyst. The yields (see Table 5.1) of the catalysts prepared by the methodology recommended in the present study, are at least three times as much as the ones shown by the catalysts listed in Table 5.2. The selectivities displayed by the hydrophobic catalysts are equally good and often superior. The only catalyst amongst the listed ones which rivals the performance of the hydrophobic catalysts is the 5% palladium supported on carbon. But in this case, the reaction pressure was 2450 kPa, approximately three times the pressure used to evaluate the activity of the hydrophobic catalysts. High pressure essentially emulates the conditions of hydrophobicity by facilitating easier transport of reactants to the catalyst surface, but burdens the process with increased costs of implementing the high pressure. The last set of values in the list provides information on the performance of the molybdenum based catalysts used in the current mode of acrylic acid manufacture, i.e., via the vapor-phase oxidation of propylene. As is evident, this process attains high propylene conversions and acrylic acid selectivities, but at the expense of severe conditions and two stages of oxidation.

5.3 Effect of metal loading

To determine the effect of metal loading on the catalyst activity, the palladium loading was varied between 5 and 15%. Specifically, three different percentage loadings of palladium at 5, 10 and 15% on support HayeSep-Q were tested under similar conditions, and the acrylic acid yield based on unit weight of the noble metal was used for comparison (presented in Figure 5.1). Figure 5.1 also plots the metal dispersion at the three different loadings. It can be observed from the graph that the metal dispersion follows a pattern similar to that of the activity of the catalyst, corresponding to the metal

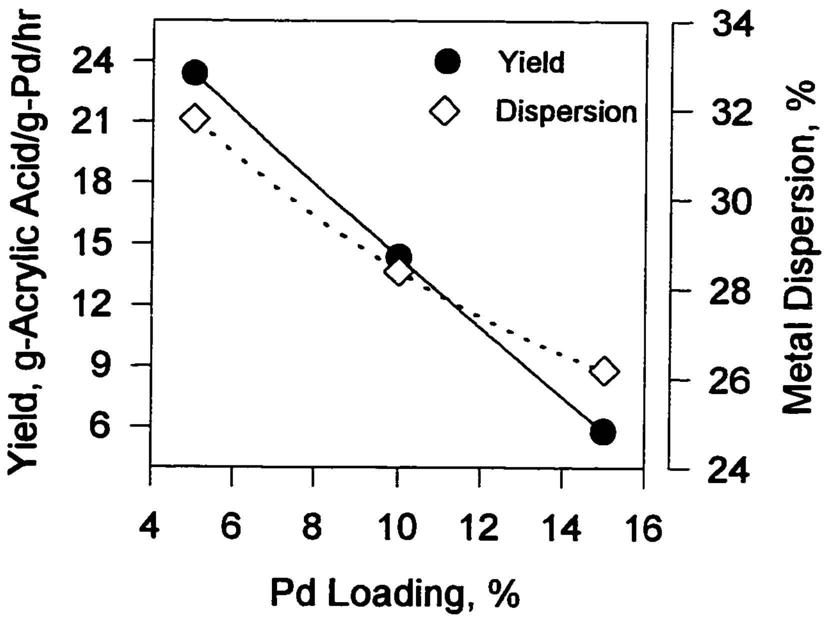


Figure 5.1 Effect of metal loading on catalyst activity (Slurry Reactor)

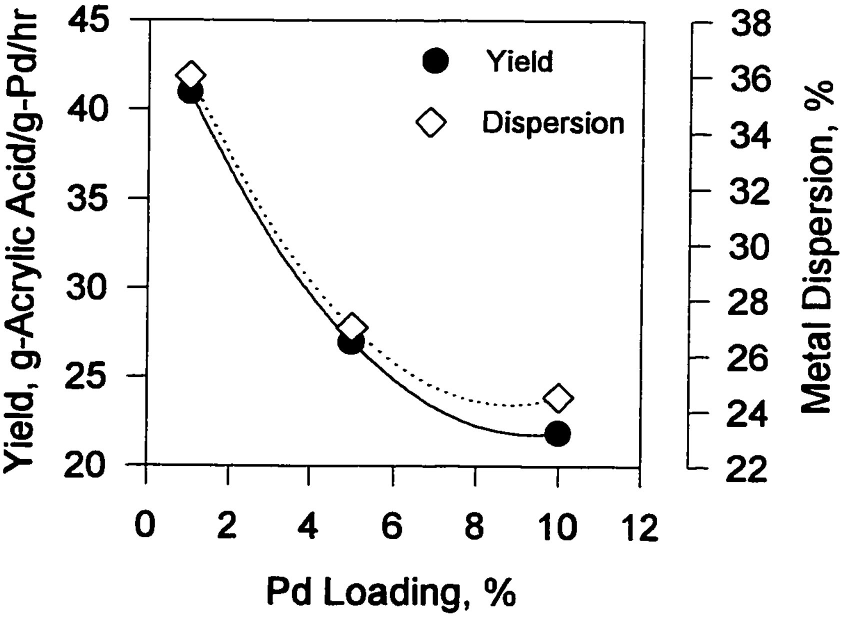


Figure 5.2 Effect of metal loading on catalyst activity (Trickle-bed Reactor)

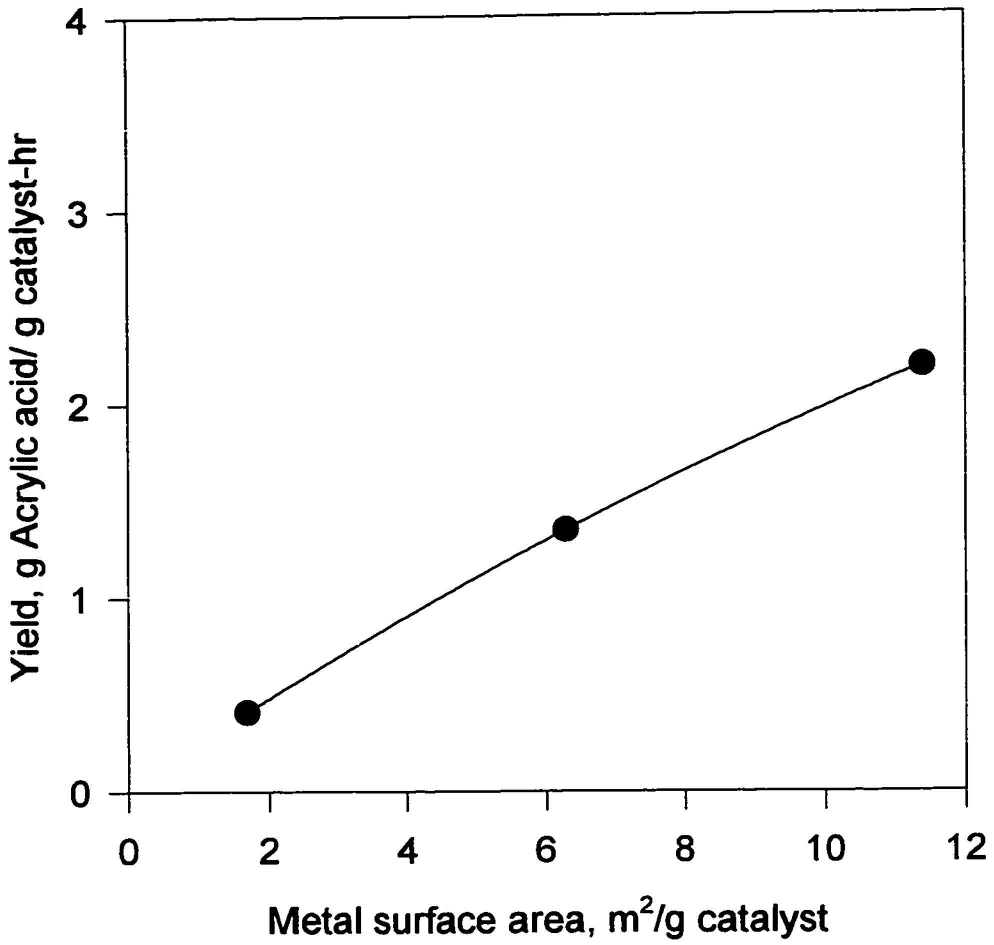


Figure 5.3 **Acrylic acid yield per gram of catalyst vs. metal surface area**

loading. The results observed above are corroborated by the observations made in a previous study in this laboratory, albeit under different conditions. The investigation differed from the present one primarily in its use of a trickle-bed reactor. Also the catalyst support used was SDB-AECL and the temperature was maintained at 140°C. Three different palladium loadings at 1%, 5% and 10% were tested. The results of this study are illustrated in Figure 5.2. Again, there is a close match between the trends in variation of the yield and metal dispersion with metal loading. A recollection of the definition of dispersion at this point would help to explain the trends seen in Figures 5.1 and 5.2. Dispersion is an indication of the efficiency of impregnation procedure to " disperse every metal atom" upon the support and thus have all the metal atoms available for reaction. It can be seen that the catalyst containing the lowest loading of metal gives the highest yields of acrylic acid based on *per gram of palladium*. This is reasonable because the metal is better dispersed at lower loading, implying that a higher fraction of metal atoms are exposed as active centers for the reaction to take place on.

A higher metal loading on the other hand implies more metal surface area, and consequently an enhanced reaction rate. This becomes apparent when the yield *per gram of catalyst* is plotted against the metal surface area, shown in Figure 5.3. The yield based on per gram of catalyst is seen to increase with metal surface area, as it is representative of the number of surface palladium atoms available for reaction. Thus at higher loadings there is a larger concentration of active sites on the catalyst surface which results in a higher yield. However in practice, a limiting metal surface area can be determined beyond which no improvement in activity can be observed (i.e., the reaction rate becomes controlled by non-chemical phenomenon, such as diffusion). Hence, if metal surface area is plotted as a function of metal loading, the picture will be that of an initial increase followed by a plateau for higher values of loading. Thus an optimum catalyst loading can be found which affords the catalyst both acceptable activity and cost-effectiveness, particularly in the case where a precious metal catalyst is involved.

5.4 Effect of catalyst composition

Small amounts of other noble metals like platinum, iridium and ruthenium were added along with palladium to see if they offered any beneficial effects in the conversion of propylene to acrylic acid. Two different supports were used to test the effects of adding different active components. In the first case, SDB-AECL was used as a support, the pressure and temperature being kept at 120 psi (827.4 kPa) and 103°C respectively. The feed composition was at 40% propylene. In the second case, HayeSep-Q was the support, and the feed composition was kept at 60% propylene. The rest of the conditions were essentially the same. The results of these experiments are tabulated in Table 5.2.

Table 5.3 Results of catalytic behavior with different active components

Active components	Propylene conversion	Acrylic acid selectivity	Yield
	SDB-AECL		
10% Pd	40	91	11.7
10% Pd + 2% Ir	28	84	9.1
10% Pd + 2% Ir + 2% Pt	28	78	8.4
	HayeSep-Q		
10% Pd + 2% Ir	6.62	90.33	3.46
10% Pd + 0.2% Ru	19.12	90.56	10.02

As can be seen from the Table above, that the addition of iridium has a deleterious effect on the performance of the catalyst. Both the activity and the selectivity suffer in the presence of iridium. Addition of platinum along with iridium causes a further degradation in the selectivity towards acrylic acid. The second set of results again prove that iridium has a retrogressive effect, causing a significant decrease in the activity of the catalyst. Trace amounts of ruthenium on the other hand do not have any positive effect on the performance of the catalyst. Therefore it appears from these observations that palladium by itself is the best candidate for the conversion of propylene to acrylic acid and an addition of other metals causes a loss in activity and selectivity.

5.5 Effect of Pressure

The effect of pressure was determined by conducting the experiments at three different pressures: 100 psig (689.48 kPa), 120 psig (827.4 kPa) and 140 psig (965.27 kPa). The catalyst used for this purpose was 5% Pd on SDB-AECL. In each of the three cases the flow rate was maintained at 0.833 mL/s and propylene composition in the feed gas mixture was kept at 40%. The reactions were conducted at 140°C. The effect of pressure on propylene conversion and acrylic acid selectivity can be seen in Figure 5.4. It is observed that propylene conversion increases with an increase in pressure. Such behavior is expected as an increase in pressure would imply increased partial pressures of the reactants in the reactor. As will be seen later on, the rate of reaction is positive order in both the reactants, and hence an increase in partial pressure would result in an enhanced rate of reaction. Also, in accordance with Henry's law, higher pressure would augment the dissolution of the gaseous reactants into the liquid phase. Perhaps a consideration of the transport of the gaseous reactants to the catalyst surface at the microkinetic level would help to elucidate the points made above. Presumably, there are two modes by which the reactants could reach the surface of the catalyst. The first mode involves the transfer of the reactants directly from the gas phase on to the catalytic centers dispersed on the solid phase. As would be the case in slurry reactors, the catalyst is well dispersed in the liquid medium, and would make contact with the gas bubbles being sparged into the aqueous phase. Since the support is hydrophobic in nature, the pores will essentially be free of any liquid. In this event, the reactants would diffuse through a gaseous phase whenever a bubble makes contact with the catalyst particles. A second possibility

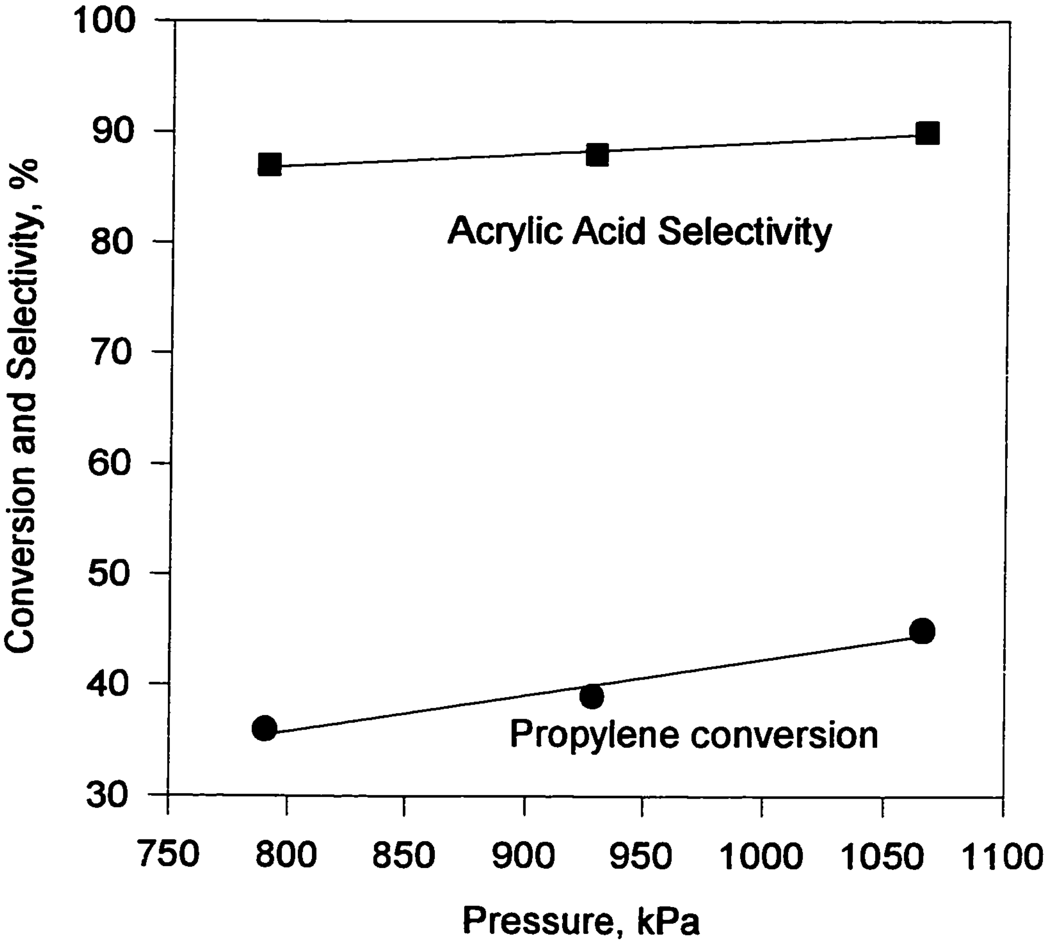


Figure 5.4 Effect of Pressure

constitutes the gas-liquid-solid route. The physical processes taking place in this mode begin with the mass transfer of the gaseous reactants from the gas phase to the liquid (water in the present case) through the gas-liquid interface; transport of dissolved reactants through the aqueous phase in the vicinity of the solid particle; transfer of the reactants at the external surface of the catalyst through the film surrounding the solid particle; and finally the reaction of the reactants at the catalyst surface. Each of these steps mentioned above in any one of the modes is aided by a higher pressure, resulting in a higher rate of propylene conversion. Based on the evidence presented by the results of the experimental runs, it can be speculated that direct gas to solid mechanism is predominant mode of the transfer of reactants to the solid surface. In any reaction that was conducted as part of this study, it was observed that the propylene conversions fell with the progress of time. This loss in activity of the catalyst during the course of a reaction can be related to the loss in hydrophobicity of the catalyst. As the reaction proceeds, an increasing amount of acrylic acid can be found in the reactor, which progressively decreases the surface tension of the liquid medium. If the Kelvin's equation stated in Chapter 3 is recalled, it can be inferred from this equation that a lower value for surface tension would cause the liquid to enter the pores, resulting in the wetting of the catalyst. As the pores get filled with the liquid, it becomes even more difficult for the gaseous reactants to reach the active sites located inside the pores, resulting in the catalyst activity to drop down. Had the second mode of transfer been dominant, such a decrease would not have been expected. Moreover, both oxygen and propylene are only sparingly soluble in water, lending credence to the supposition that the gas to solid mode of transfer is prominent in the present context. This reasoning is backed up by the observation that the hydrophobic catalyst actually sinks when immersed in a solution of acrylic acid, signifying a loss in the hydrophobic property of the catalyst. The critical juncture where the catalyst begins to sink occurs when the acrylic acid concentration is approximately between 5-6%. This was verified by immersing fresh samples of the catalyst in varying concentrations of acrylic acid.

Another possible reason which could contribute to the increased activity at higher pressure is that the reaction leading to the synthesis of acrylic acid from propylene is decreasing in the number of moles. In accordance with Le Chatelier's principle, an increase in pressure would drive the equilibrium in favor of the products. The effects of high pressure are easily observable in the experiment reported by Hinnenkamp *et al.*, where a pressure of 2150 kPa was used, and the authors were able to achieve a high yield of 11.0 (g acrylic acid/ g Pd-hr).

5.6 Effect of temperature

The experimental runs described in section 4.3 were carried out at different temperatures primarily to determine an optimum operating temperature for the reaction. Past studies show that the reaction for the conversion of propylene to acrylic acid over palladium catalyst is best carried out under mild conditions, and the surveyed literature shows that the reaction had been carried out in the range of 65°C to 120°C. These experiments were conducted with 10% palladium supported on SDB-AECL, with a uniform set of conditions of 0.833 mL/s feed flow rate, 40% propylene feed composition, and 120psi (827.4 kPa) system pressure. Figure 5.5 plots the propylene conversions versus time at five different temperatures of 87°C (360 K), 91°C (364 K), 103°C (376 K), 114°C (387 K) and 125°C (398 K). The figure clearly indicates an increase in the rate of reaction with the increase in temperature. Such behavior is expected considering the dependence of the rate constant on temperature, which can be explained on the fundamental level by the collision theory. The figure also shows that the conversion of propylene decreases with the progress of time in each of the cases. Figure 5.6 plots average propylene conversion and acrylic acid selectivity against temperature, and gives a better picture of the effects being brought about by the change in temperature. The average propylene conversion increases with the increase in temperature, but the increase is more pronounced at lower temperatures than at higher temperatures, there being a tapering of the propylene conversions at higher values of temperature. This suggests external-diffusion regime

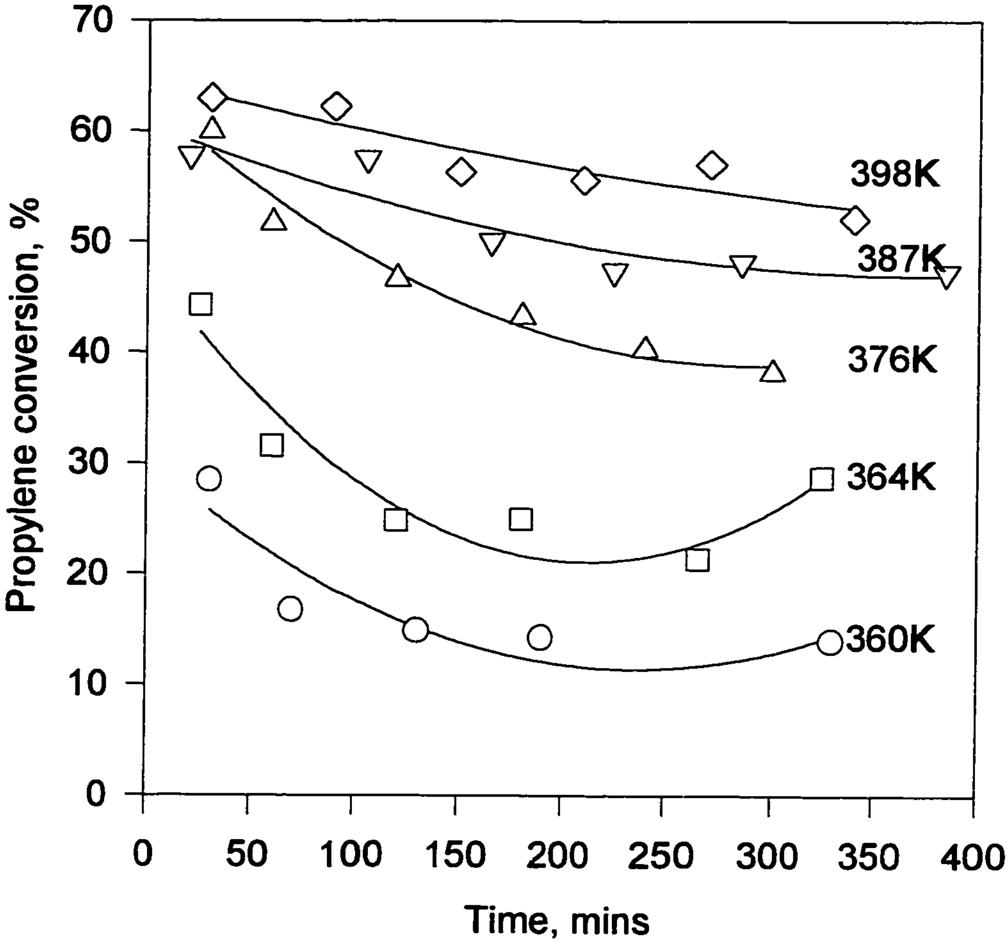


Figure 5.5 Propylene conversion vs time at different temperatures

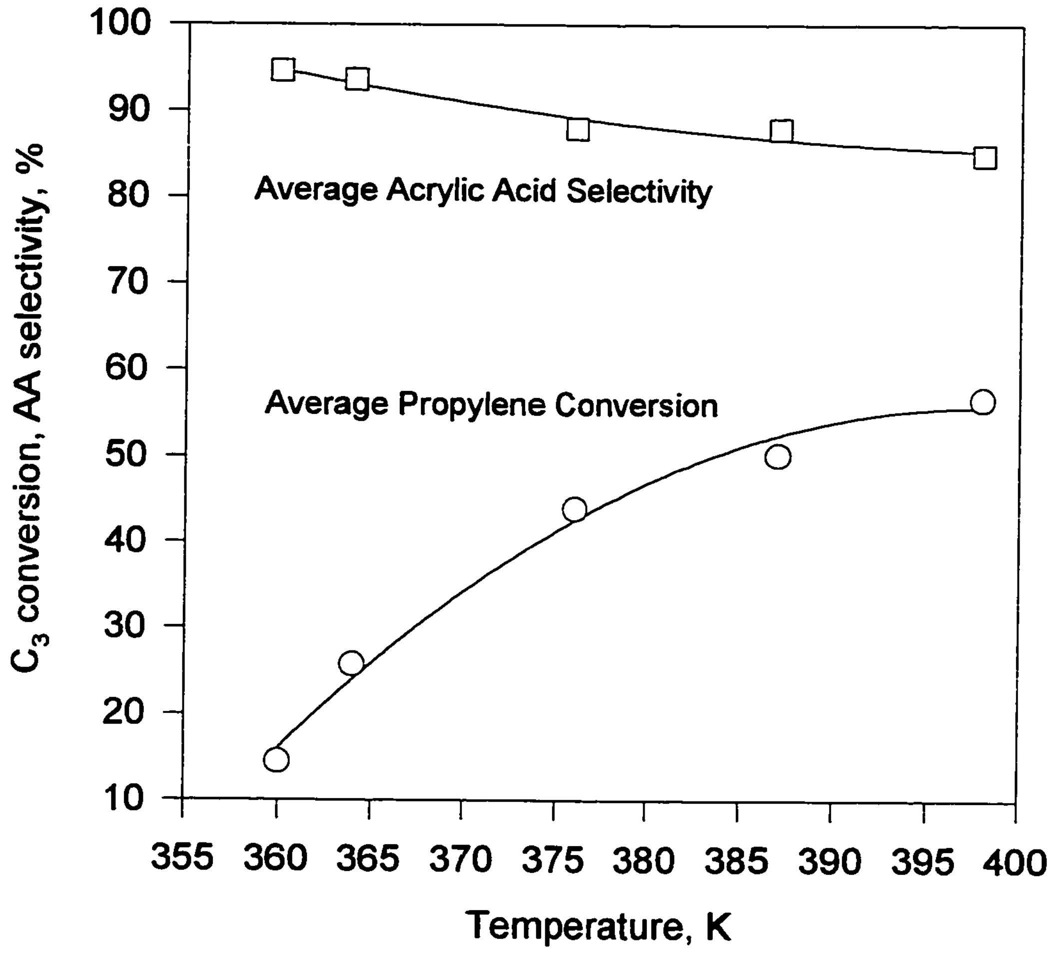


Figure 5.6 Effect of temperature on catalyst activity

being encountered at higher temperatures. The average acrylic acid selectivity on the other hand goes down with the increase in temperature. A possible explanation for the decrease in acrylic acid selectivity is that higher temperatures aid the oxidation of acrylic acid to carbon dioxide. To confirm that the principal source of carbon dioxide in the reaction was from the oxidation of acrylic acid, an experimental run was conducted with only oxygen (i.e. in the absence of propylene) being fed to the reactor containing the solution left after the completion of a normal run. This solution would primarily contain acrylic acid produced during the course of a single experimental run. In a normal run, where fresh catalyst was used with the usual supply of oxygen and propylene, the exit carbon dioxide flow rate varied from 0.00833 mL/s to 0.05 mL/s with the progress of time. In the run conducted with only oxygen fed to the reactor, the carbon dioxide flow rate was observed to be 0.045 mL/s. This value was attained relatively faster after an initial increase from a minuscule value, and remained constant thereafter. This observation lends credence to the supposition that as temperature is increased, more acrylic acid gets oxidized to carbon dioxide, affecting the acrylic acid selectivity. Also, an increase in temperature could cause side-reactions to proceed to a greater extent. This could be the case in the present system, as some of the side reactions like the production of acetic acid cause carbon dioxide to be given off, while the main reaction producing acrylic acid does not.

In such a case where activity and selectivity conflict with the change in temperature, it becomes necessary to choose an optimum temperature, where a balance between these two factors can be achieved. Higher temperature is not desirable because in addition to the promotion of the undesirable thermal reactions, it shortens the life of the catalyst. Based on the test results, the temperature of 103°C (376 K) seems to be an appropriate point for conducting the reaction, as reasonably high conversions are possible without sacrificing selectivity.

Since the plot of average propylene conversion against temperature suggests a mass transfer limited regime being encountered at higher temperatures, an Arrhenius type plot of logarithmic [observed rate (of propylene conversion)] versus the inverse of absolute temperature would confirm such a suspicion. In the absence of mass transfer limitations, the plot between log R and 1/T would essentially be a straight line, in accordance with the Arrhenius equation. However, if diffusion regimes exist and these are neglected in computing the rates used for the Arrhenius diagram, the plot will not be a straight line. Figure 5.7 depicts the Arrhenius type diagram for the present case, at 60 minutes past the initiation of the reaction., and strongly suggests that diffusion controlling phenomena are present. As pointed out in Figure 5.8 (C.N. Satterfield, 1980), three different catalytic regimes may be observed. This figure has been provided as a basis for reference, and bears a close resemblance to Figure 5.7. At sufficiently low temperatures the rate of the reaction will be so low that the potential required to provide the diffusion flux is insignificant and intrinsic kinetics will be rate controlling. With increased temperature, the rate of diffusion per unit potential difference (the diffusion coefficient) increases but slowly, as diffusivity is proportional to the square root of temperature, whereas the intrinsic rate constant rises exponentially. Hence a significant concentration gradient of the reactant then develops through the pellet (concentration gradients within the catalyst pores usually become significant before those in the ambient fluid). This second regime where pore diffusion becomes significant, is termed as the *internal-diffusion regime*. As the temperature is further increased, reactant is effectively consumed before it can penetrate far into the pellet. The concentration difference between the bulk of the fluid and the outside of the catalyst pellet becomes significant. In this reaction regime, often termed as the *external-diffusion* regime, the concentration of the reactant at the outside surface of the catalyst pellet approaches zero. The rate-limiting process is one of mass transfer from the ambient fluid and shows the same characteristics as bulk diffusion. An encounter of each of these regimes can be envisaged in the case of the catalysts being used in present investigation, with the progression in reaction temperature. These catalysts are essentially high surface area catalysts with small particle sizes in the range of 20-100 mesh. Due to the highly porous structure of these catalysts, which effectively relates to small pore sizes, rate limitations imposed by internal diffusion are expected to arise.

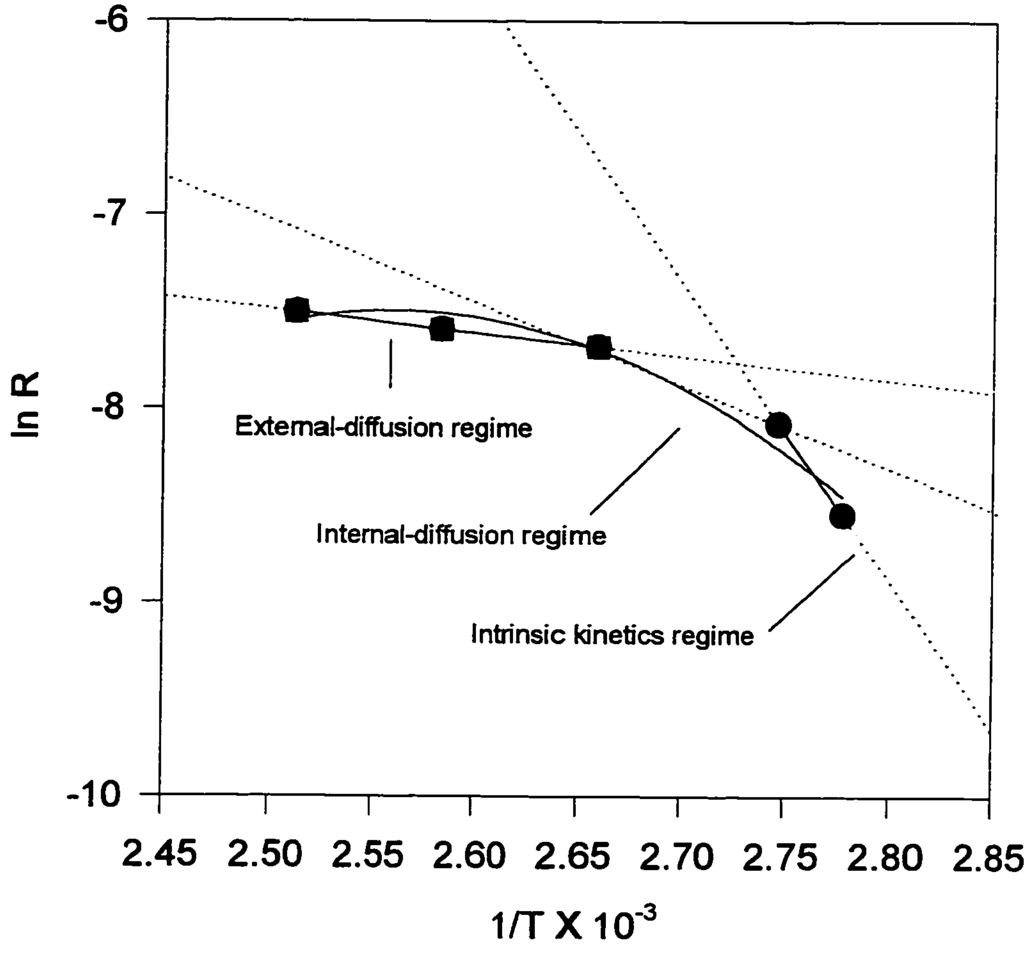


Figure 5.7 Arrhenius-type plot at 60 minutes

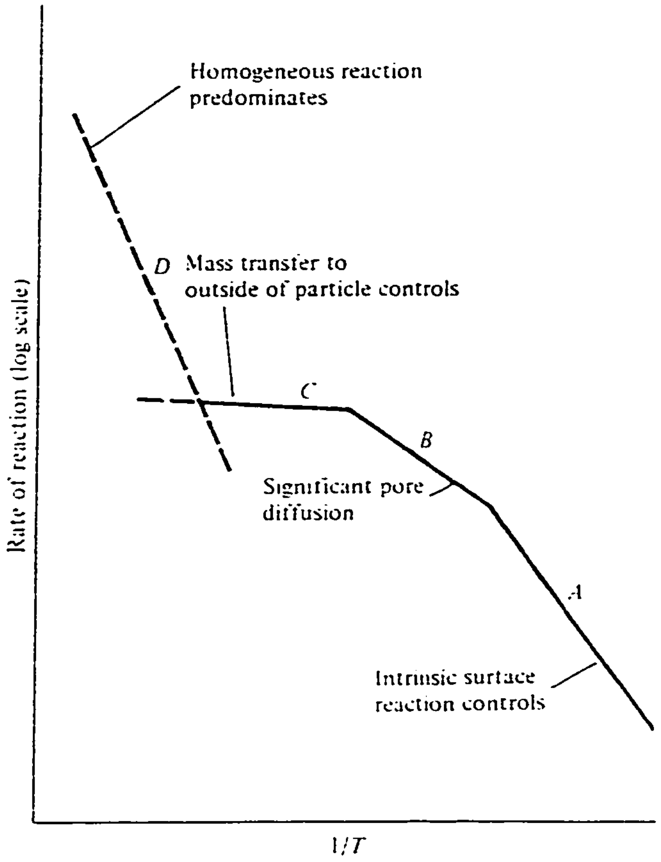


Figure 5.8 Possible kinetic regimes in a gas phase reaction occurring on a porous solid catalyst (C.N. Satterfield, 1980)

A theoretical explanation for this rate behavior with temperature can be proposed on a mathematical basis, if one considers the equations for bulk diffusion and surface reaction at steady state:

$$r = k_m a_m (C_b - C_s)$$
$$r = \eta k (C_{sA}) (C_{sB})$$

where C_b and C_s are the concentrations of the reactants in the bulk fluid and at the surface respectively (C_{sA} and C_{sB} represent surface concentrations of reactants A and B respectively, where A is assumed to be propylene and B to be oxygen). In the first expression, k_m is the mass-transfer coefficient between bulk gas and the solid surface, and a_m is the external surface area per unit mass of the pellet. In the second expression, k represents the observed reaction rate constant, and η is the effectiveness factor. At steady state, if the rates of diffusion and reaction are assumed to be the same, then

$$k_m a_m (C_b - C_s) = \eta k (C_{sA}) (C_{sB})$$

Assuming $C_A >> C_B$, i.e. assuming oxygen is the limiting reactant, then solving for C_{sA}, the concentration of propylene on the surface of the catalyst,

$$C_{sA} = \left(\frac{k_m a_m}{\eta k C_{sB} + k_m a_m}\right) C_{bA}$$

Then the net rate of reaction can be written as:

$$r = \eta k \left(\frac{k_m a_m}{\eta k C_{sB} + k_m a_m}\right) C_{bA} C_{sB}$$

At high temperature, the reaction rate constant k will be much greater than the diffusion coefficient k_m. Under these conditions, the rate of reactant depletion at the surface of the catalyst will be much faster than its replenishment permitted by diffusion to the outer surface of the catalyst. This implies that,

$\eta\ k\ (C_{sB}) >> k_m\ a_m$ and the expression for rate reduces to:

$r = k_m\ a_m\ C_{bA}$

The reaction order essentially reduces to one, because the mass transfer across the bulk fluid is a first order process.

At the other extreme, when the temperature is low,

$k_m\ a_m >> \eta\ k\ (C_{sB})$

$r = \eta\ k\ (C_{bA})\ (C_{sB})$

$r = \eta\ A_0\ e^{-E/RT}\ (C_{bA})\ (C_{sB})$

In this case the mass transfer resistance is small compared to the kinetics of the surface reaction. The last equation explains the linear increase of log rate with temperature at lower values. In the case where mass transfer effects are significant, and these limitations are neglected, the Arrhenius expression if used to compute the activation energy, would give an apparent activation energy, different from the true activation energy observed in the case of intrinsic kinetics. A quantitative evaluation of the apparent activation energies can be made from the slopes of the Arrhenius plot for the three controlling regimes described earlier in this section. Table 5.3 lists the values for each of the three cases. Alongside the general range of values of the activation energies for heterogeneous reactions expected in these three regimes is provided as reference (Farrauto *et al.*, 1986). The values for activation energy obtained for the present case are in close agreement with those presented by the reference. These values serve as a means for the assessment of the rate limiting step, and support the observations made from the Arrhenius plot in Figure 5.7.

Table 5.3 Apparent activation energies obtained from Arrhenius plot

Controlling Regime	Activation Energy kcal/mole	Reference values
Chemical or Kinetic Control	30.57	E ≥ 8 kcal/mole
Pore Diffusion Control	8.958	E ≥ 4-8 kcal/mole
Mass Transfer Control	2.437	E < 4 kcal/mole

5.7 Effect of feed composition

To test the effect of feed composition, the propylene to oxygen ratio in the feed was varied between 0.33 to 3, in the following configurations:- 1:3, 1:2, 1:1.5, 1:1, 1.5:1, 2:1, 3:1., All other conditions were kept constant. Although the relative proportions of propylene and oxygen can be varied widely, but for safety reasons explosive mixtures should be avoided. The explosive limits for propylene in molecular oxygen lie in the range of 2.1-53% propylene, placing propylene to oxygen ratios above 1.5:1 in the safe zone of operation. Figures 5.9, 5.10, 5.11 depict the propylene conversions, oxygen conversions and the carbon dioxide selectivity respectively, with the passage of time. The feed mixture with the lowest propylene concentration gives the highest propylene conversions. This is explicable as propylene is the limiting reactant at this composition, and a greater percentage of it reacts. The propylene conversions decline with the increase in the propylene to oxygen ratio, the lowest conversions being displayed at the ratio of 3:1. Oxygen conversions show a similar trend in the reverse direction with respect to the propylene concentration in the feed. It can be seen that for the first four ratios, i.e. 3:1, 2:1, 1.5:1 and 1:1, the oxygen conversion goes through a maxima with respect to time, and then drops off. This is because oxygen is a limiting reactant in these cases, and the oxygen consumption rises to a maximum before the decreasing rate of reaction pulls the rate of oxygen conversion down. For the remaining ratios, where oxygen is present in

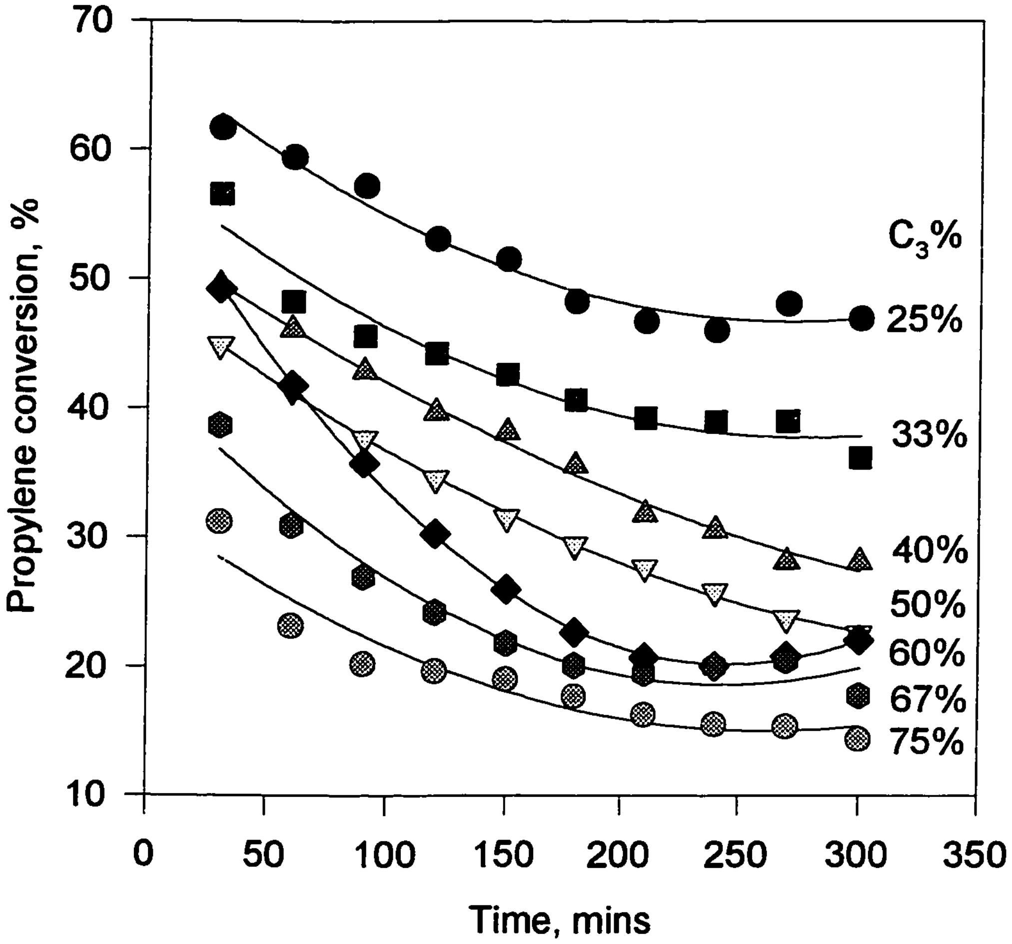


Figure 5.9 Propylene conversions vs time at varying feed compositions

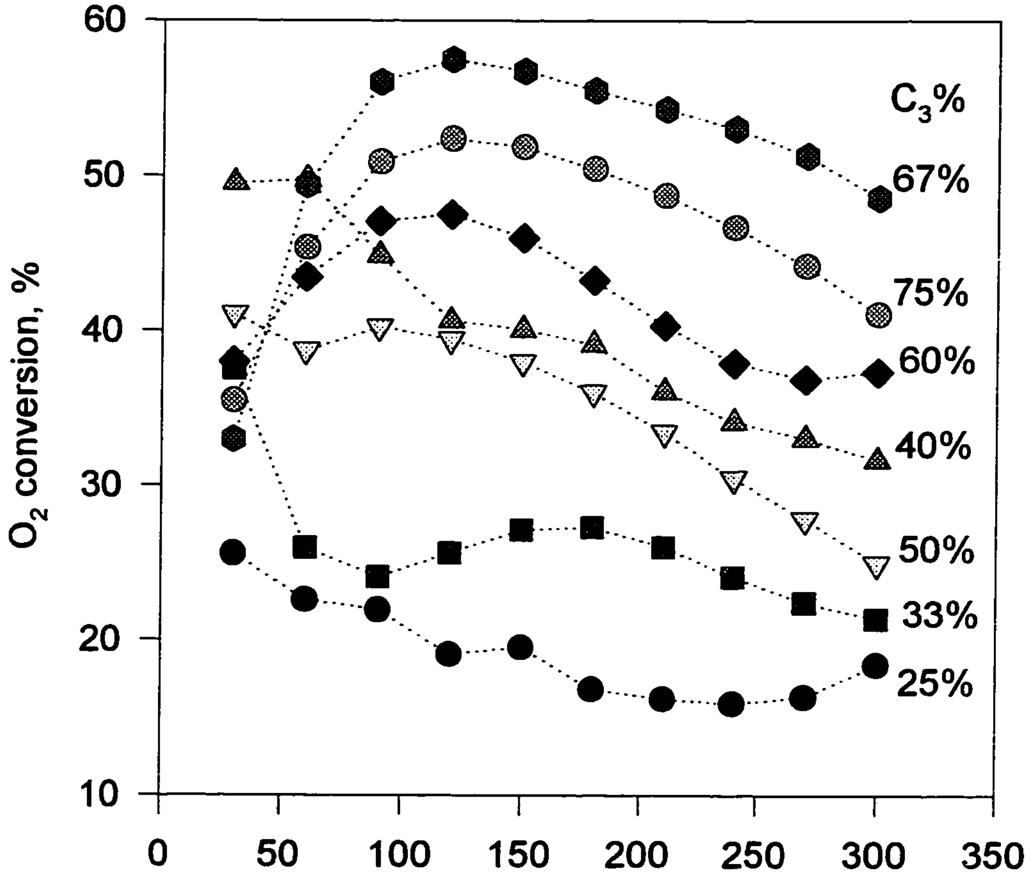


Figure 5.10 Oxygen conversions vs time at varying feed compositions

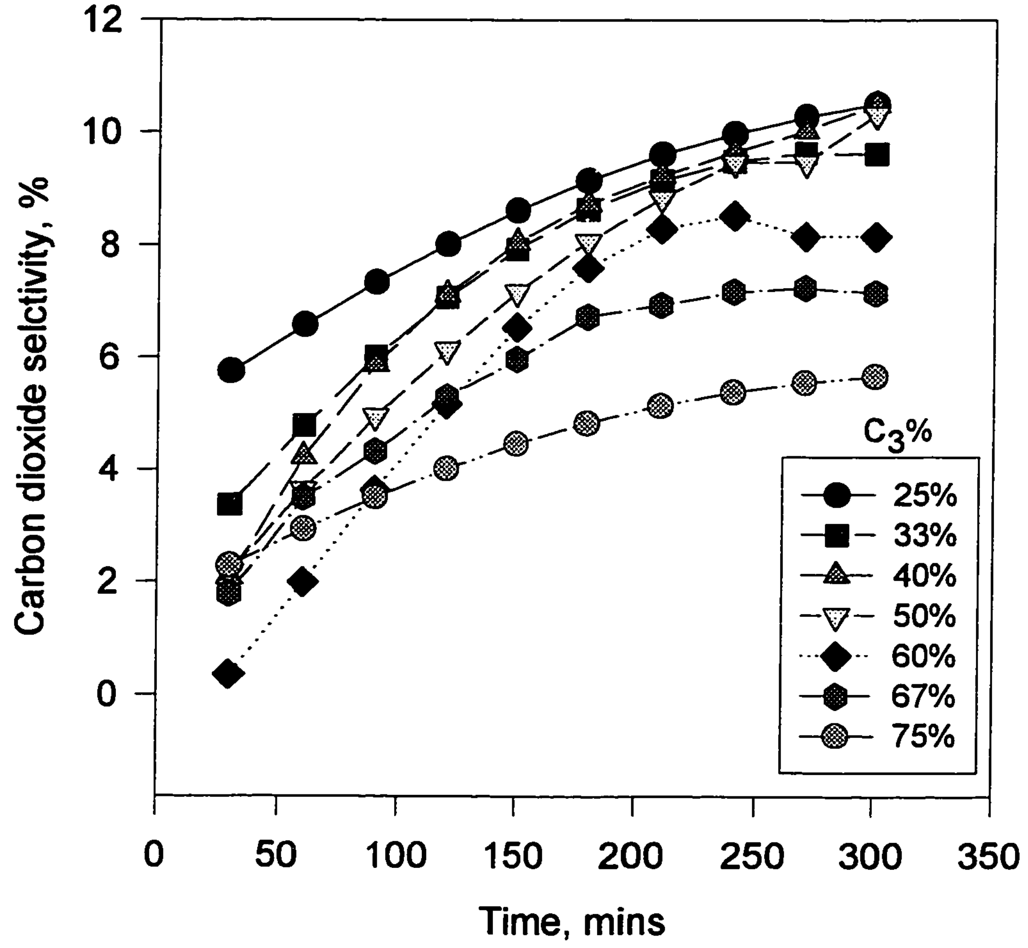


Figure 5.11 Carbon dioxide selectivity vs. time at varying feed compositions

sufficient quantity, the conversions drop off uniformly. The carbon dioxide selectivity, which signifies the rate of carbon dioxide production increases with time, but shows a tapering off towards the end of the experiment, suggesting a constancy being reached after a period of time. The increase in selectivity can be explained on the basis that with the passage of time more acrylic acid is available for oxidation to carbon dioxide. Also the side reactions like production of acetic acid and acrolein, which give off carbon dioxide may proceed to a greater extent. A similar reasoning can be applied to the fact that carbon dioxide selectivity is more at lower concentrations of propylene in the feed. This is shown in Figure 5.11. At these ratios, more oxygen is available for oxidation as the flow rate is maintained constant, implying more oxygen available for the conversion of acrylic acid to carbon dioxide. Thus it can be said that the acrylic acid selectivity increases with the prevalence of propylene concentration in the feed.

However, the rate of propylene conversion, defined as the moles of propylene converted per gram of catalyst per minute, presents a different picture, and does not follow the same trend as the propylene conversion with respect to the feed composition. Figure 5.12 plots the rate defined above against time for varying feed compositions. The highest rate of reaction is exhibited at the feed ratio of 1.5: 1. The rate however decreases with the progress of time. It would be worthwhile to plot the rate at different times against the propylene to oxygen ratio to illustrate this behavior. In Figure 5.13 it becomes quite clear that the rate passes through a maximum value which occurs somewhere between the propylene to oxygen ratio of 1 and 1.5. The nature of this plot also proves that the reaction is positive order with respect to both reactants. Since the plot has been constructed for various reaction times, the rate is seen to be decreasing with the progress of time.

The nature of the data collected for these experimental runs allows a preliminary kinetic evaluation, since the reactor outlet gas composition assays were made periodically at equal intervals in each of the cases. A linear regression performed between the instantaneous rate of propylene consumption per unit time, per gram of catalyst (which

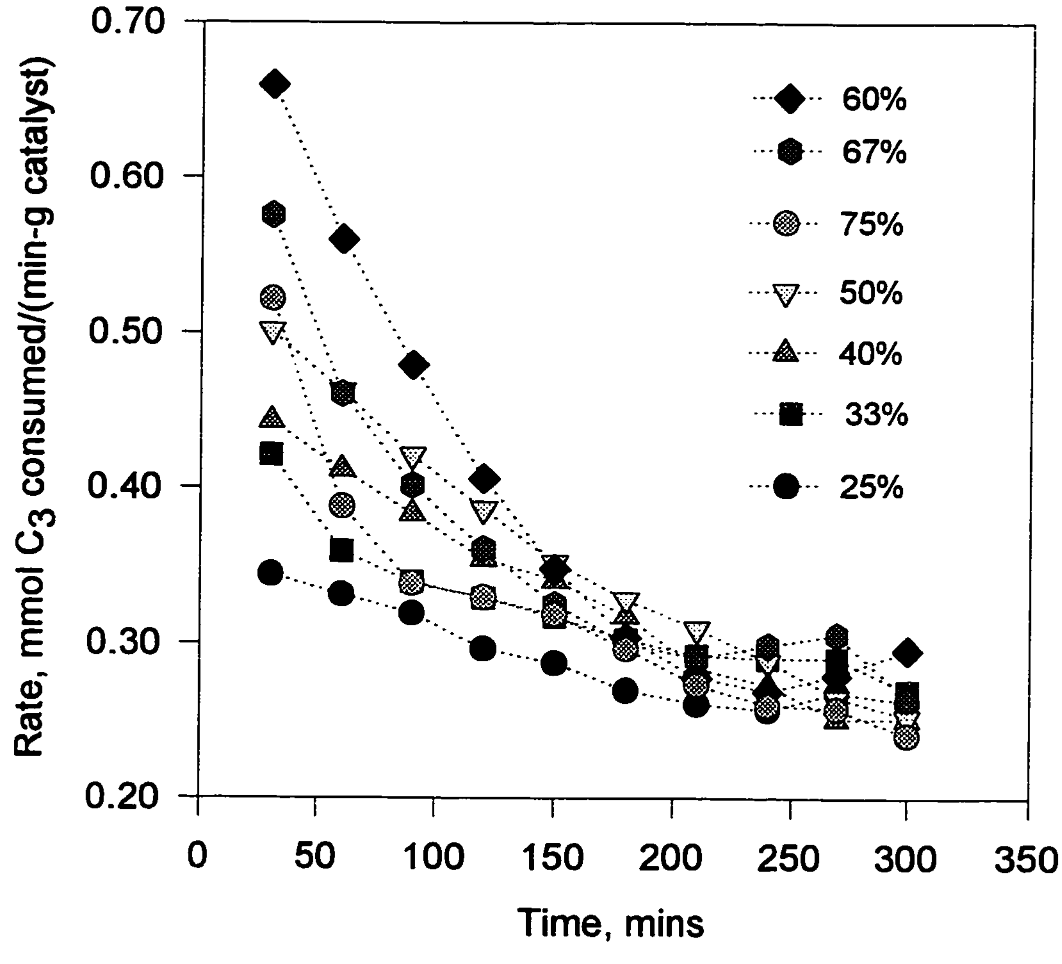


Figure 5.12 Rate of propylene conversion vs time for varying feed compositions

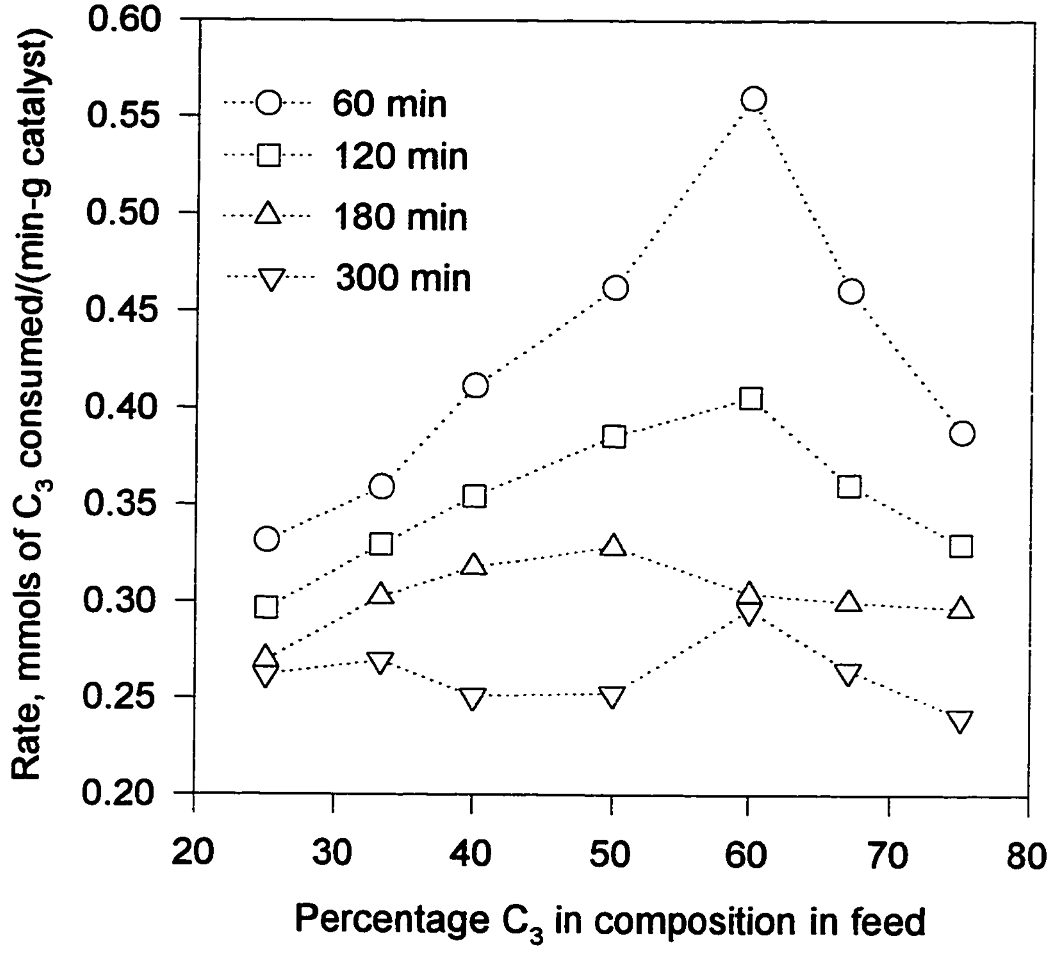


Figure 5.13 Rate of propylene conversion vs feed composition

can be referred to as the heterogeneous rate) and the reactant concentrations inside the reactor, estimates the rate constant and the order of the reaction with respect to the reactants. It should be mentioned that the observed rate of reaction is representative of the global or overall rate of reaction, and does not refer to the intrinsic rate of reaction. Therefore the regression has been performed by using the overall rate of reaction. The reactant concentrations used in this regression were taken to be the outlet concentrations in the gases exiting the reactor, on the assumption that the reactor can be modeled as a continuous-flow, stirred tank reactor, and the reactants are perfectly mixed in the entire reactor volume, such that the reaction mixture is uniform in all parts of the reactor. Since the gas flow is maintained on a continuous basis, the gaseous composition in the exit stream can be essentially equated to the concentration inside the reactor. It should be mentioned that the rate constant in this case has not been evaluated by the simultaneous solution of the equations for the rate of reaction and mass and energy transfer. If all these equations are linear in the concentrations and temperatures, an analytical solution is possible. If any of the equations are non-linear, numerical solution becomes necessary. In the present study, the non-steady nature of operation of the reactor, introduces non-linear terms into the mass transfer equations. Also the presence of a multitude of reactions increases the complexity of the equations. A numerical solution of these equations was constrained by the lack of sufficient data, and also by the fact that product analysis was done only at the end of the experimental run. A more formal treatment based on a mechanistic model has also not been attempted. Thus what has been attempted is an empirical correlation between the rate of the reaction and the concentrations of the reactants to develop a power-rate equation. Essentially this is the Arrhenius expression with power functions of reactant concentrations, the exponents being arbitrary adjustable constants, the rate being the observed global rate of reaction, with mass-transfer and internal diffusion effects possibly being included.

The values of the rate constant obtained by the linear regression performed between the instantaneous rates and the concentrations of the reactants for varying feed compositions are plotted against time in Figure 5.14. These results are in agreement with the decreasing rate of reaction. The shape of the curve for rate constant follows the trend exhibited by the propylene conversions or the rate of the reaction for that matter. However due to the transitory nature of the rates and the concentrations measured at instantaneous points of time, the regression does not yield constant values of the order with respect to the reactants. These values are listed in Table 5.4. The orders of the reaction with respect to both propylene and oxygen display a decreasing trend with the passage of time, and seem to commensurate with the falling rates and rate constants. The reaction orders are positive with respect to both the reactants, however there is more dependence on concentration of propylene than on that of oxygen.

5.8 Stability tests

Activity and selectivity are not the only criteria that influence the ultimate industrialization of the catalyst. It becomes imperative to exclude from the list of contender catalysts which are not likely to be stable under operating conditions because of such things as poisons in the feed, loss of active agents, inactivation by one or more products, or loss of activity due to crystallographic changes. A catalyst with good stability will change only slowly over several years under conditions of use.

To test the stability of the catalysts employed in the present investigation, the catalysts were subjected to extended cycles of reaction. The catalyst was recovered after each run, washed thoroughly in water and dried for use in the next experimental run. The stability of the catalysts were determined by following the changes in activity during the course of the operating conditions. The operating conditions in each successive experimental run were maintained constant. It should be mentioned that the activity of the catalyst fell during the course of a reaction for reasons which are attributable to the loss of hydrophobicity of the catalyst. This has already been discussed in Section 5.5. Also the increasing amounts of acrylic acid in the reactor as a result of its accumulation, suppress

the forward rate of reaction towards the desired product. However, the conversions should recover in the successive run to values displayed in the prior runs, once the catalyst has been washed and the reaction resumed under fresh conditions. Some loss of activity is expected in the initial stages, before the catalyst activity reaches a constant value. Theoretically this value should remain unchanged over long periods of time, if industrial implementation is being contemplated. Or alternatively, there should be means by which the catalyst could be easily regenerated, if the catalyst loses activity in a relatively short period of time.

Figure 5.15 shows the propylene conversions against time over 8 cycles of reaction, carried out with 10% Pd on SDB-NHL. The runs were conducted under a system pressure of 120 psi (827.4 kPa) at 103°C and 60% propylene feed composition in a total gas flow rate of 0.833 mL/s. The figure shows that the propylene conversions decrease with each successive run. The initial conversion is not able to bounce back to the value displayed in the preceding run. Figure 5.16 plots the average acrylic acid yield over the runs, and gives another representation of the decreasing trend in the catalyst activity. A similar trend was observed in other catalysts which were tested beyond the initial run. In the experimental program adopted as part of this investigation, any catalyst which showed some promise was usually subjected to five cycles of testing. Based on an observation of the average conversions during these runs, and the results evident from the Figures 5.15 and 5.16, there is an unmistakable deactivation of the catalysts, resulting in a decrease in the propylene conversions. This poses a serious problem with regard to the upgradation to pilot-scale stage of testing, and stalls any chance whatsoever of commercialization of the process. It thus becomes mandatory to investigate the causes of deactivation of the catalyst and to explore possibilities of regeneration of the catalyst. It should be stated that a rigorous and comprehensive investigation of the deactivation process is a daunting task, and is outside the scope of this thesis. However a preliminary inquiry to ascertain the cause(s) of the loss in activity of the catalyst was attempted. A general discussion of the causes of deactivation of a catalyst is presented, and alongside the reasoning for acceptance or rejection of a cause for the inactivation of the hydrophobic catalyst used in

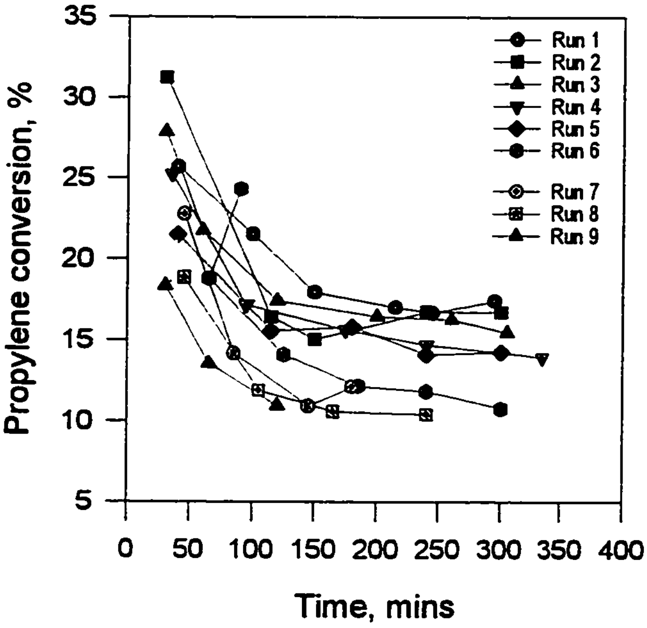


Figure 5.15 Aging Tests (C_3 conv. vs time)

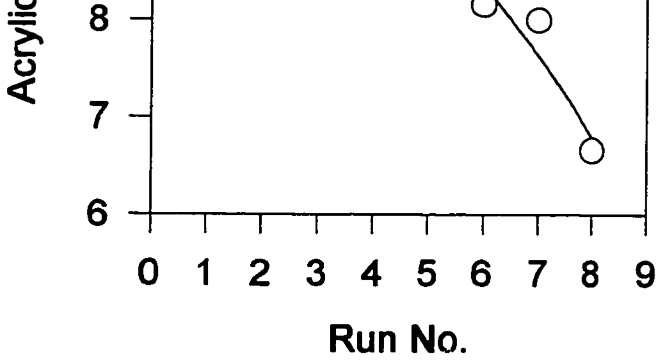


Figure 5.16 Decrease of acrylic acid yield with each successive run

this study is also furnished, based on evidence collected from certain tests performed on the catalyst.

There are three main classes of catalyst deactivation: chemical, thermal and mechanical. Both thermal and mechanical deactivation have been ruled out for the present case, as the support styrene divinylbenzene is known to be thermally stable up to a temperature range of 250-300°C, and is a mechanically strong support. The temperatures under which the oxidation reactions were carried out lie in the range of 80-140°C, much below the temperatures at which the support loses its stability. Also inspection of the catalyst reveals that the catalyst suffers no physical damage such as abrasion or deformation due to the stirring action inside the reactor.

Chemical deactivation involves a chemically induced change in catalyst activity. This change may be related to the loss of active species; to the physical blockage of the pore structure (fouling); to the competitive, reversible adsorption of the poison precursor (inhibition); or to the irreversible adsorption, deposition, or reaction of the poison precursor on or with the surface (poisoning); or to the poison induced restructuring of the surface. These may occur singly or in combination, but their net effect always is to remove active sites from the surface.

Loss of active species means the leaching of the noble metal into the liquid phase. The catalyst in this case was subjected to vigorous agitation in acrylic acid solution (6% by weight) for a period of 5 days, and tested for any traces of palladium in the solution. No such loss of the active components in the surrounding solution was observed. These tests were conducted by the Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES) method of detection in the Department of Chemistry. Fouling of the catalyst by physical blockage by deposits of dust or fine powder deposits is also excluded because of the absence of impurities in the feed or the possibility of the production of coke.

Catalyst poisoning can be classified into three main categories: poison adsorption, poison-induced surface reconstruction, and compound formation between poison and the catalyst. According to the precursor of the poisoning event, impurity poisoning may be distinguished from self-poisoning; in the latter case one or more of the reaction participants (reactants, products, intermediates) serve as poison precursors. There are numerous ways in which adsorption of poisonous species can affect catalytic activity, but one of the most common mechanisms is through the competitive adsorption with reactant species. Poison adsorption can be termed as reversible or irreversible, where reversibility is either defined by the recovery of the activity of the catalyst upon removal of the poison from the feedstream under actual reaction conditions, or by the recovery of activity upon changing the feedstream or the operating conditions (regeneration). Inhibition is the consumption of active sites by the competitive, reversible adsorption of a poison precursor on the sites, effectively reducing the active centers for the desired reaction to take place. The possibility of inhibition is ruled out for the present case of deactivation, because of the preclusion of any impurity in feed stream, which may adsorb on the surface. As an extension of the reasoning above, it can be satisfactorily concluded that there is no impurity poisoning in the present context because of the lack of any such poison from an external source. This directs the investigation into the deactivation process towards the possibility of self-deactivation or self-poisoning by a reaction product. This poisoning may be due to purely physical means or could be the result of a chemical combination between the poison precursor and the catalyst. In addition to poison adsorption, chemically induced surface reconstruction may also significantly alter the state of activity of the catalyst. An example of this kind of poisoning is the surface morphological changes brought about by sulfur in the crystal structure of nickel. However the most serious form of catalyst deactivation is represented by compound formation between a poison precursor and the catalyst. This is sometimes indistinguishable from the stronger chemisorptive interactions discussed earlier. An example of this kind of poisoning is the sulfur poisoning of base metal catalysts in an oxidizing environment, such as in automobile exhaust. Another possibility for deactivation is by the carbonaceous deposits on the catalyst, by the process which is generally referred to as coking, and described by some researchers as self-poisoning. These carbonaceous deposits are a consequence of side reactions and are considered to be macromolecules of empirical composition approaching CH. Coking differs from poisoning in that the deactivation effect is accomplished primarily by the covering over of the active sites by the macroscopic deposits; and the reactants are denied access to the active sites by physical screening rather than competitive chemisorption at work in poisoning. These deposits build up to the point where they block the pores in the internal volume of the catalyst, restricting access of the reactive molecules to the active surface. Yet another deactivating mechanism could arise due to support effects, whereby the support may either adsorb a poison or react with it. Indeed, the exclusion of this mode of deactivation cannot be made, considering the polymeric nature of the support offering reactive nodes for polymeric products of this reaction. Having listed the causes which could be responsible for the deactivation in the present context, it is most likely that the deactivation is as a result of the last two modes described, namely physical blockage by a product tantamount to fouling, or the product poison precursor support interaction. The possibility of product interaction with palladium has remote chances, either in the adsorptive form, surface reconstruction of the crystallite structure, or reactive coupling. It should be noted that there is a presence of minute quantities of bye-products as indicated by the liquid chromatography analysis, as also evident from the color imparted to the incumbent liquid in the reactor. Acrylic acid is colorless, as also the other prominent products acetic acid and acrolein. The surrounding aqueous liquid should also imbibe the same color, but it has a yellowish tinge imparted by the presence of reaction by-products. These products are essentially organic in nature, primarily polymerization products of acrylic acid. Free radical initiated polymerization of the double bond is a very common reaction for acrylic acid and presents a troublesome aspect of its manufacture. On storage or at elevated temperatures, acrylic acid has a tendency to dimerize easily. It is quite possible that other polymeric products are also being produced as a result of interaction with other products. In the present situation, it is speculated that the polymeric product, which is macromolecular with relatively large physical dimensions, causes the physical blockage of reactive species to the active sites on the surface of the catalyst. A more serious concern arises from the possibility of the reaction of this product(s) with the polymer support.

Although the root cause of the deactivation can at best be presented as speculative, there is conclusive evidence of the actual deactivation taking place on the basis of certain characterization studies undertaken. The results of these tests buttress the observed loss in activity of the catalyst. A BET surface area measurement of the catalyst before and after use shows a considerable decrease in surface area. The catalyst put to test in this case was 10% Pd on HayeSep-Q. The fresh catalyst had a surface area of 637 m^2/g, which dropped to 237 m^2/g after five runs. This represents a drop of almost 63% in a span of five cycles of reaction i.e., roughly 30 hours of operation, suggesting significant coverage of active surface area on the catalyst. This is further concluded from the examination of the Infra-red Spectroscopy spectra for identical cases of observation, i.e., before and after use of the catalyst. Figures 5.17 (a) and (b) show the spectra for the two cases. These characterization studies were also performed on the same catalyst, i.e. 10% Pd on HayeSep-Q. Figure 5.17 (a) depicts the spectroscopic spectra for a fresh catalyst, and shows the absorption band for benzene skeletal structures (Bellamy *et al.*, 1980), known to occur at frequencies of 800 to 1600 cm^{-1}. The second figure clearly show absorption frequencies around the bands for the aromatic rings, and at frequencies of 3000 cm^{-1}. An inspection of the organic group absorption frequencies shows that α,β-unsaturated carboxylic acids have strong absorption bands in the frequency range of 1680-1715 cm^{-1}, suggesting that these could belong to acrylic acid or a dimeric form of it. However the exact compound cannot be identified, based on the information provided by these studies. But it does provide the basis to speculate on the nature of the poisoning agent.

Further qualitative support for the deactivation of the catalyst is provided by X-Ray Diffraction (XRD) tests conducted on the same catalyst. The larger the crystals of a given component the sharper the peaks on the x-ray diffraction pattern for each crystal plane. Thus, the breadth of the peak can be related to the crystal size which subsequently relates

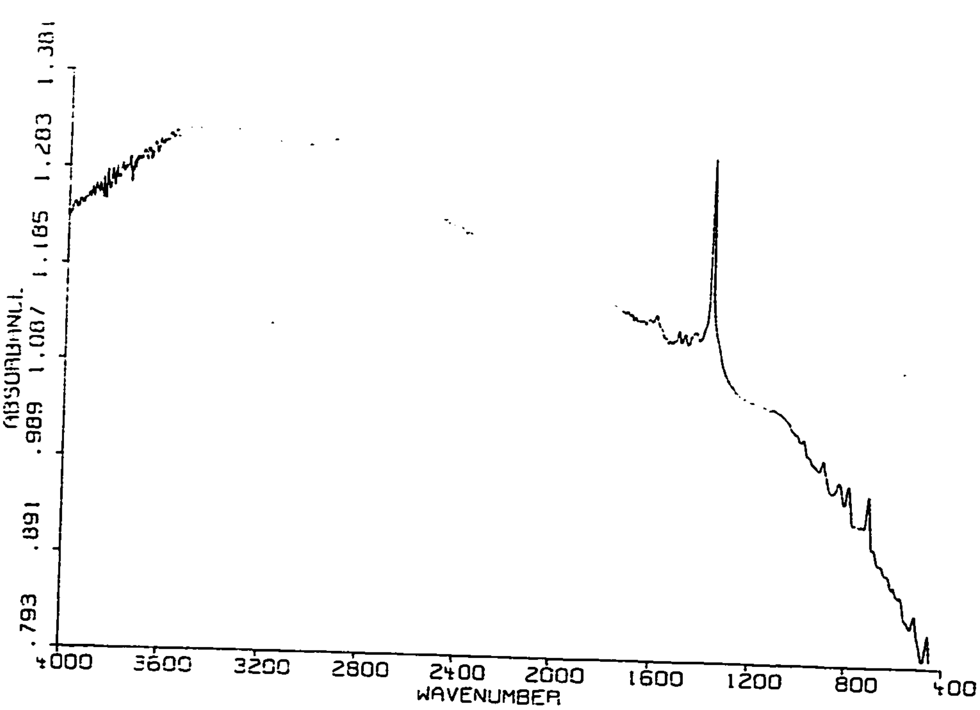


Figure 5.17 (a) IR spectroscopic pattern for fresh catalyst

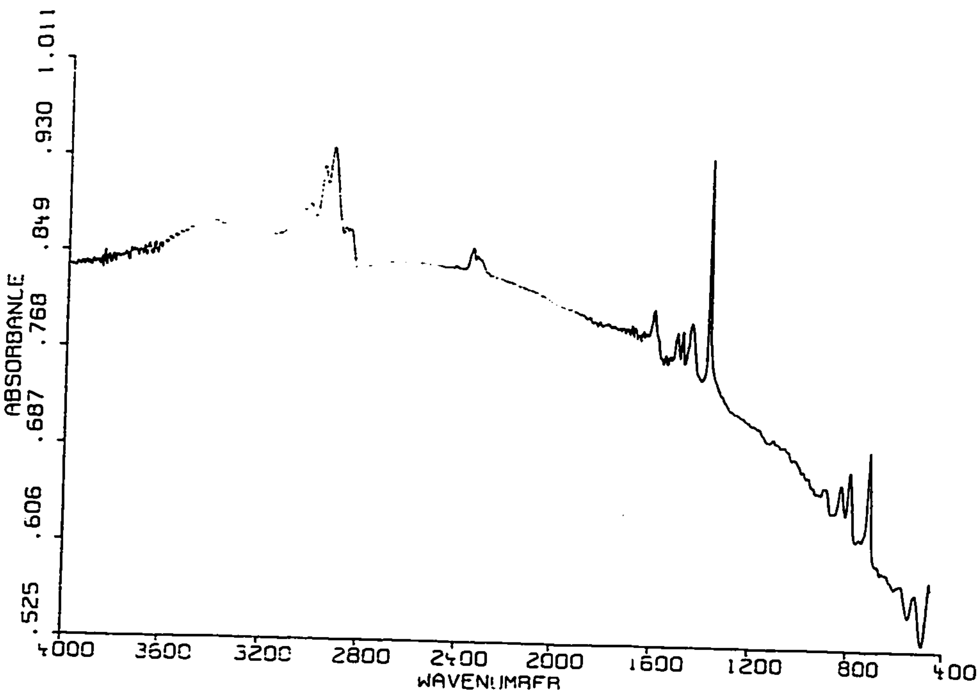


Figure 5.17 (b) IR spectroscopic pattern for used catalyst

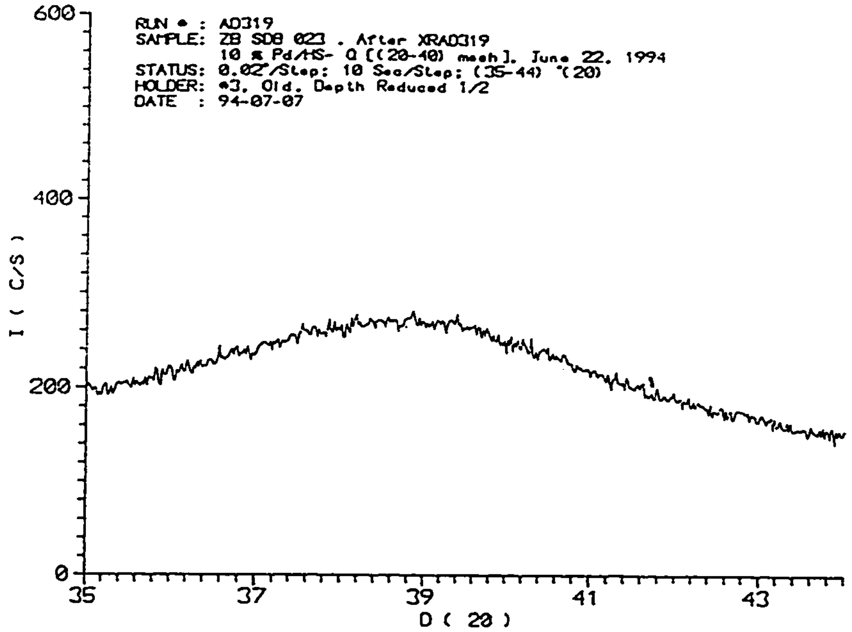


Figure 5.18 (a) X-ray diffraction pattern for fresh catalyst

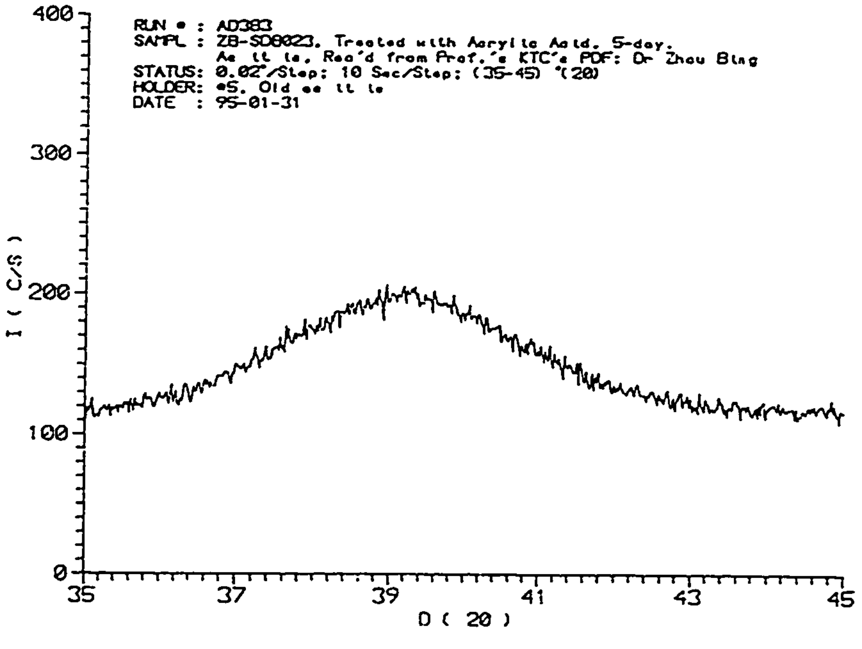


Figure 5.18 (b) X-ray diffraction pattern for used catalyst

to the catalytic components available to the reactants, i.e., the catalytic area. The breadth at half peak height of an x-ray diffraction line is inversely proportional to the size of the crystallites. Figures 5.18 (a) and (b) show the diffraction patterns obtained for the fresh sample of 10% Pd on HayeSep-Q and that of the used catalyst. It can be observed that the diffraction pattern for the fresh catalyst is broad, and there is an accentuation of the peak for the used catalyst, denoting a growth in the size of the crystallite particle. This suggests that sintering of the supported metal catalyst could be yet another mechanism by which the catalyst loses its activity. However, this seems to be only transitory phenomenon in the initial stages of the catalyst utilization. Indeed, the growth of palladium crystallites is significant only after the first run. This observation is supported by the fact that the maximum drop in propylene conversion takes place after the first run for the catalyst. Finally, sintering is a phenomenon which occurs via actual structural alteration of the catalyst, and is most commonly a thermally activated process with a physical basis, rather than a chemical one. Apart from the initial restructuring that is not precluded, the possibility of continued deactivation by sintering is not envisaged in the present case. Therefore the deactivation can be sufficiently concluded to have been caused by either the physical coverage of active sites or the blockage of pores by a reaction product, or the chemical combination of this reaction product with the polymer support.

Chapter 6

Summary and Conclusions

A **hydrophobic** catalyst process for the single-step oxidation of propylene to acrylic acid was developed. Several catalysts containing various ingredients on different supports were examined for their ability to efficiently oxidize propylene to acrylic acid. Palladium metal dispersed on styrene divinylbenzene copolymer (SDB) proved to be the most effective catalyst for the required conversion. The hydrophobicity of styrene divinylbenzene copolymer resulted in significant improvements in propylene conversions over palladium supported on conventional supports used by other researchers in the past. Of the various SDBs that were tested, the highest activities were displayed by Porapak-Q and HayeSep-Q, both supports being characterized by high surface areas.

During the course of process development, the behavior of the catalyst under various operating conditions was observed. It was found that the catalyst was better dispersed at lower metal loadings, but reaction rate was higher at higher loadings of palladium. The addition of other catalytic components like platinum, iridium or ruthenium had a deleterious effect on the catalytic activity. Increasing pressure and temperature had a favorable influence on propylene conversions. However selectivity towards acrylic acid was found to deteriorate with the increase in temperature, due to the increase in oxidation of acrylic acid to carbon dioxide. In addition an Arrhenius type plot for logarithmic rate versus temperature revealed the presence of both internal and external mass transfer regimes being encountered at higher temperatures. Feed composition also played an important role in the rate of reaction. The heterogeneous rate of reaction was observed to go through a maxima with varying feed composition. This maximum rate was displayed at 60% propylene in the feedstream. This observation also conclusively indicated that the rate was positive order with respect to both the reactants. However, propylene conversion and the reaction rate were found to decrease with chronological time during the progress of the reaction. Accumulating amounts of acrylic acid in the reactor is speculated to be the reason behind the loss in activity, resulting in the loss of hydrophobic attributes of the catalyst due to a decrease in the surface tension of the surrounding aqueous solution. Apart from this abatement in the activity of the catalyst while the reaction was in progress, there was a decrease in the intrinsic activity of the catalyst when it was tested for more than one experimental run. All the catalysts that were examined displayed this deactivation when subjected to extended cycles of reaction.

This deactivation of the catalyst is a disturbing phenomenon, and stands as a stumbling block in the way of upgradation of the process to the pilot-scale stage of testing. Moreover, it jeopardizes the objective of this research undertaking to ultimately carry the process to the commercial stage. Although a detailed investigation into the deactivation process was not possible, with the help of deductive reasoning and the evidence collected by certain characterization studies, the loss of activity could be linked to self-deactivation by a reaction product. This deactivation could either be due to the physical coverage of active sites or pore blockage by the reaction product or the chemical combination of this product poison with the polymer support.

It is mandatory that the exact reason for the deactivation process be ascertained, so that a preventive measure could be devised or suitable steps could be taken to explore the possibility of regeneration of the catalyst. This would only be possible if an appreciation for the chemistry of the reactions involved is developed, assisted by further characterization studies. A possible solution could lie in the use of polymerization inhibitors like hydroquinone or butylated hydroxytoluene (BHT). Amongst other things which need further thought and experimentation is the problem of separation of product acrylic acid from the aqueous solution it dissolves into. Due to the loss of activity of the catalyst resulting from the decrease in surface tension of the liquid, it becomes necessary to remove the solution at an acrylic acid concentration no greater than 6%, so as to maintain the hydrophobic nature of the catalyst. This is a very dilute solution of acrylic acid, and the recovery procedure has to take into account the costs involved. At this concentration, distillation would prove to be expensive. The answer would probably lie in solvent extraction or membrane separation technologies.

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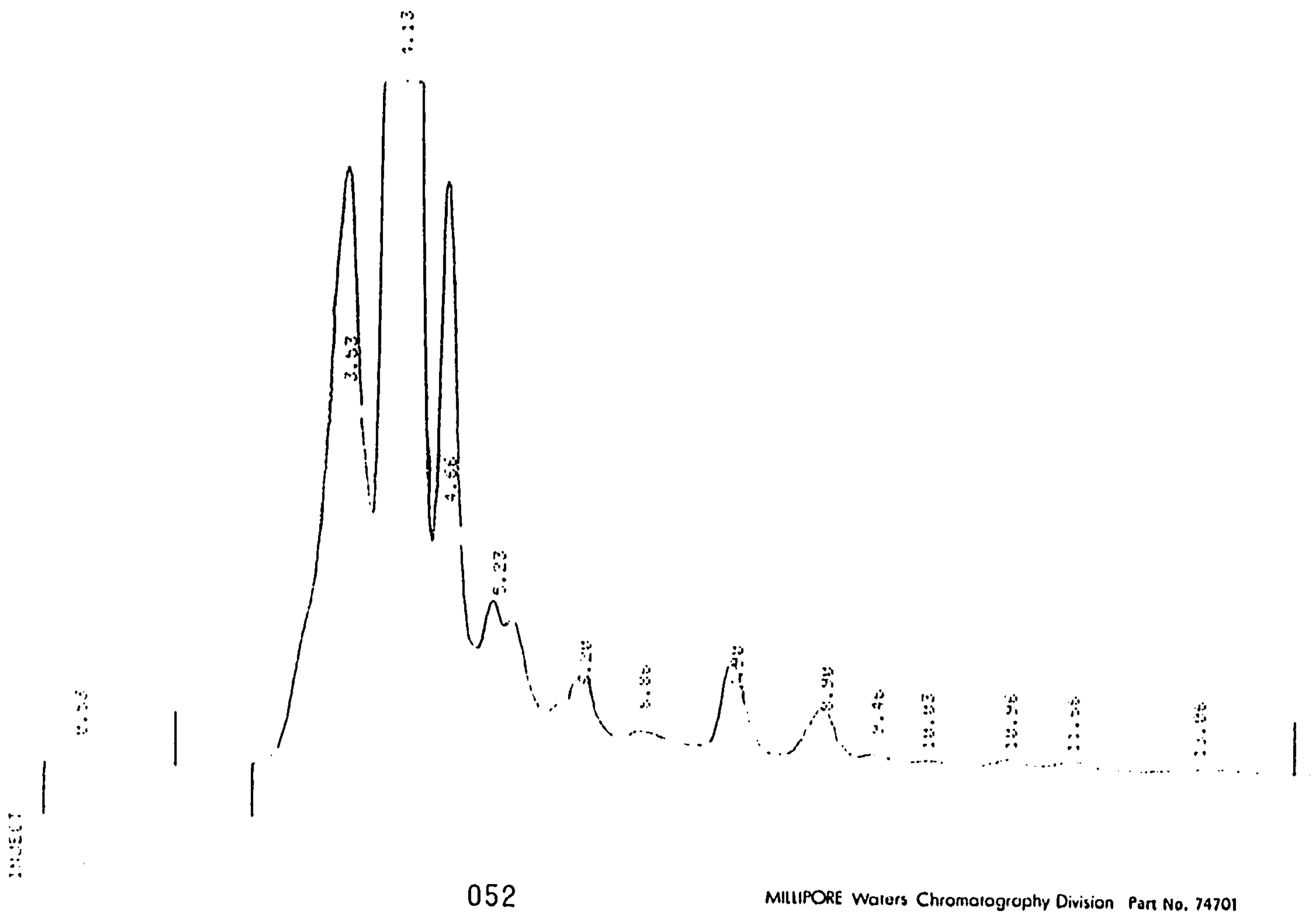
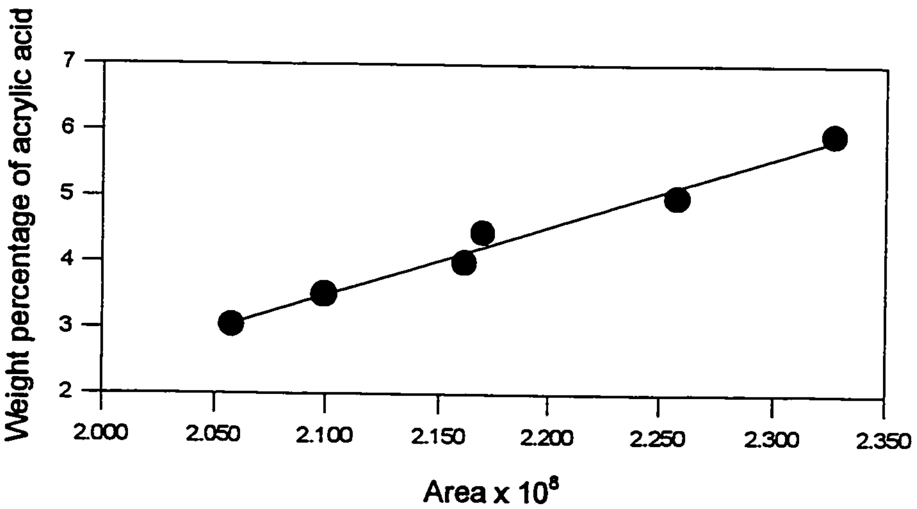
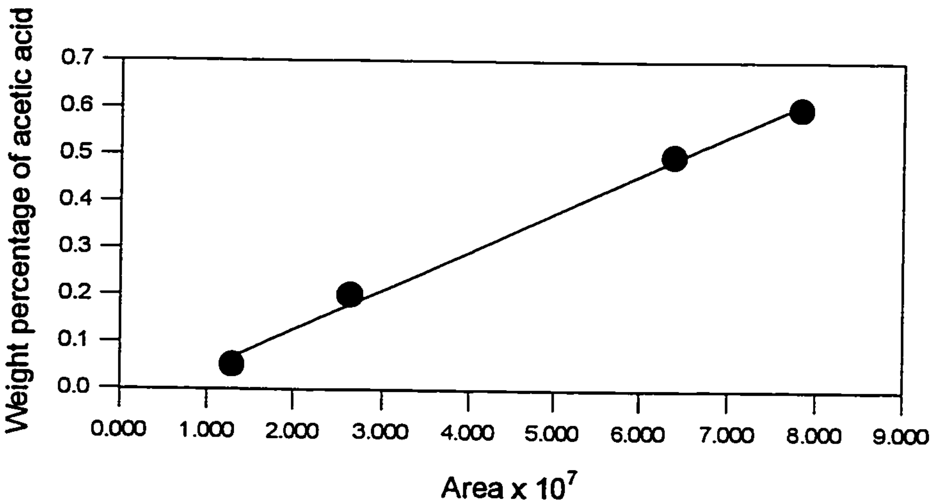


Appendix A1 Liquid Chromatograph spectrum for a typical product assay

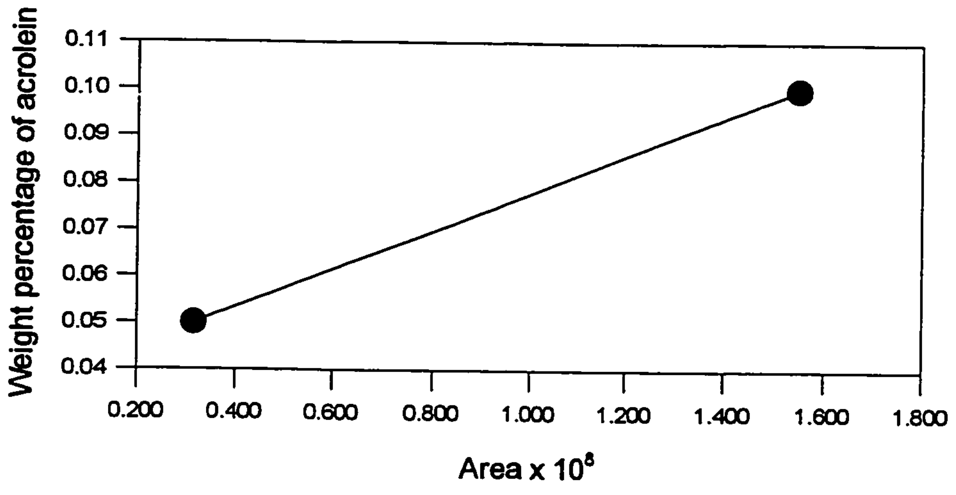
Appendix A2 Calibration curves for liquid chromatograph



Calibration curve for acrylic acid



Calibration curve for acetic acid



Calibration curve for acrolein