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The University of Alberta

Removal of Carbon Monoxide From Polluted Air

by

Ravindra Yaparpalvi ©

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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THE 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 **Removal of Carbon Monoxide From Polluted Air** submitted by **Ravindra Yaparpalvi** in partial fulfillment of the requirements for the degree of Master of Science.

KT Chuang

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Dr. N. O. Egiebor

Date: October 11, 1990

Abstract

Air fed to air-separation plants and compressors producing pressurized air for breathing purposes must be free of **carbon monoxide**(CO). In the present work a **catalytic process** for the purification of humid air containing low (ppm) levels of carbon monoxide was developed. During preliminary screening many supported metal catalysts containing various active ingredients were examined for room temperature oxidation of CO. The results indicate that platinum supported on **hydrophobic** styrene-divinylbenzene(SDB) copolymer meets the catalyst requirements. It was observed that the activity of this catalyst was enhanced by water vapor. This is a marked contrast to platinum on hydrophilic supports such as alumina (Al_2O_3), silica(SiO_2) etc., which deactivates in presence of water vapor due to capillary condensation.

In the course of process development, the behavior of the catalyst during CO oxidation was studied. The reason for enhanced activity of the (Pt-Ir)/SDB catalyst by water vapor has been attributed to the change in adsorption characteristics of CO and/or O_2 by water adsorbed on the surface. In the absence of water vapor, adsorbed CO was found to inhibit the adsorption of oxygen and hence the rate of oxidation. This strong adsorption of CO resulted in catalyst poisoning. However, the Pt-Ir catalyst supported on the hydrophobic SDB support was readily regenerable at room temperature by contact with a CO-free air,

thus indicating that the active ingredient and/or support surface may play an important role in the regeneration.

Similar to CO oxidation at high CO concentrations and high temperatures, steady-state multiplicity and kinetic oscillations were observed. The observed oscillations are believed to have been caused by varying surface concentrations of the reacting species.

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Chapter 1

Introduction

Carbon monoxide(CO) is a priority air pollutant in a variety of industrial and domestic environments. Ranging from the long-term effect of cardiomegaly to the immediate consequences of angina, CO pollution has a lengthy history of serious health implications, particularly for those who live and work in urban areas. (Stewart, 1975).

A combination of the widespread occurrence of low (ppm) level concentrations of CO in the ambient air, mostly generated by vehicular emissions, and reports of its adverse effects upon long-term exposure to even ppm level concentrations has created great concern (Greek and Dorweiler, 1990; Canada EPS report 7/Up/3, 1990), prompting development of methods that control exposure of CO to humans both in industrial and non-industrial environments. Control of such emissions via **catalytic oxidation** offers potential advantages over other methods, e.g. adsorption, in terms of equipment size and operating simplicity. However, apart from being low in CO concentration, the polluted air is often saturated with water and available only at room temperatures. Hence the catalysts must be active at room temperatures and must not be poisoned by the presence of water vapor.

Catalytic oxidation of CO has received extensive attention in the literature. The majority of these studies has, however, been carried mainly in relation to automobile emission control and, therefore, reaction conditions involve temperatures in excess of 300 °C. There are innumerable situations in industrial and domestic sectors wherein the use of clean air for various applications is imperative. Typical examples are breathing air, workshop air, air for agitation in fermenters etc. While the current technology appears to be satisfactory in removing various air-borne contaminants like dirt particles, oil etc., the same can not be said for the removal of low level CO at ambient temperatures. This has largely been due to the failure of the commercial **hopcalite** catalyst to effectively remove CO from air in the presence of water vapor. Furthermore, in purifying large volumes of air ambient temperature operation which requires no feed preheating is preferred.

Two classes of catalyst are normally used for the oxidation of CO by O_2. They are the supported noble metals and the oxides of transition metals. All the noble metal based catalysts investigated so far are mostly supported on highly porous materials such as SiO_2, Al_2O_3, etc. However, these catalysts must be heated to prevent a gradual loss in activity due to the accumulation of capillary condensed water in the catalyst support. Similarly, the metal oxide catalysts show no activity when exposed to air containing water vapor.

It has been reported that water vapor does not adsorb on Pt-group metals appreciably (Katz, 1953). If the noble metals are supported on a hydrophobic material, the presence of water vapor in the feed air will not cause capillary condensation and, therefore, the reactant molecules can always reach the catalyst active sites. Polymeric supports for catalysts have been recognized (Chauvin *et al.*, 1977; Lieto *et al.*, 1983) and used for the oxidation of hydrogen (Chuang *et al.*, 1987). These catalysts are hydrophobic and remain active in the presence of moisture.

The main objective of the present work is to develop a **catalytic** process suitable for the removal of CO from polluted air streams. According to Hiross Canada Inc. (2550 Dunwin Dr., Mississauga, Ontario L5L 1J5), a pollution control device manufacturer, the reactor should operate at room temperature with a space velocity (defined as the total volumetric flow rate of the polluted air stream divided by the catalyst bed volume) of greater than 400,000 h^{-1} to be economically competitive. This very high value of space velocity was desired since the manufacturer found in most practical applications that the polluted air is available in pressurized form at approximately 700 kPa.

The suitability of a **hydrophobic** catalyst for use in humid air will be the focus of this thesis. However it is also decided to test during the development stage various supported catalysts as candidates for room temperature oxidation of CO to identify a catalyst which will satisfy the requirements of the present work. It is not the intent of this study to investigate the mechanism of CO oxidation. Nevertheless, behavior of the candidate catalyst will be studied and the existing knowledge will be used to interpret and predict the catalyst behavior under the operating conditions which may be encountered in industrial applications.

Chapter 2

Literature Review

2.1 Introduction

Literature on catalytic oxidation of CO is legion. This is because oxidation of CO to CO_2 is an important reaction technologically and environmentally and a complex and interesting reaction scientifically. In most cases, the reaction is carried out in order to remove CO as an environmental hazard. Studies of this system, therefore, have concentrated on fundamental phenomena as well as issues of applied catalysis. Hence a complete summarization of the available reports would be far beyond the scope of any single contribution and can be found to some extent in review articles on different aspects of CO oxidation (Katz, 1978; Engel and Ertl,1979; Golodets, 1983; Razon and Schmitz,1986). The literature review presented here pertains only to those topics which have relevance to the problem under study. The survey has been formatted as follows:

- Background
- Oxidation over noble metal catalysts.
- Oxidation over metal oxide catalysts.

- **Adsorption on a metal surface.**

- **Reaction Mechanisms.**

- **Multiplicity and kinetic oscillations.**

2.2 Background

The oxidation reaction

$$CO + \frac{1}{2} O_2 \longrightarrow CO_2 \tag{2.1}$$

at ordinary temperatures of catalysis is irreversible, the value of ΔG^0_{298} for the reaction being equal to – 61.4 kcal/mol. The main contribution to ΔG^0 is by a high negative value of ΔH^0 ($\Delta H^0_{298} = -$ 67.6 kcal/mol). The entropy change for the reaction is negative ($\Delta S^0_{298} = -26.7$ cal/K mol).

The CO oxidation in an excess of oxygen proceeds readily at high temperatures, but requires the presence of certain contact material to enable it to proceed at low temperatures (below flame or explosion temperatures). Two classes of catalysts are normally used for the oxidation of CO by O_2. They are supported noble metals and the oxides of transition metals.

2.3 Oxidation over noble metal catalysts

The active catalysts for CO oxidation are supported platinum(Pt) group metals, which are usually active in the temperature range 100 - 600 ^{0}C (Brown *et al.*, 1960; Daglish and Eley, 1961). Published results using noble metal catalysts at or near room temperatures have been scarce compared to high temperature studies. In general, platinum has been found to be more active for CO oxidation compared to palladium(Pd) or silver(Ag). With metals purified in ultra vacuum, the activity order Pt>Pd≫Ag has been obtained (Sklyarov *et al.*, 1969; Tretyakov *et al.*, 1970, 1971).

Recent interest in the development of low temperature CO oxidation catalysts has been mainly focused on carbon dioxide(CO_2) lasers, to recombine the CO and O_2 formed as a result of CO_2 dissociation. Reports (Schryer and Hoflund, 1990; Sheintuch *et al.*, 1989) have claimed that platinum and/or palladium when supported on tin(IV) oxide(SnO_2) shows good activity for CO oxidation at room temperatures compared to the results obtained using Al_2O_3, SiO_2 etc., as supports. The reason for the enhanced activity of platinum and/or palladium on SnO_2 has been attributed to a synergistic interaction between SnO_2 and the noble metal (Bond *et al.*, 1975, 1977). Similarly Norman *et al.* (1990) have reported that the activity of Pt/SnO_2 catalyst depends on the gas composition and catalyst pretreatment conditions. Additionally humidification of the reaction gas mixture (test gas: 1% CO + 0.5%O_2 in He, 0.1 mole% H_2O, 85 ^{0}C, 5 SCCM) has been reported by Norman *et al.* (1990) to further improve the Pt/SnO_2 catalyst performance. They have hypothesized that the effect of humidification is to increase the concentration of OH groups on the catalyst surface which play a role in the reaction mechanism. However the effect of varying water vapor content in the feed on the catalyst activity was not discussed in their results. The majority of the test results published using SnO_2 supported catalysts has been in the temperature range 50 to 100 ^{0}C (Croft and Fuller, 1977; Sheintuch *et al.*, 1989; Schryer *et al.*, 1990; Norman *et al.*, 1990).

Papp and Kamp (1988) have obtained good catalyst activity using a dry feed ($CO+O_2$) with palladium supported on titania(TiO_2) at 30 ^{0}C. Heterogenized Wacker catalyst ($PdCl_2$ - $CuCl_2$) has been reported to possess a high activity for CO oxidation at temperatures around 60 ^{0}C, but it maintains activity only with water saturated feeds. Typical experimental conditions used were space velocity 58,000 h^{-1}, 333 K, 0.0584 g catalyst (Desai *et al.*, 1983).

Previous work on gold catalysts has been reviewed by several authors (Bond, 1972; Bond and Sermon, 1973; Schwank, 1983). The chemical reactivity of gold catalysts has been studied for the oxidation of CO by oxygen or nitrogen oxides (Benton and Elgen, 1927; Yates, 1969; Cant and Fredrickson, 1975; Hodges and Roselaar, 1975). However, the conventional gold catalysts prepared by impregnation have been reported to be usually far less active than platinum-group catalysts. Haruta *et al.* (1987, 1989) report enhanced catalyst activity for CO oxidation using a gold catalyst combined with the transition metal oxides such as $\alpha-Fe_2O_3$, Co_3O_4, NiO etc., even at temperatures as low as -70 ^{0}C and with 76% relative humidity feed.

Cant *et al.* (1978) found that the CO oxidation activity of noble metal catalysts such as Pt, Pd, Ru, Ir on supports such as cabosil HS5 silica, $\gamma-$ alumina, etc., at relatively low temperatures (330-480 K) was high in the beginning and then reduced to a constant value. They found that CO/O_2 ratio and temperature were the critical factors.

2.4 Oxidation over metal oxide catalysts

The active catalysts for CO oxidation under this category have been found to be the oxides of cobalt, manganese, copper and to a lesser extent nickel (Katz, 1953). Benton (1923) observed that the activity drops in the order: $Co_3O_4 > CuO > MnO_2 > Fe_2O_3 > V_2O_5 > SiO_2$. Manganese dioxide ($MnO_2$) has been reported to be one of the most active catalytic agents near room temperature (Whitesell and Frazer, 1923), however it is deactivated rapidly by adsorbed water and hence requires heating to regain the catalyst activity. Similarly, Engelder and Blumer (1932) found that a catalyst containing 30% cobalt oxide (Co_2O_3) and 70% iron oxide(Fe_2O_3) was sufficiently active to cause substantially complete oxidation of $\frac{1}{2}$% CO in air at 0 ^{0}C and a flow rate of 250 L/h gas per 17 g of catalyst. However, adsorption of 2.5% of its weight of water was observed to cause deactivation. Benton (1923) has studied the adsorption of oxygen and CO on cobalt oxide at 0 °C and at −79 °C. Bone (1926) has studied the oxidation of CO with oxides of nickel and copper.

The work of Lamb, Bray and Frazer (1920) has resulted in the discovery of a group of catalysts, called the *hopcalites.* These catalysts have been found to be highly active for CO oxidation at room temperature and consist essentially of a co-precipitate of oxides of manganese, copper etc. Although catalysts of this class possess a very long life in the presence of dry gas, they have been found to deactivate rapidly in the presence of water vapor which is adsorbed strongly (Katz, 1953).

2.5 Adsorption on a metal surface

2.5.1 Carbon monoxide

Adsorption of carbon monoxide on noble metal surfaces has been investigated in detail and available reports have been summarized (Ford, 1970; Engel and Ertl, 1979). Carbon monoxide adsorption has been reported to take place in molecular form. The commonly assumed configurations of chemisorbed CO on a metal surface are the *linear* (M-CO) and the *bridged* (M-CO-M) forms and the linear species has been reported to be catalytically more active. It is believed that the CO molecule is chemisorbed through the carbon atom, the molecular axis being perpendicular to the surface plane. The adsorption of CO on a metal surface is illustrated in Figure 2.1. Cortes and Droguett (1975) studied temperature programmed desorption of CO from supported cobalt and concluded that the linear species may be the precursor needed to form the bridge-bonded species. Tucker (1964) based on a LEED study has concluded that there may be limited mobility of CO on the Pt(100) surface at room temperature. Similarly, an initial sticking coefficient of 0.92 for carbon monoxide on platinum surfaces near room temperature has been reported (Campbell *et al.*,

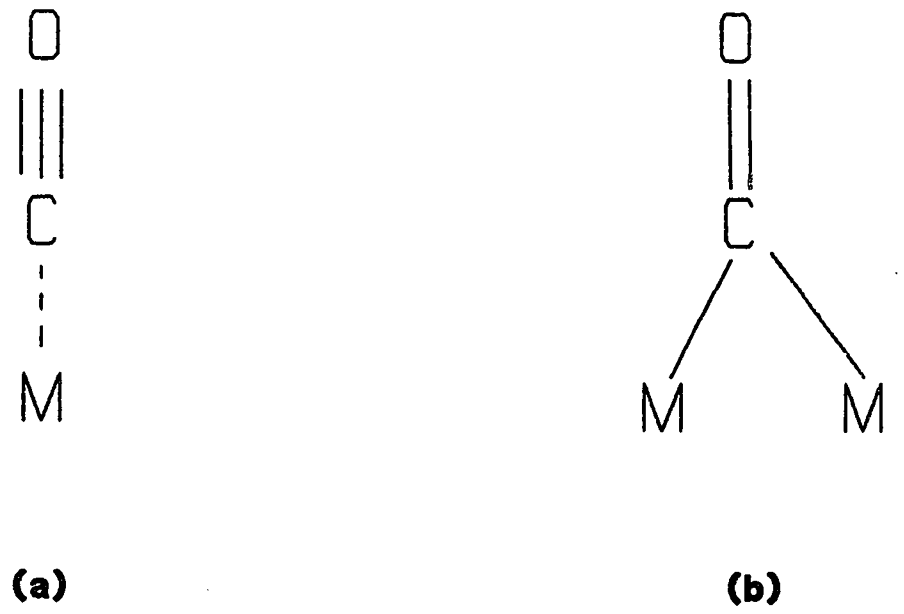


Figure 2.1: Adsorption of CO on a metal surface. (a) Linear bond. (b) Bridge bond

1981). Therefore CO is believed to adsorb on the platinum surface very strongly. Some studies report the existence of a chemisorbed and a physisorbed state for CO adsorption. The physisorbed form has been assumed to be a mobile state or a precursor which permits a CO molecule to move over the adsorbate layer until it reaches a vacant site (Kisliuk, 1957,1958; Weinberg *et al.*, 1976).

The saturation coverage of CO on platinum has been reported to depend on the size of the metal crystallites. Freel (1972), Dorling and Moss (1967), and Yao *et al.* (1979) have determined that for supported platinum with a small average particle size (less than 5 nm), the maximum ratio of adsorbed CO molecules to Pt surface atoms is 0.87 ±0.07. For a catalyst with a large crystallite size, the ratio of CO:Pt can be as low as 1:3. These observations have usually been explained by assuming bridge bonding on large crystallites and linear bonding on highly dispersed platinum.

2.5.2 Oxygen

The adsorption of oxygen on platinum group metals has been observed to be of more complex nature than CO adsorption since molecular adsorption, dissociative chemisorption, and oxide formation are all possible on a given surface in different temperature and pressure ranges (Engel and Ertl, 1979). Oxygen has been found to adsorb dissociatively on the platinum group metals above 100 K (Wilf and Dawson, 1975). The nature of the bond to the surface has been reported to depend on the temperature and pressure range in which the adsorption is carried out. The existence of a weakly held molecular form at low temperatures has been concluded from thermal desorption data for platinum (Norton, 1975) and iridium (Taylor *et al.*, 1979). Studies have revealed that it is more difficult for oxygen to adsorb on a surface already covered with CO than in the reverse situation of CO adsorbing on a surface pretreated with oxygen (Bonzel and Ku, 1972; Conrad *et al.*, 1978; Matsushima, 1978). A suggested explanation for this is that since O_2 dissociates, hence needs a larger vacant area than CO does before adsorption can occur. Similarly, Norton *et al.* (1984) have studied interaction of O_2 with Pt(100) at 298 K and have reported an initial sticking coefficient close to 0.1 (Griffiths *et al.*, 1984). The variation in sticking coefficient with coverage for oxygen adsorption on a platinum surface is illustrated in Figure 2.2. Adsorbed oxygen has been found to form islands on Pt(110) (Bonzel and Ku, 1972).

2.5.3 Carbon monoxide and Water

Although CO is probably the single most extensively studied molecule in surface science and while water has been investigated on a wide variety of surfaces (Thiel and Madey, 1987), relatively little attention has been paid to $CO+H_2O$ co-adsorption. Wagner *et al.* (1988) have studied the co-adsorption of CO and H_2O at 100 K on rhodium(Rh(111)) and platinum(Pt(111)). They have concluded that co-adsorption of low coverages of CO with water on Rh(111) in UHV yields a mixed phase in which CO and water molecules occupy adjacent sites, with net attractive CO-H_2O interactions, i.e. hydrophilic co-adsorption, and on Pt(111) co-adsorption of CO with water yields separate patches of the two species, with net repulsive CO-H_2O interactions, i.e. hydrophobic co-adsorption.

2.5.4 Nitrous oxide

CO oxidation by nitrous oxide(N_2O) has been included in the present investigation to compare the results obtained from using oxygen(air) as the oxidant, since the reaction mechanism in both cases is similar and differs only in the way the oxidant is formed on the surface, i.e. dissociative adsorption of O_2 needs two vacant sites whereas N_2O requires only one site.

Nitrous oxide(N_2O) molecule is asymetric and best decribed by the two canonical structures, $^-N{=}N^+{=}O$ and $N{\equiv}N^+{-}O^-$. Adsorption of nitrous oxide(N_2O) has been a subject of debate concerning whether the bonding on a metal surface occurs through the terminal

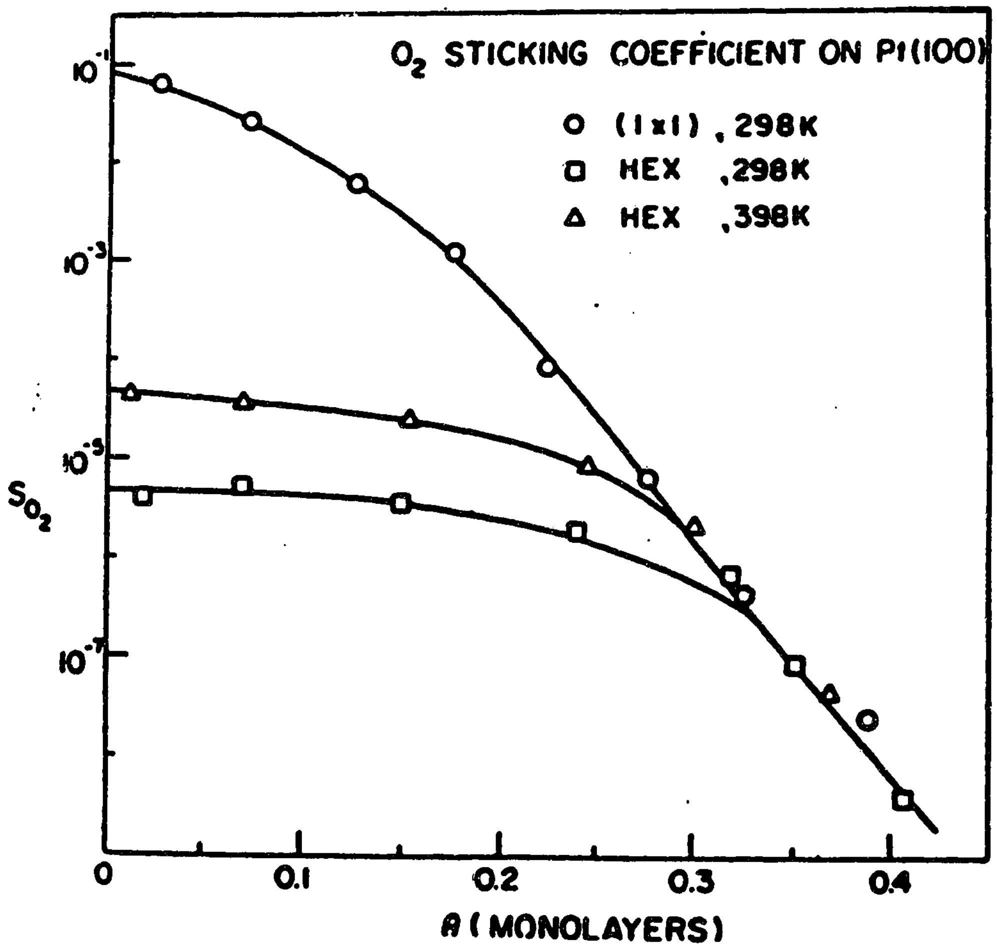


Figure 2.2: Sticking coefficient of oxygen on Pt(100) surfaces

N or O ends of the molecule. On the basis of electron energy loss spectroscopy(EELS) and thermal desorption spectroscopy(TDS), Avery (1983) reported that, on Pt(111) at a temperature of 78 K, molecular adsorption occurs by bonding through N end. No evidence for N_2O dissociation was found on this surface at 78 K. Weinberg (1973) used the bond energy bond order model of chemisorption to describe the interaction of N_2O with both clean and carbon covered Pt surfaces. The similar conclusion was reached that N_2O binds to the platinum surfaces through the nitrogen atom.

Alnot *et al.* (1974) compared adsorption of N_2O with O_2 on platinum polycrystalline ribbons. The adsorption of N_2O was accompanied by the evolution of molecular N_2 in the gas phase, even in the 300 to 500 K range. They found that the N_2O sticking coefficient varied with the surface coverage.

2.6 CO oxidation mechanism over noble metals

2.6.1 CO oxidation by O_2

There have been two schools of thought concerning the possible reaction paths in CO oxidation over noble metals. These were expressed by Langmuir (1922). According to one school both carbon monoxide and oxygen must be adsorbed on the catalyst surface to form the reaction product. On the other hand, according to the other only one reactant need be adsorbed on the surface while the other must originate from the gas phase. The first of these paths is called *Langmuir-Hinshelwood* mechanism, whereas the second mechanism is named after *Eley and Rideal.* This latter mechanism could also involve a weakly held species rather than a direct impact. The reaction product is carbon dioxide(CO_2). These mechanisms are described by the following elementary steps:

$$CO(g) + M \rightleftharpoons CO - M \qquad (2.2)$$

$$CO - M + O - M \longrightarrow CO_2 + 2M \tag{2.3}$$

$$CO(g) + O - M \longrightarrow CO_2 + M \tag{2.4}$$

where, M denotes a free adsorption site. Carbon dioxide does not appreciably adsorb on platinum (Conrad *et al.*, 1978), but it does adsorb strongly on catalyst support such as Al_2O_3. However the adsorption of CO_2 on a support has been reported to have negligible effect on the reaction rate (Engel and Ertl, 1979).

In large excess oxygen and at the conditions under study, it would be reasonable to expect a combination of both types of mechansims to influence the CO oxidation rate, i.e. a Eley - Rideal type mechanism at very low CO concentrations wherein the catalyst surface is largely covered with O_2 and a Langmuir - Hinshelwood type mechanism at high CO concentrations wherein CO populates the catalyst surface (Nishiyama and Wise, 1974; McCarthy *et al.*, 1975).

Based on the above mentioned reaction paths a considerable effort has been focused on the study of kinetics of carbon monoxide oxidation. Hawkins (1978) and Holliday (1981) have summarized the published experimental data and the models proposed to correlate them. Most of them have been *Langmuir-Hinshelwood-Hougen-Watson*(LHHW) type models.

2.6.2 CO oxidation by N_2O

Several N_2O + CO reaction paths have resulted from high temperature studies over noble metal catalysts (Lorimer and Bell, 1979; Lintz, 1981; Hardee and Hightower, 1984). These mechanisms can be classified into two categories: one involves the dissociative chemisorption of N_2O, the other involves the decomposition of adsorbed N_2O.

Lintz (1981) claimed that the reaction involved four elementary steps:

$$CO(g) + M \rightleftharpoons CO - M \tag{2.5}$$

$$N_2O(g) + M \longrightarrow N_2(g) + O - M \tag{2.6}$$

$$CO - M + O - M \longrightarrow CO_2(g) + 2M \tag{2.7}$$

$$CO(g) + O - M \longrightarrow CO_2(g) + M \tag{2.8}$$

In this mechanism, the dissociative chemisorption of N_2O results in the production of molecular nitrogen. It was found that the reaction probability of this process is very low (at 500 K).

A different mechanism has been proposed by Winter (1969), in which the dissociative chemisorption of N_2O is used in the preceding mechanism.

$$N_2O(g) + M \rightleftharpoons N_2O - M \tag{2.9}$$

$$N_2O - M \longrightarrow N_2(g) + O - M \tag{2.10}$$

It was assumed that the decomposition of the N_2O surface complex is the rate-limiting step.

Yet another surface reaction has been proposed by Hendershot and Hansen (1986), who investigated the reduction of nitric oxide(NO) with CO on a Rh(100) single crystal surface. They assumed that an adsorbed nitrous oxide intermediate was involved in the reaction process. The surface N_2O reacts with adsorbed CO, with gas phase nitrogen and carbon dioxide as the products.

$$N_2O - M + CO - M \longrightarrow N_2(g) + CO_2(g) + 2\,M \tag{2.11}$$

They showed that this step was consistent with both steady-state kinetics and surface characterization results. Similar to CO oxidation by O_2, it would be reasonable to expect a combination of Eley-Rideal and Langmuir-Hinshelwood type mechansims to influence the CO oxidation rate, at very low and high CO concentrations respectively.

2.7 CO oxidation mechanism over metal oxides

In this case, the reaction is believed to proceed through a variation of the oxidation state of the metal cations, i.e. via oxidation/reduction cycles of the topmost atomic layers. A detailed explanation of the different mechanisms proposed by various authors has been compiled by Golodets (1983). Since the feed in the present study will always contain water vapor, metal oxides are not suitable and hence no attempt has been made to review critically the pertinent literature.

2.8 Multiplicity and kinetic oscillations

2.8.1 Multiplicity

Steady-state multiplicity and oscillations have been reported in the oxidation of CO on platinum at high CO concentrations and high temperatures (Razon and Schmitz, 1986). Isothermal multiplicity in CO oxidation on platinum was first reported by Beusch *et al.* (1972) using a 3 × 3 mm cylindrical catalyst pellet. Hysteresis was observed by Beusch *et al.* to be independent of the total volumetric flow rate and hence they argued that multiplicity must be a result of interaction between reaction and chemisorption rate. Assuming an Eley-Rideal mechanism with oxygen reacting with adsorbed CO and a Langmuir-Hinshelwood model for the adsorption of CO, Beusch *et al.* showed that multiple steady states could occur if the intrinsic rates of the reaction and chemisorption steps are of roughly the same magnitude. Various authors have shown theoretically that if a reactant concentration gradient occurs with reactions described by Langmuir-Hinshelwood models in which one of the reactants is strongly adsorbed, isothermal multiplicity could arise. Reactions of the above sort exhibit negative orders through a portion of the composition range. Thus, an alternate explanation of multiplicity is the interaction of intra particle diffusion and a surface reaction of a sorption step involving at least one strongly adsorbed reactant. Multiplicity could also arise from the coupling of a reaction step with a strong concentration gradient external to the catalyst particle.

Carbon monoxide oxidation rate hysteresis has been studied experimentally by investigators besides Beusch *et al.*, mainly using Pt or Pd catalysts supported on alumina (Padberg and Wicke, 1967; Fieguth and Wicke, 1971; Votruba and Hlavacek, 1974; Oh *et al.*, 1978; Cutlip and Kenney, 1979). In addition to Wei and Becker (1975), Smith *et al.* (1975), Schmitz (1975) and Hegedus *et al.* (1977) demonstrate that diffusion-reaction interactions can lead to multiplicity. On the other hand, Eigenberger (1978) showed that two or more surface rate steps of roughly same magnitude could give isothermal multiplicity in a gradient less reactor. Recent experimental work suggests most hysteresis observations with CO oxidation arise from diffusion-reaction interaction. Hegedus *et al.* (1977) found that by increasing the intra-pellet diffusion resistances of the Pt/Al_2O_3 catalyst by aging, the region of multiplicity was significantly widened. Oh *et al.* (1979) showed that hysteresis can be eliminated if the catalyst particle size is made very small. Tamhankar and Lacava (1989) observed steady-state multiplicity at low temperature and with low level CO concentrations and have attributed the cause to a change in the reaction mechanism.

2.8.2 Kinetic oscillations

Oscillatory phenomena which have been reported for CO oxidation over platinum catalysts are summarized in several review papers (Sheintuch and Schmitz, 1977; Slin'ko and Slin'ko, 1978). Numerous causes of oscillations have been suggested in the literature. These include:

- Surface temperature fluctuations (Jensen and Ray, 1980).
- Surface coverage dependent activation energies (Sheintuch and Schmitz, 1978).
- Slow adsorption and desorption of an inert species (Eigenberger, 1978).

- Slow alternate oxidation and reduction of the catalyst surface (Sales *et al.*, 1982).
- Periodic transformations of the catalyst surface structure (Cox *et al.*, 1983).

The literature review presented so far pertains only to some of the observations made by various reports and provides the necessary background for the interpretation of experimental results obtained in this work.

Chapter 3

Catalyst preparation

In this chapter, the various supported metal catalysts prepared in this investigation for testing as candidates for room temperature oxidation of CO are outlined. First the basis for the selection of catalyst support material for use in humid air is explained followed by preparation methods adopted for the catalysts.

3.1 Selection of catalyst support

A conventional noble metal catalyst supported on highly porous hydrophilic supports such as Al_2O_3, SiO_2, etc., loses its activity when exposed to humid air (Leder and Butt, 1966; Sherwood, 1981; Jones and Nevell, 1990). Under these conditions, pore condensation takes place until it reaches thermodynamic equilibrium dictated by the Kelvin equation (Golodets, 1983) as follows:

$$ln(\frac{P}{P_0}) = -\frac{2V\gamma cos\theta}{rRT} \tag{3.1}$$

where,

r = radius of the capillary

V = molar volume of the liquid

γ = surface tension

θ = angle of contact

The above equation indicates that for values of the contact angle θ less than 90^0, liquid condenses in the capillary at a pressure P less than the saturated vapor pressure P_0 at temperature T. For example, for alumina catalysts the contact angle with water is close to zero. The catalyst deactivation would continue until thermodynamic equilibrium conditions are reached by which time the catalyst activity would be very low. These phenomena have been reported by Sherwood (1981). Furthermore, the equation (3.1) also implies that increasing contact angle reduces pore condensation.

It has been reported (Katz, 1953) that water vapor does not adsorb appreciably on platinum group metals. If these metals are supported on a hydrophobic material, the presence of water vapor in the feed will not cause capillary condensation and, therefore, the reactant gases can always reach the catalyst active sites. Polymeric supports for catalysts have been widely recognized (Chauvin *et al.*, 1977; Lieto *et al.*, 1983) and used for the oxidation of hydrogen (Chuang *et al.*, 1987). These supports are **hydrophobic** in nature and have been reported to offer the advantages of being inert, easily functionalized and prepared with a wide range of physical properties. The disadvantage of a polymer support is lack of stability at high temperatures, which is not a concern in the present study. The use of polymer support in the present investigation seems to be very promising for maintaining the catalyst activity in humid air. Furthermore among the polymer supports investigated in literature, poly(styrene-divinylbenzene) has been reported to offer the advantages of high-purity catalyst supports (Lieto *et al.*, 1983). Therefore, it was decided to use **styrene-divinylbenzene copolymer** (SDB) support for the catalyst in the present investigation.

3.2 Preparation of catalysts

3.2.1 Pt-Ir/SDB, Pd/SDB, Au/SDB and Ru/SDB

The SDB support was obtained by polymerizing divinylbenzene in ethyl vinylbenzene. The reaction was carried out in 2-methyl-1-pentanol using 2,2-azobis (2-methylpropionitrile) as initiator. The SDB so obtained was crushed and screened to different sizes. It had a BET area of 465 m^2/g.

The Pt-Ir/SDB catalysts were prepared by the impregnation of SDB with an ethanol solution containing a given amount of chloroplatinic acid, H_2PtCl_6 and iridium chloride, $Ir(NH_3)_5Cl_3$. The mixture was installed in a rotary evaporator which operated at 95 ^{0}C and under a slight vacuum. The dried product was then reduced in hydrogen at 200 ^{0}C until the pH of the furnace became neutral. The platinum was found by X-ray analysis to distribute on the SDB support uniformly and the metal area was determined by H_2/O_2 titration. The characterization studies of the Pt-Ir/SDB catalysts were carried out at Chalk River Nuclear Laboratories, Chalk River, Ontario. The percentage loading of the catalyst was based on the initial weight of the metal complexes. The characteristics of the Pt-Ir/SDB catalysts containing different percentage loadings of the active material are listed in Table 3.1. It can also be seen in Table 3.1 that the Pt/Ir metal ratio is 9:1 in each of the catalysts. This ratio was selected based on the preliminary tests conducted at Chalk River Nuclear Laboratories which revealed that this combination of Pt+Ir metal is more effective compared to equivalent loadings of Pt or Ir metal alone. Further details such as pore size distribution, pore volume etc., are proprietary of Atomic Energy of Canada Limited and hence has not been discussed here.

The above paragraph pertains to the preparation method of Pt-Ir/SDB catalysts. However, a similar approach was also used for preparing SDB supported catalysts containing active ingredients such as palladium(Pd), gold(Au), and ruthenium(Ru). These catalysts are listed in Table 3.2.

Although studies (Sklyarov *et al.*, 1969; Tretyakov *et al.*, 1970, 1971) have concluded that platinum is more active for CO oxidation compared to palladium, silver etc., it was decided to prepare and test various catalysts containing different active ingredients on different supports as candidates for room temperature oxidation of CO to compare the results and select the most effective and reliable catalyst to meet the requirements of the present investigation. Accordingly, different catalysts were prepared and are outlined in the following sections.

3.2.2 Pd/Al_2O_3 and Pt/Al_2O_3

The preparation method followed for alumina supported catalysts is similar to the one described by Stiles (1983). γ-Alumina spheres (Kaiser, BET surface area 341 m^2/g) were heated to 200 ^{0}C in order to remove any adsorbed moisture. The total pore volume of the spheres was determined by weighing a quantity of the spheres, immersing them in water and allowing them to remain immersed until they are completely saturated, removing the spheres from the water, blotting the surface dry from excess water then weighing them again. The difference in weight is the total pore volume of the alumina spheres. The spheres were then made alkaline by preparing a 5% sodium bicarbonate solution to be exactly equal to the total pore volume of spheres involved. Next the weight or volume of spheres to be treated was taken in a beaker and the beaker was placed on a rotating device and the volume of sodium bicarbonate solution corresponding to the total pore volume was poured in to the beaker. After complete coating, the spheres were dried.

A solution of palladium chloride/nitrate (palladium chloride, Terochem; palladium(II) nitrate, Aldrich) was prepared which contained the proper quantity of palladium to be impregnated onto the surface of the spheres and was equal to the total pore volume of the spheres already determined. The spheres, while being rotated were next coated with the

Cat.#	% metal loading	%Pt	%Ir	metal area, $\frac{m^2}{g}$	size, mesh
1	2.0	1.8	0.2	3.05	10-14
2	6.0	5.4	0.6	4.18	10-14
3	9.0	9.0	1.0	10.0	10-14

Table 3.1: Characteristics of Pt-Ir/SDB catalysts

Cat.#	% metal loading	%Pd	%Ru	%Au	size, mesh
1	2.0	-	2.0	-	10-20
2	2.0	-	-	2.0	10-20
3	8.0	6.0	2.0	-	10-20
4	8.0	2.0	6.0	-	10-20

Table 3.2: SDB supported catalysts

Cat.#	% metal loading	%Pt	%Pd	%Ce
1	0.2	0.2	-	-
2	6.0	3.0	-	3.0
3	3.0	-	3.0	-
4	6.0	-	3.0	3.0

Table 3.3: Alumina supported catalysts

exact volume of palladium chloride (or nitrate) solution stipulated in the previous step; rotation was continued until the spheres are completely and uniformly coated. Rotation was continued for an additional 20 minutes and the spheres were then washed to remove the halide and sodium by running distilled water. The spheres were next removed from the rotating equipment and dried. Reduction was carried out in hydrogen/nitrogen stream at 523 K. For the purpose a U-glass tube was used. The sample was taken in the U-tube which was then placed in a furnace and hydrogen/nitrogen mixture, in equal volumes (100 ml/min) was flown through the U-tube. The temperature was increased in incremental steps and maintained at the reduction temperature for 8 h and then cooled in a nitrogen stream for a similar period.

The above method of preparation describes the procedure adopted for preparing palladium supported on alumina. A similar method was also used to prepare platinum on alumina catalyst. In this case hexachloroplatinic acid($H_2PtCl_6.6H_2O$, Engelhard Industries) was used. A semi-hydrophobic type alumina support supplied by Met Pro was also used in preparing platinum metal (0.2 wt.%) catalyst. Details of this catalyst are proprietary of Met Pro company. Table 3.3 lists the alumina supported catalysts prepared. The metal loadings indicated are in weight percent.

3.2.3 Pt-Ce/Al_2O_3 and Pd-Ce/Al_2O_3

Addition of cerium oxide has been reported to increase the CO oxidation efficiency of fresh platinum, palladium based catalysts. Cerous nitrate ($Ce(NO_3)_3.6H_2O$, purified, Fisher Scientific) solutions were impregnated onto porous γ-alumina spheres(Kaiser, BET area 341 m^2/g). These solutions were acidified with hydrochloric acid (pH approximately 1.2) in order to place the cerium(Ce) uniformly along the pellet radius. After calcining in air (673 K, 5 h), the noble metals (Pt or Pd) were placed uniformly on supports which contained 3.0 wt.% Ce. This was accompanied by impregnating HCl solutions (pH 1.2) of either $H_2PtCl_6.6H_2O$ (Engelhard Industries) or $PdCl_2$ (Terochem, Aldrich) on to the supports, air drying and then calcining the catalysts in air (623 to 673 K). These catalysts were then reduced in nitrogen/hydrogen stream at 623 to 673 K for 8 h and then cooled in a nitrogen stream for a similar period. Table 3.3 lists the alumina supported catalysts prepared.

3.2.4 Pt/Y-zeolite and Pd-Ce/Y-zeolite

The Y-zeolite support used was obtained from Union Carbide (type AW500, Union Carbide). The Pt, Pd or Ce were introduced onto this support by ion-exchanging the support with tetra-amine platinum(II) dichloride, $Pt(NH_3)_4Cl_2.H_2O$, tetra-amine palladium(II) dichloride (Engelhard Industries), $Pd(NH_3)_4Cl_2.H_2O$, cerous nitrate, $Ce(NO_3)_3.6H_2O$ (Fisher Scientific). Essentially the procedure consisted of placing the supported immersed in a measured amount of water in a beaker. The beaker was placed on a hot plate and the water temperature was maintained at around 60 ^{0}C. The Pt, Pd or Ce containing solutions prepared were added from a burette slowly (drop wise, typically 3 to 4 drops per minute) with a periodic stirring of the solution containing the support. After the transfer of noble metal containing solution, the beaker was left on the hot plate until the entire solution evaporated. The support was next dried in a furnace maintained at 60 ^{0}C overnight, calcined in air at 623 to 673 K for 8 h and next reduced in hydrogen/nitrogen stream at 623 to 673 K for 8 h, then cooled in a nitrogen stream for a similar period. The catalysts so prepared are listed in Table 3.4.

3.2.5 Pt/Silicalite, Pt-Rh/Silicalite and Pd/Silicalite

Silicalite supported catalysts were prepared by impregnation of the support (SR-115, UOP) by appropriate solutions of the corresponding metal salts, namely, $H_2PtCl_6.6H_2O$ (Engelhard Industries), $Pd(NO_3)_2$, $RhCl_3$ (Aldrich), $Cu(NO_3)_2.6H_2O$. Following drying each preparation was calcined at 573 to 673 K and subsequently reduced at 523 to 673 K with a hydrogen/nitrogen gas stream and then treated overnight with flowing nitrogen alone for a similar period. For catalysts with more than one active ingredient on the support, impregnation was carried out in two steps. The catalysts thus prepared are listed in Table 3.5.

3.2.6 Pt/Tin oxide

The tin (IV) oxide supported catalyst used in this investigation was 2%(by weight) Pt/SnO_2 powder obtained from Engelhard Industries. This catalyst had an average particle size of 1μm and a BET surface area of 6.9 m^2/g. The powder obtained was mixed with small quantities of Alon powder, to act as a binder, and compressed into small pellets for easier handling. The pellets so prepared were used for testing catalyst activity.

In addition to all the catalysts prepared and listed so far, few other catalysts such as palladium supported on titania extrudated (Engelhard Industries), copper chromite catalysts (consisting essentially of Cu, Mn, Cr, Ba - 4.5 mm × 4.5 mm pellets -United Catalysts Inc.) were also obtained for testing. These are listed in Table 3.6.

Cat.#	% metal loading	%Pt	%Pd	%Ce
1	5.0	5.0	-	-
2	6.0	-	3.0	3.0

Table 3.4: Y-zeolite supported catalysts

Cat.#	% metal loading	%Pt	%Rh	%Cu
1	2.0	1.8	0.2	-
2	10.0	5.0	-	5.0
3	10.0	-	5.0	5.0

Table 3.5: Silicalite supported catalysts

Cat.#	% metal loading	%Pt	%Pd	%Au	%Cu	%Cr	%Mn
1	2.0	-	-	2.0	-	-	-
2	2.0	2.0	-	-	-	-	-
3	5.0	-	5.0	-	-	-	-
4	100.0	-	-	-	39.0	37.0	3.0
5	100.0	-	-	-	35.0	31.0	2.0

Table 3.6: Other catalysts: Pt/SnO_2, Au/Cab-o-sil, Pd/Titania, Copper Chromite

Chapter 4

Experimental equipment and procedure

This chapter describes the experimental program adopted to test CO oxidation efficiencies of the catalysts prepared, as outlined in chapter 3. The equipment used is described first, followed by the method adopted for the analysis of carbon monoxide in air and the experimental procedure respectively.

4.1 Description of experimental equipment

Experimental runs were carried out using a flow reactor system consisting essentially of a feed manifold, a purification train, a water vapor saturator and a fixed-bed integral reactor. Two reactors of different dimensions were employed in the present study. A primary reactor of 38.1 mm ID × 345 mm L was used to demonstrate catalyst performance under operating conditions encountered in practice, while a secondary reactor of 25.4 mm ID × 190 mm L was used to test for catalyst activities during development stage. The smaller size secondary reactor was used primarily for economic reasons, since with this reactor it was possible to carry out experiments with a limited quantity of expensive noble metal catalysts and at low air flow rates. Both the reactors are made of stainless steel. The inlet and outlet lines to the primary reactor system consist of 12.7 mm ID copper pipe, whereas a 6.35 mm ID high strength Teflon tubing served as inlet and outlet lines for the secondary reactor.

The main inlet gas to the reactor system was air. This air was drawn from a compressed air supply line (approximately 600 kPa) and was bone dry (pressure dew point -40^0C). A stabilizer was installed in the line to subdue any fluctuations in supply air pressure. The air was further purified, to remove any air borne contaminants, by passing it through a purification train in four stages of filtration as follows:

- Stage 1 - Domnick Hunter grade AO 1 micron pre-filter for particulate removal.
- Stage 2 - Domnick Hunter grade SL soda line filter for CO_2 removal.
- Stage 3 - Domnick Hunter grade AA .01 micron high efficiency coalescing filter.
- Stage 4 - Domnick Hunter grade AC activated carbon filter for organic vapor removal.

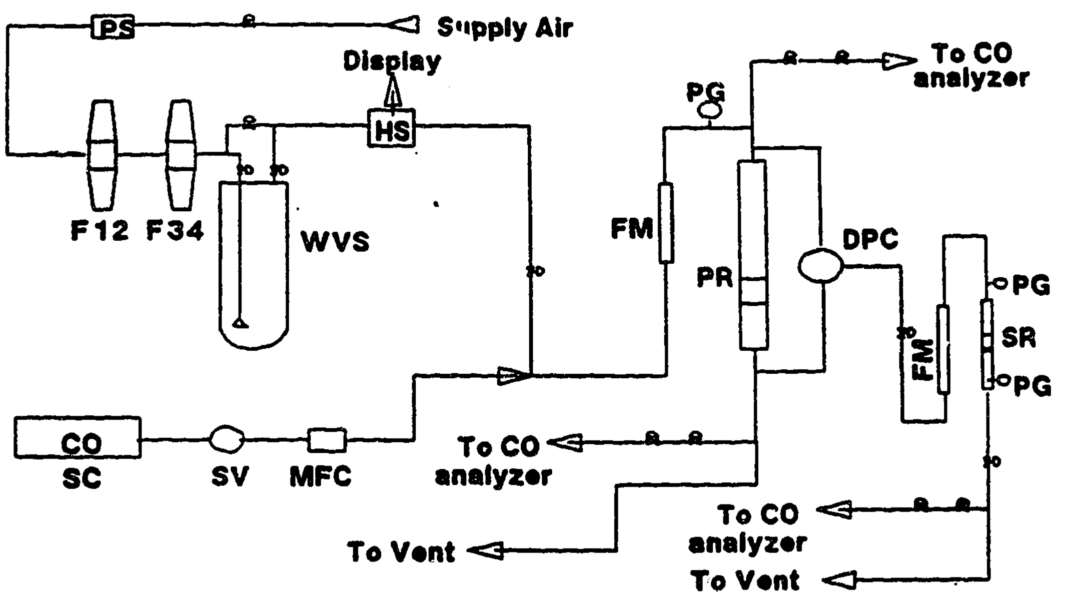
The operation of the purification stages is as follows. In the first two stages of air purification dust particles, which may have entered from the piping system, and any CO_2 present are removed. The air next flows through the grade AA filter element in the bottom section from inside to out. This element traps the solid particles in its filter layers, oil/water aerosols are coalesced and form bulk liquids. The bulk liquid gravitates in the anti re-entrainment barrier (outer porous plastic foam) to form a wet band of coalesced liquid at the bottom of the filter element. The separated liquid then falls through the resultant quiet zone to the filter bowl, where it is removed by the drain.

The air then flows through the grade AC filter element in the top section. The grade AC filter element contains activated carbon which adsorbs oil vapor and odors. The air passes from the bottom section of the filter assembly up through the adsorption element. A filter tube prevents the migration of any particles in to the air stream.

Either part of or all of the purified air was then passed through a water vapor saturator to obtain desired humidity. The saturator was a 152.4 mm L × 914.4 mm H stainless steel column and was filled with water to the required level. The dry air flows to the bottom of saturator, via a pipe which runs along the depth of the saturator, wherein it was bubbled into water, at room temperature, by means of a sparger. A shower head attached to the end of pipe served this purpose. A by-pass line was provided to skip the saturator stage in order to carry out experimental runs with dry air. The humidity and temperature of air just before it enters the reactor were continuously monitored using a VAISALA Series HMP 124B (Cole - Parmer) humidity and temperature transmitter for pressurized spaces. This sensor has a temperature measurement range of -20 to $+80^0$C and relative humidity measuring range of 0 to 100 %RH. The impurity level of CO in air was achieved by continuously injecting the appropriate amount of CO. Essentially, CO flow from source cylinder (Technical grade, Linde-Union Carbide) was controlled by means of a mass flow controller (Unit Instruments) in order to obtain the desired concentrations in inlet air. The catalyst in the reactor was supported on a fine stainless steel wire mesh along with glass wool/glass beads packing in order to arrest any catalyst movement. A schematic diagram of the complete flow reactor system is shown in Figure 4.1.

4.2 CO analysis

The Canadian standards association CSA standard Z223.21 - M 1978 outlines in detail the procedure to be followed for measurement of CO in air. In the present investigation, CO concentrations in air at the reactor inlet and outlet were continuously monitored and recorded using a portable 2000 Series ECOLYZER CO analyzer. The instrument accom-



Key:
PS-Pressure Stabilizer
F12-Filtration stages 1&2
F34-Filtration Stages 3&4
WVS-Water Vapor Saturator
SR-Secondary Reactor
MFC-Mass Flow Controller
SV-Solenoid Valve
HS-Humidity & Temperature Sensor
FM-Flow Meter
PG-Pressure Gauge
PR-Primary Reactor
DPC-Diff.Press.Cell
SC-Source Cylinder

Figure 4.1: Schematic diagram of the flow reactor system

plishes this by drawing in and analyzing the air by means of an electrochemical sensor. The sensor produces an electrical current output whose magnitude represents the level of CO in the sampled air. The resulting current causes a meter indication showing the level of CO in parts per million (PPM).

The operating principle of the CO analyzer is as follows. Carbon monoxide is electro-oxidized to carbon dioxide at a catalytically active electrode such as platinum in an aqueous electrolyte according to the equation

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e \tag{4.1}$$

In the CO analyzer, this electrochemical process occurs at a potential- controlled electrode. This electrode is maintained at a potential of 0.15 V versus the reference electrode. Under these conditions, the current measured upon introducing a carbon monoxide sample to the detector is the result of the electro-oxidation of carbon monoxide, and it is proportional to the partial pressure of carbon monoxide in the gas sample.

This analyzer had two scale ranges of 0 - 60 ppm and 0 - 600 ppm. The rise time (90%) of the instrument was 25 seconds. The precision, minimum detectable sensitivity of the analyzer were ±1%(full-scale) and 0.5% (full-scale) and the performance of the instrument was not affected by the presence of gases like CO_2, NH_3, N_2O, SO_2, etc. in the environment. The analyzer was calibrated on a regular basis to ensure accuracy and reproducibility in analysis using standardized CO in air mixtures. For the purpose, two cylinders containing CO concentrations of 6 ppm, 197 ppm respectively in air were obtained and used (supplied by Matheson). The calibration procedure essentially consisted of passing the standard air+CO mixture through the analyzer and noting the CO ppm level on the display. Any deviation in the CO analyzer reading from standard value was corrected by adjusting the span potentiometer.

4.3 Experimental procedure

During preliminary screening experiments, the catalysts outlined in chapter 3 were examined for room temperature CO oxidation catalyst activity. This procedure essentially consisted of evaluating performance parameters such as CO outlet concentration with respect to a fixed value of inlet CO concentration as a function of the total air flow rate, water vapor content in the feed etc. The main purpose of these initial runs was to identify a few candidate catalysts which would meet the requirements of the present study, i.e. exhibit activity for CO oxidation at high flow rates in humid air. Upon identification of potential catalyst(s), subsequent experimental runs were mainly directed towards investigating the effect of CO concentration in the inlet air on the catalyst activity measured in terms of steady-state conversions of CO (**conversion** in this study is defined as ppm of CO oxidized divided by CO ppm level in the inlet air and has also been referred to as oxidation efficiency). Similarly runs were conducted to study the effect of various operating variables such as catalyst composition, water vapor content in inlet air, total flow rate, etc. on the oxidation efficiency of the catalyst. In a typical run, the experiment would begin by setting air flow rate etc., to a desired value and adjusting the inlet CO concentration to the lowest value of interest. When steady-state was reached, as indicated by a constant outlet concentration of CO on the analyzer, the CO ppm level in inlet air was given a step-raise and again the steady-state outlet concentration was noted. This incremental increase in inlet CO concentration was continued until the catalyst oxidation efficiency dropped to the low conversion regime. In reverse direction experiment, the run ended when the CO inlet concentration was decreased from its highest value in steps to its lowest value. Multiplicity of steady-states was observed and has been discussed in the next chapter. Regeneration of the catalyst was carried out by shutting-off CO feed and flushing with purified air at room temperature for a period of approximately one hour. This procedure was found to recover the catalyst activity previously poisoned by CO. The reason for catalyst poisoning by CO and catalyst regeneration studies have been discussed in detail in the next chapter.

Chapter 5

Results and Discussion

The experimental results obtained using the catalysts, outlined in chapter 3, are presented in the following sections along with a discussion of the key findings. The experimental conditions, such as the total air flow rate, the feed CO ppm level, the amount of moisture in air etc., were varied over a wide range in this investigation. The objective of these experiments was to study the behavior of the catalyst under various operating conditions which may be encountered in industrial applications and to identify the operating limits.

5.1 Catalyst screening

Each catalyst prepared in this investigation was screened in the secondary reactor for its ability to oxidize CO at room temperature. The objective of this preliminary screening was to identify the few candidate catalysts that might have the potential to meet the requirements of the present work. Sufficient care was taken to maintain similar experimental conditions such as flow rate, catalyst volume etc in all the runs. In a typical experiment, the conditions such as air flow rate etc., were adjusted to a desired value and performance parameter such as CO outlet concentration with respect to a fixed value of inlet CO concentration was evaluated. Specifically, the reactor was filled with desired volume (5 to 30 mL) of the catalyst. Throughout the series of experiments carried out here, to begin with the room temperature oxidation efficiency of the catalyst at a space velocity of 8000 h^{-1} was tested. All these experiments were carried out using dry air. If the catalyst showed any activity, additional experiments were carried out at higher flow rates. The results have been presented in Table 5.1. Since only Pt-Ir/SDB, Pt/Y-zeolite catalysts showed activity for CO oxidation at the conditions under study further experimentation was carried out using these catalysts.

5.2 Extraneous Catalytic Effects

Before presenting the experimental results, it is worthwhile to address the issue of transport disguises. It is known that heat or mass transfer effects, caused by intra reactor, interphase or intra particle gradients, can disguise the results and lead to misinterpretations.

A blank experimental run, carried out without the catalyst in the reactor, exhibited no CO conversion indicating the reactor material to be non-catalytic. In the flow system, the flow rate was varied while the space velocity, defined in this study as the volumetric flow rate of the combined gas stream (i.e. air + CO + water vapor) entering the catalyst bed, divided by the volume of the catalyst bed, was kept constant. Accordingly, runs were carried out using different catalyst bed depths, and in the meantime, maintaining the same space velocity. It was observed that similar values of CO conversions were obtained at a fixed space velocity, thus indicating the absence of mass transfer effects. Typical results are shown in Figure 5.1. Since the CO feed concentrations used in this study were less than 300 ppm and in most runs below 100 ppm, the temperature increases as a result of heat released from the CO oxidation was less than 3.0 ^{0}C. This was confirmed by similar readings of the thermocouples at the inlet and outlet of the reactor. Hence it can be

Cat.#	Catalyst	Result
1	1.8%Pt-0.2%Ir/SDB	active
2	5.4%Pt-0.6%Ir/SDB	active
3	9.0%Pt-1.0%Ir/SDB	active
4	6.0%Pd-2.0%Ru/SDB	inactive
5	2.0%Pd-6.0%Ru/SDB	inactive
6	2.0%Ru/SDB	inactive
7	2.0%Au/SDB	inactive
8	0.2%Pt/alumina	inactive
9	3.0%Pt-3.0%Ce/alumina	inactive
10	3.0%Pd/alumina	inactive
11	3.0%Pd-3.0%Ce/alumina	inactive
12	5.0%Pt/Y-zeolite	active
13	3.0%Pd-3.0%Ce/Y-zeolite	inactive
14	1.8%Pt-0.2%Rh/silicalite	inactive
15	5.0%Pt-5.0%CuO/silicalite	inactive
16	5.0%Pd-5.0%CuO/silicalite	inactive
17	2.0%Pt/tin oxide	inactive
18	2.0%Au/cabosil	inactive
19	copper chromite	inactive

Table 5.1: Preliminary screening results

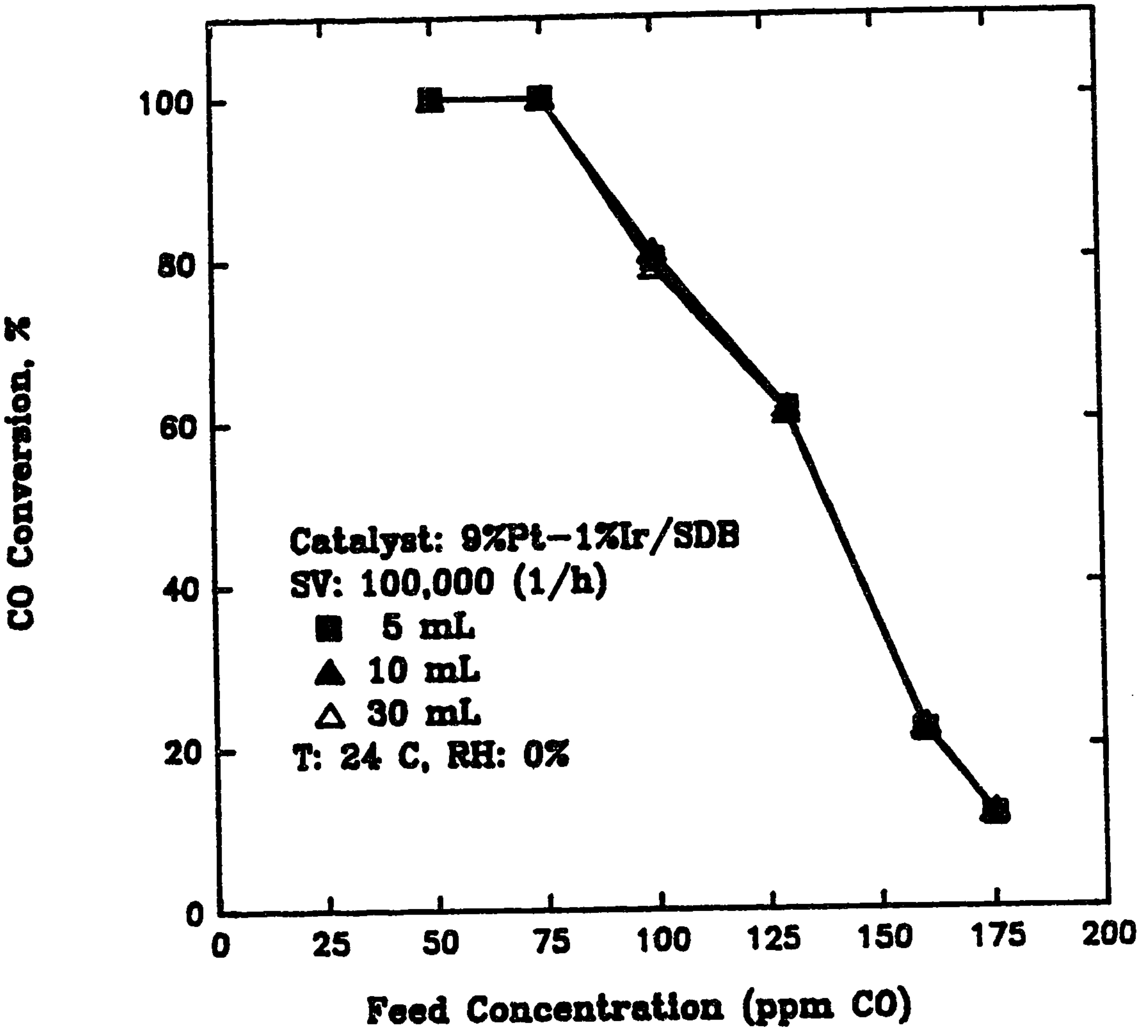


Figure 5.1: Effect of external mass transfer

assumed that the reactor was operated isothermally for all the experiments.

5.3 Effect of CO concentration

Three catalysts listed in Table 3.1 were tested to determine the effect of feed concentration on catalyst activity. Figure 5.2 shows the steady-state CO conversion versus feed concentration, at two different flow rates for each catalyst. When the total flow rate and hence the space velocity(SV) decreased, the overall conversion increased. Therefore, the curve for the higher flow rate appears on the left side of the lower flow rate curve. As CO feed ppm level was increased from zero to higher values, the reactor outlet conversion was close to about 100 percent, defined as ***high conversion*** regime. After inlet CO concentration was raised to a certain point the conversion dropped to a low value, defined as ***low conversion*** regime. The exact point of drop depended mainly on the CO inlet concentration, air flow rate, loading of active material and catalyst particle size. The features observed during this transition from a high conversion regime to low conversion regime have been further discussed in the following paragraphs.

The steady-state conversions of CO as a function of inlet concentration in consecutive cycles using 9%Pt-1%Ir/SDB catalyst are presented in Figure 5.3. Similar to many reports on CO oxidation (Razon and Schmitz, 1986) hysteresis phenomena were observed. The term hysteresis here refers to a multiplicity of steady states, and the actual steady state was observed to depend on the past history of operation of the reactor. In particular, different CO conversions were obtained for the same inlet CO concentration depending on the direction in which the CO inlet concentration was varied. Beginning with a regenerated catalyst, desired inlet conditions were maintained at a low CO inlet concentration until steady-state was reached, giving one data point on the top part of the curve. Then the inlet CO concentration was raised, and the experiment again proceeded to a steady-state,

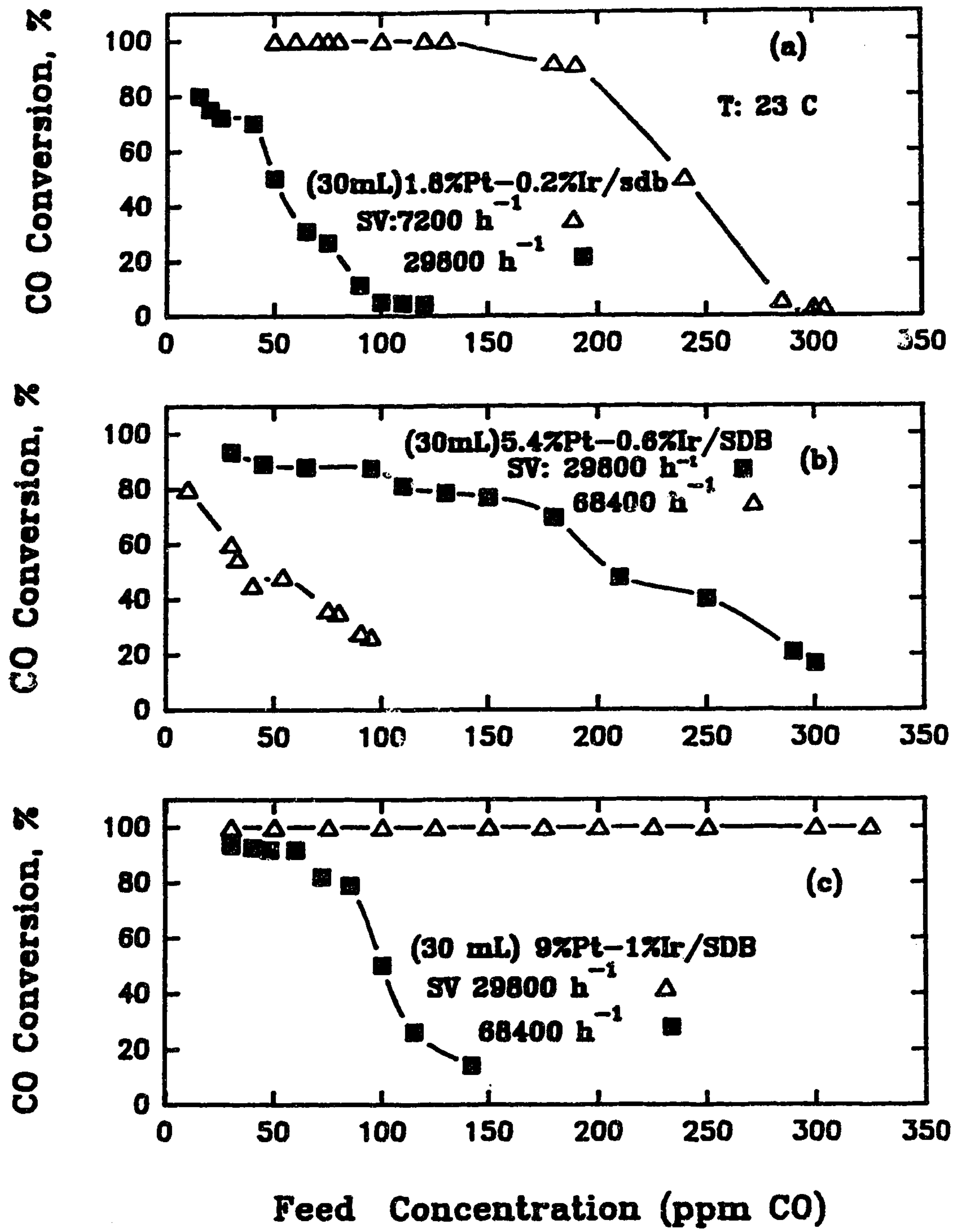


Figure 5.2: Effect of feed concentration on conversion

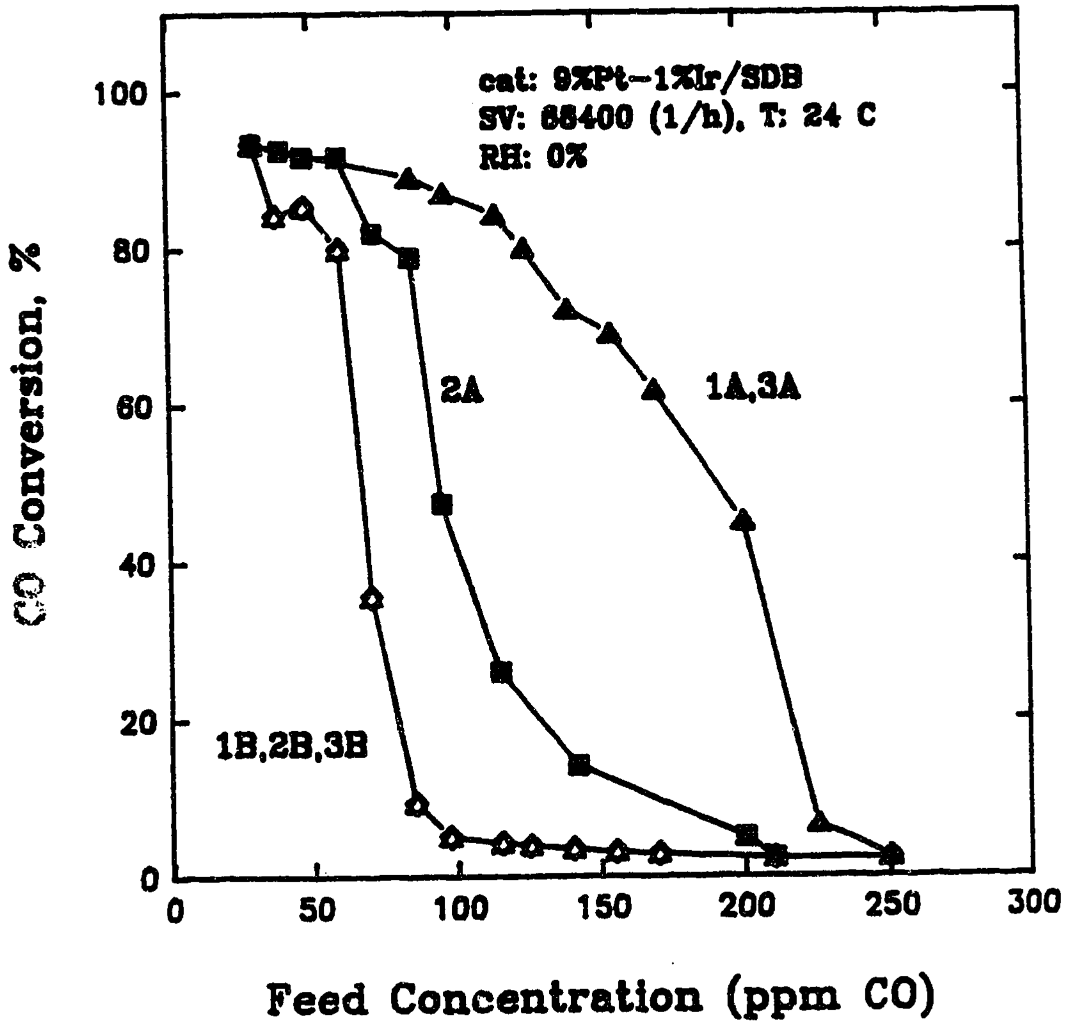


Figure 5.3: CO conversion hysteresis

giving another data point. This procedure was repeated in obtaining the curve denoted in Figure 5.3 as 1A. The CO concentration was then decreased, step by step, until a new steady-state was reached each time. This gave rise to the curve denoted as 1B in Figure 5.3. Thus for a given CO inlet concentration between the high conversion and low conversion regimes, there was a *transition* regime, which shows different steady state conversions. During the transition regime, oscillations in conversion were always observed. These oscillations started when the inlet CO concentration reached a certain point and ended when the CO concentration fell below this value during experimental run in the reverse direction. These observations, along with different explanations suggested by various authors (Razon and Schmitz, 1986; Imbihl, 1989) for observed oscillations at high temperatures and concentrations, lead us to believe that the oscillations in this study were caused by varying surface concentrations of the reacting species. Furthermore, because of the low CO concentrations involved, long transients for a complete transformation from a high conversion regime to low conversion regime were observed during tests. The time required to reach a complete saturation of CO on the surface was of the order of hours.

Figure 5.3 also shows that the catalyst activity was reduced in going from the first to the second cycle. The second cycle run, represented by curves 2A and 2B, was carried out immediately following the cycle 1 run without regenerating the catalyst. This suggests that in the absence of the regeneration step, the adsorbed CO from the previous experiment was not completely removed and therefore the transition from the high to low conversion regime occurred at a lower ppm. Following cycle 2, the catalyst was flushed with purified air for a period of approximately one hour and the activity was again tested in cycle 3. The catalyst exhibited the same activity as that obtained in cycle 1, thus indicating that the activity can be recovered by flushing with air at ambient temperature. Cant *et al.* (1978) and Tamhankar and LaCava (1989) have reported that the initial interaction of the platinum surface with CO permanently blocked some of the active sites and required high temperature for regeneration. In our study, the Pt-Ir catalyst supported on the hydrophobic SDB seems readily regenerable at low temperatures, indicating that the active ingredient and/or support surface may play an important role in the regeneration.

The occurrence of two conversion regimes and an unstable region wherein multiplicity and oscillations occur may be explained by the ability of platinum to adsorb CO and O_2 at various operating conditions. It is generally agreed that the rate of CO oxidation is controlled by the reaction between the adsorbed CO and O_2. At room temperatures CO is adsorbed more strongly than O_2 (Engel and Ertl, 1979) on the platinum surface. Thus adsorbed CO inhibits the adsorption of oxygen. The large CO coverage at high ppm values results in low conversion regime due to the lack of adsorbed oxygen. On the other hand, the adsorption of CO is not affected by the presence of adsorbed oxygen at the beginning of the experimental run. This results in high conversion regime where the CO molecules impinging upon the catalyst surface react with high probabilities. As the CO concentration in the feed is continually increased, the number of adsorbing CO molecules exceed the number of CO molecules removed by the oxidation and a transition to CO covered surface occurs. At this point the catalyst activity is dependent on the rate of oxygen adsorption and its subsequent dissociation on the surface. The following rate expression has been found by many studies (McCarthy *et al.*, 1975) to satisfactorily reflect the reaction kinetics of CO oxidation in air:

$$r = \frac{k[CO]}{(1 + K[CO])^2} \tag{5.1}$$

At low CO ppm levels the above equation reduces to $r = k[CO]$, which implies that the reaction rate on surface covered predominantly by oxygen is proportional to the impingement rate of CO molecules. At higher CO ppm levels, the rate becomes inversely proportional to CO concentration; i.e. $r = \bar{k}/[CO]$, which indicates that the CO oxidation reaction is inhibited by the presence of CO in the feed air.

5.4 Effect of metal loading

To determine the effect of metal loading on the catalyst activity the amount of noble metals(Pt-Ir) present in the catalyst sample was varied from 124 to 760 milligrams. The flow rate per milligram of metal present in the catalyst sample was used to compare the catalyst activity. A typical comparison at a fixed CO feed concentration is presented in Figure 5.4. It can be seen that the catalyst containing the lowest loading of metal (1.8%Pt-0.2%Ir) yields the best conversion of CO per unit weight of noble metal. This is reasonable because the noble metal is better dispersed at a lower loading. On the other hand the higher the loading the higher is the total metal area obtained. This can be seen from data given in Table 3.1. The reaction rate was found to increase with increasing total metal area and hence the catalyst containing the highest loading (9%Pt-1%Ir) exhibited the best catalyst activity.

5.5 Effect of water vapor

All the experimental results presented so far pertain to catalyst activities obtained under dry feed conditions. To determine the influence of water vapor on the catalyst activity, additional experiments were carried out with humid air. Two noble metal supported catalysts were used for the purpose: one supported on SDB (9%Pt-1%Ir/SDB) and the other supported on Y-zeolite with similar platinum content, each representing *hydrophobic* and *hydrophilic* type catalysts. Figure 5.5 compares the performance of the two catalysts under dry and humid feed conditions. It can be seen that in the case of a hydrophilic support, the catalyst is active under dry conditions but almost inactive in the presence of water vapor. This is due to the accumulation of capillary condensed water in catalyst pores similar to that observed by Sherwood (1981). The condensation results in increased diffusional resistance for the reactants across the liquid film covering the catalyst active sites. On the other

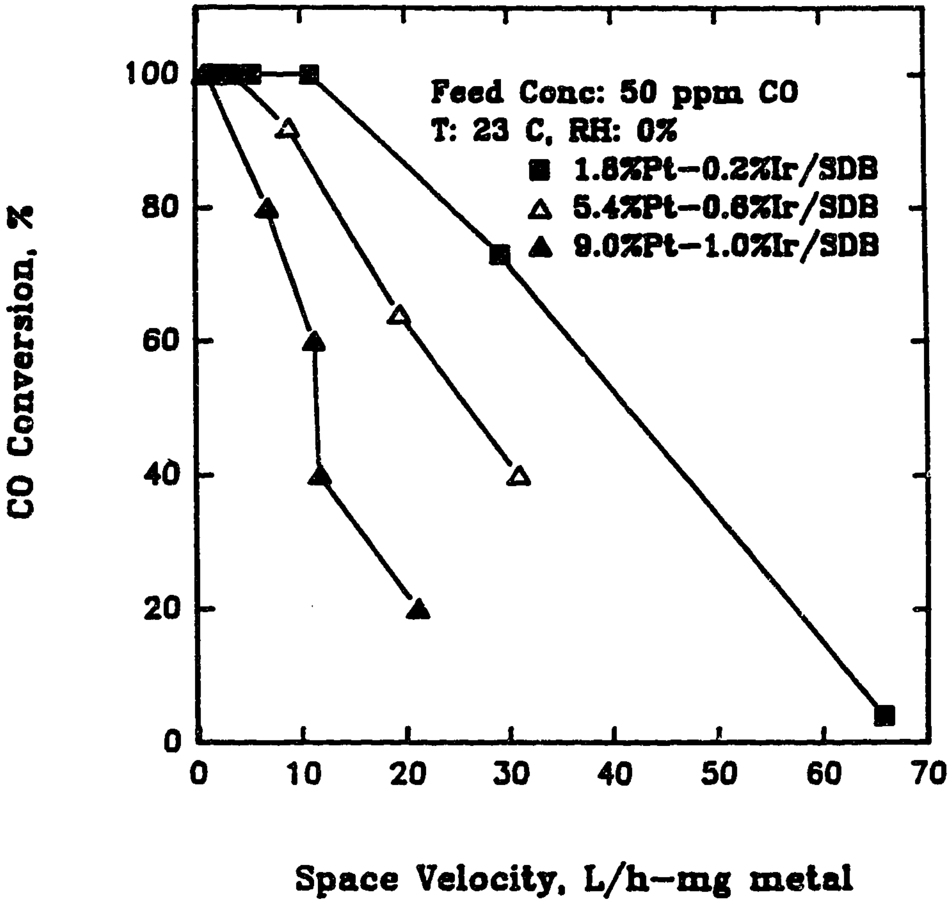


Figure 5.4: Effect of noble metal loading on catalyst activity

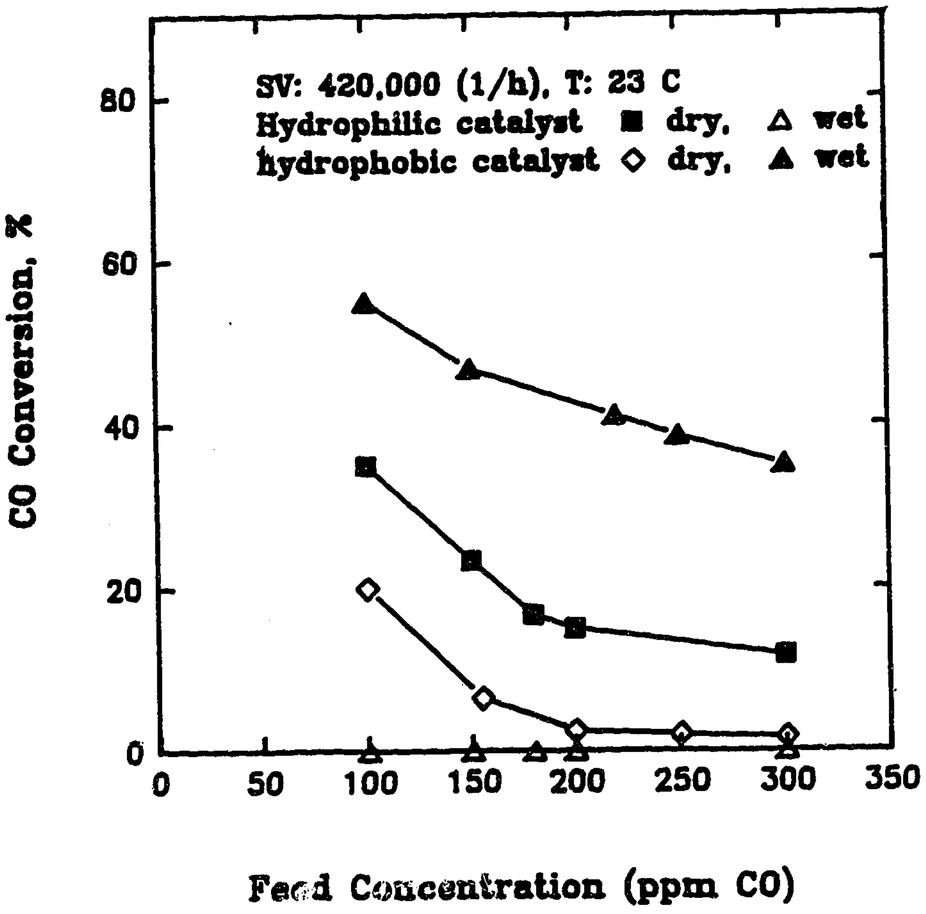


Figure 5.5: Effect of water vapor on catalyst activity

hand, the hydrophobic catalyst is not very active under dry conditions, but its activity increases when water vapor is introduced into the feed gas. The reason for the improvement in catalyst activity may be attributed to the change in adsorption characteristics of CO and/or O_2 by water adsorbed on the surface. In the case of hydrophobic catalysts, the surface is free of adsorbed water when the dry air is used. Since adsorbed water can only be obtained through the moisture mixed in the feed, it is reasonable to assume that adsorbed water has beneficial effects for the oxidation of CO. With hydrophilic catalysts, there always exists adsorbed water and surface hydroxyl groups at room temperatures and thus the catalysts showed good activity under dry feed conditions. Again, hydrophilic catalysts are not suitable for humid feeds because of capillary condensation.

5.6 CO oxidation by N_2O

The oxidation of CO by nitrous oxide (N_2O) was carried out to compare the results obtained from using O_2(air) as the oxidation agents. Since the reaction mechanism in both the cases is similar and differs only in the way the oxidant is formed on the surface, i.e. dissociative adsorption of O_2 needs two adjacent vacant sites whereas N_2O needs only one site. Tests were conducted with dry and humid feed using 9%Pt-1%Ir/SDB catalyst. Before each run the catalyst was flushed with N_2O (Purified grade, Linde - Union Carbide) for a period of approximately six hours. A typical set of results is presented in Figure 5.6. The data show similar observations to those made during the runs with dry and humid air. In the beginning of the run, the catalyst surface was essentially covered with adsorbed N_2O. Addition of low ppm CO into the feed stream resulted in rapid formation of CO_2, confirmed by the complete conversion of CO. When the available oxidant on the surface was continually removed by the reaction, a transition from N_2O to CO covered surface occurred. As a result, the catalyst exhibits low conversion. Similar to oxidation using air, oscillations

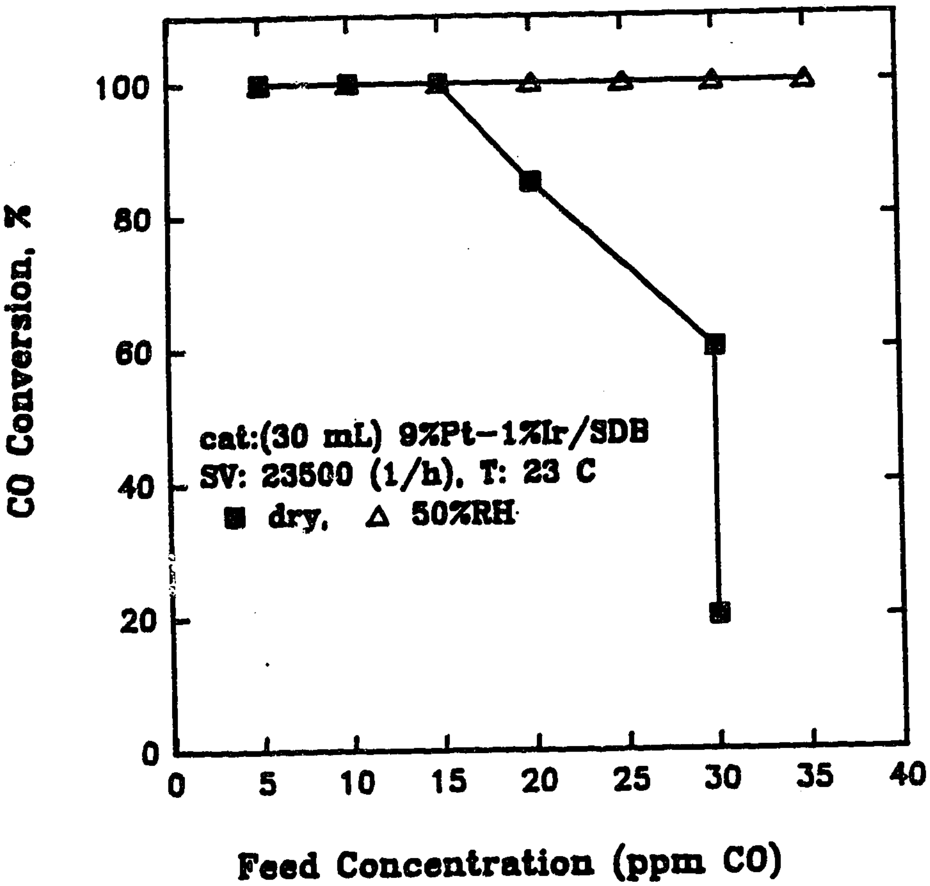


Figure 5.6: CO oxidation by N_2O

were also observed during the transition regime. Complete conversion of CO was obtained when water was introduced into the N_2O stream. This is also shown in Figure 5.6. The similarity of the results indicate that either two adjacent vacant sites are not essential for the dissociation of adsorbed O_2 into atomic form or the atomic oxygen is mobile so that the availability of any two vacant sites is the only requirement for dissociative adsorption. Therefore it may be concluded that the the adsorption of oxidant controls the rate at high CO concentrations.

5.7 Effect of catalyst particle size

Since platinum was found by X-ray analysis to deposit on the SDB support uniformly across the catalyst particle, the influence of intra particle diffusion on catalyst activity was studied by varying the particle size. For the purpose, the catalyst (9%Pt-1%Ir/SDB) in three different sizes, 5/9, 14/20, 20/35 mesh, were tested. Figure 5.7 shows the conversion of CO as a function of inlet concentration under dry air conditions. The results indicate that the catalyst activity varies with the particle size. It is clear from the figure that the catalyst with smallest particle size (20/35 mesh) drops to low conversion regime faster than the other two sizes. One possible explanation is that CO tends to adsorb on the outer layer of the particle and large portion of the platinum deposited on small particles is covered by adsorbed CO. The high CO coverage results in low catalyst activity. On the other hand, the platinum located in the internal of a large particle may be exposed to a lower CO concentration due to diffusional effects. Therefore, the rate of CO oxidation may be expressed by

$$rate = k_1[CO] + k_2/[CO] \tag{5.2}$$

The first and second term in the right hand side of the equation represents respectively,

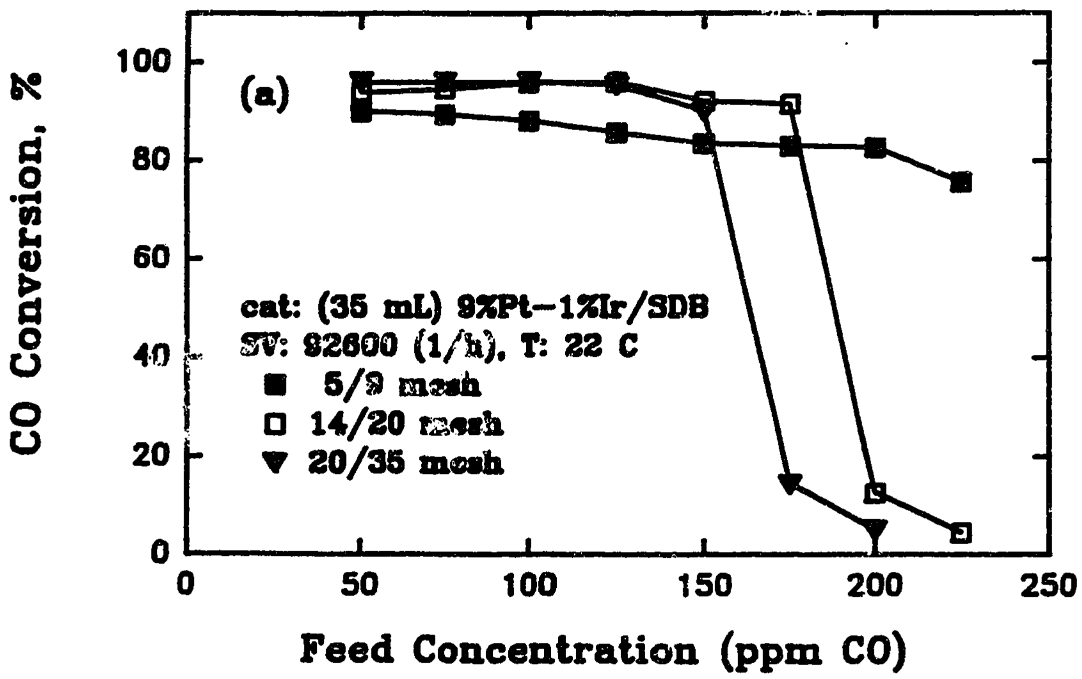


Figure 5.7: Effect of catalyst particle size on activity - dry feed conditions

the internal and external contribution to the reaction. It can be concluded that small particles are better for applications involving low CO concentrations. The particle size should be increased as the feed concentration increases. Hysteresis phenomena in CO conversion were also observed with all the particle sizes investigated. These have been shown for 5/9 mesh and 20/35 mesh particle size catalysts in Figures 5.8 and 5.9 respectively. In these figures, curves 1A and 1B correspond to steady-state CO conversions obtained by varying the feed CO concentrations in increasing and decreasing directions respectively.

The effect of feed humidity on catalyst activity for the three particle sizes was also investigated. Figure 5.10 shows the performance of the catalysts at a fixed inlet CO concentration by comparing the observed CO conversion as a function of amount of water vapor in the inlet air. The results obtained are in marked contrast to those obtained in the absence of water vapor. The catalyst with smallest particle size (20/35 mesh) was poisoned by CO at an inlet concentration of 185 ppm. However, in the presence of water vapor, complete conversion was obtained with 25% relative humidity(RH) in the feed. To ascertain the effect of water vapor on the catalyst activity, a test run was carried out for a period of ten hours (instead of the normal three hours), keeping the CO concentration at 185 ppm and maintaining 25% RH in the feed. No change in catalyst activity was observed at the end of the experiment, thus affirming the role of water vapor in improving the catalyst activity. By increasing water vapor content from 25% to 50% and higher relative humidity, a slight 'dip' in conversion was observed with particle sizes 5/9 mesh and 14/20 mesh, while no appreciable 'dip' was noticed with 20/35 mesh size.

5.8 Catalyst regeneration/reaction studies

The catalyst, when used in practice, would encounter various environmental conditions: humidity, temperature etc. In order to assess the behavior of the catalyst to these changes,

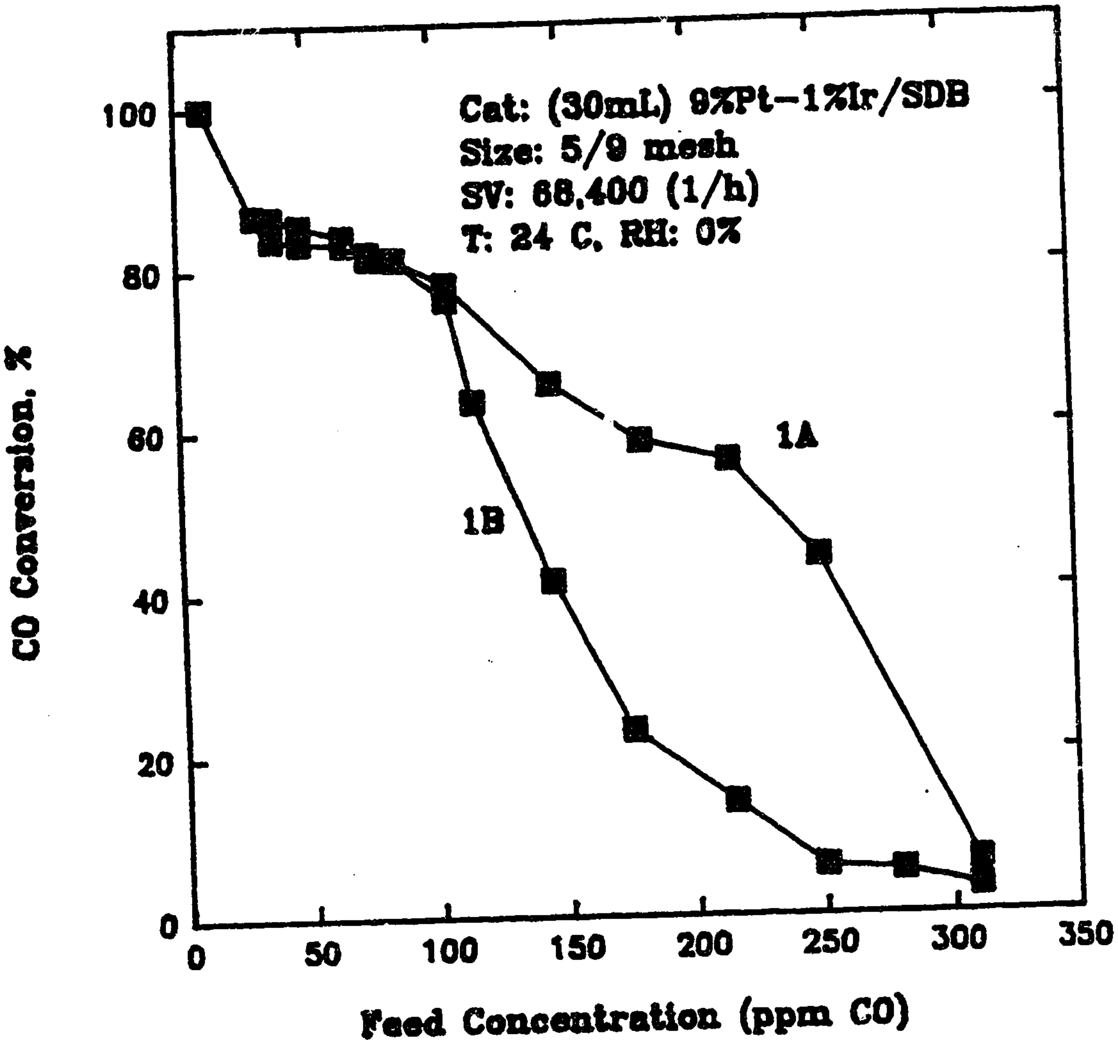


Figure 5.8: CO conversion hysteresis

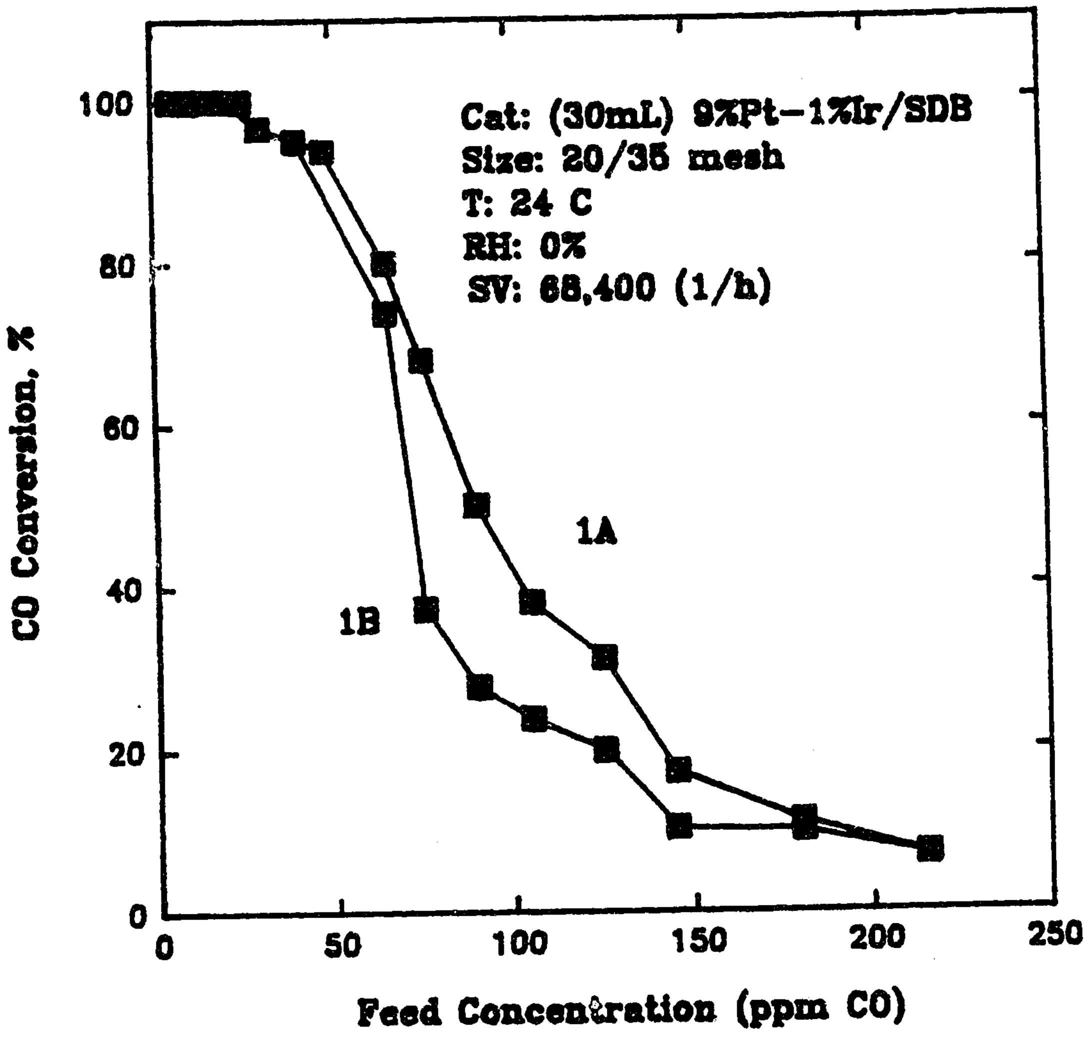


Figure 5.9: CO conversion hysteresis

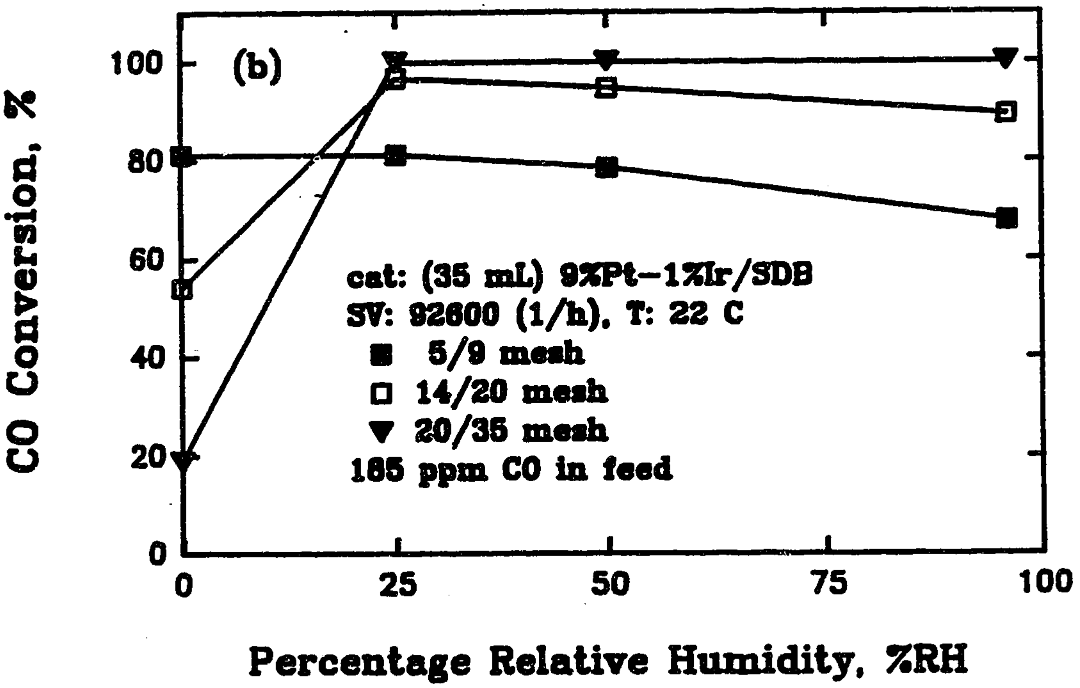


Figure 5.10: Effect of catalyst particle size on activity - humid conditions

experimental runs were carried out under the following conditions:

1. dry air reaction / dry air regeneration.
2. dry air reaction / wet air regeneration.
3. wet air reaction / dry air regeneration.
4. wet air reaction / wet air regeneration.

Figure 5.11(a) shows the results obtained during dry air reaction and dry air regeneration (case 1). It can be seen that in the absence of water vapor and at the high space velocity employed, the catalyst activity drops steadily in the first hour of operation. After the reaction reached the low conversion regime, the catalyst regeneration was carried out by shutting-off CO feed and flushing with air for a period of 45 minutes. The run was repeated with the regenerated catalyst and it was observed that the catalyst retraced the same activity profile. This suggests that the catalyst activity can be regained without using a high temperature regeneration procedure.

In dry reaction/wet regeneration (case 2) experiments, the reaction was carried out under dry air conditions at a CO concentration of 50 ppm. The regeneration step involved a contact of catalyst with CO-free air at 5% and 92% relative humidity. Upon regeneration, the reaction was once again carried out under dry conditions. It was observed that higher the relative humidity used in the regeneration the greater was the initial activity obtained. But after 45 minutes of operation the conversion dropped to a value similar to that in the dry regeneration. This is presented in Figure 5.11(b). It seems that water adsorbed during wet regeneration momentarily improved the activity and once the adsorbed water was removed from the catalyst surface, the catalyst repeated its performance under dry air conditions. The conversion data for cases 3 and 4 are summarized in Figure 5.11(c). Clearly, both dry and wet air regeneration were effective so long as the reaction was carried out

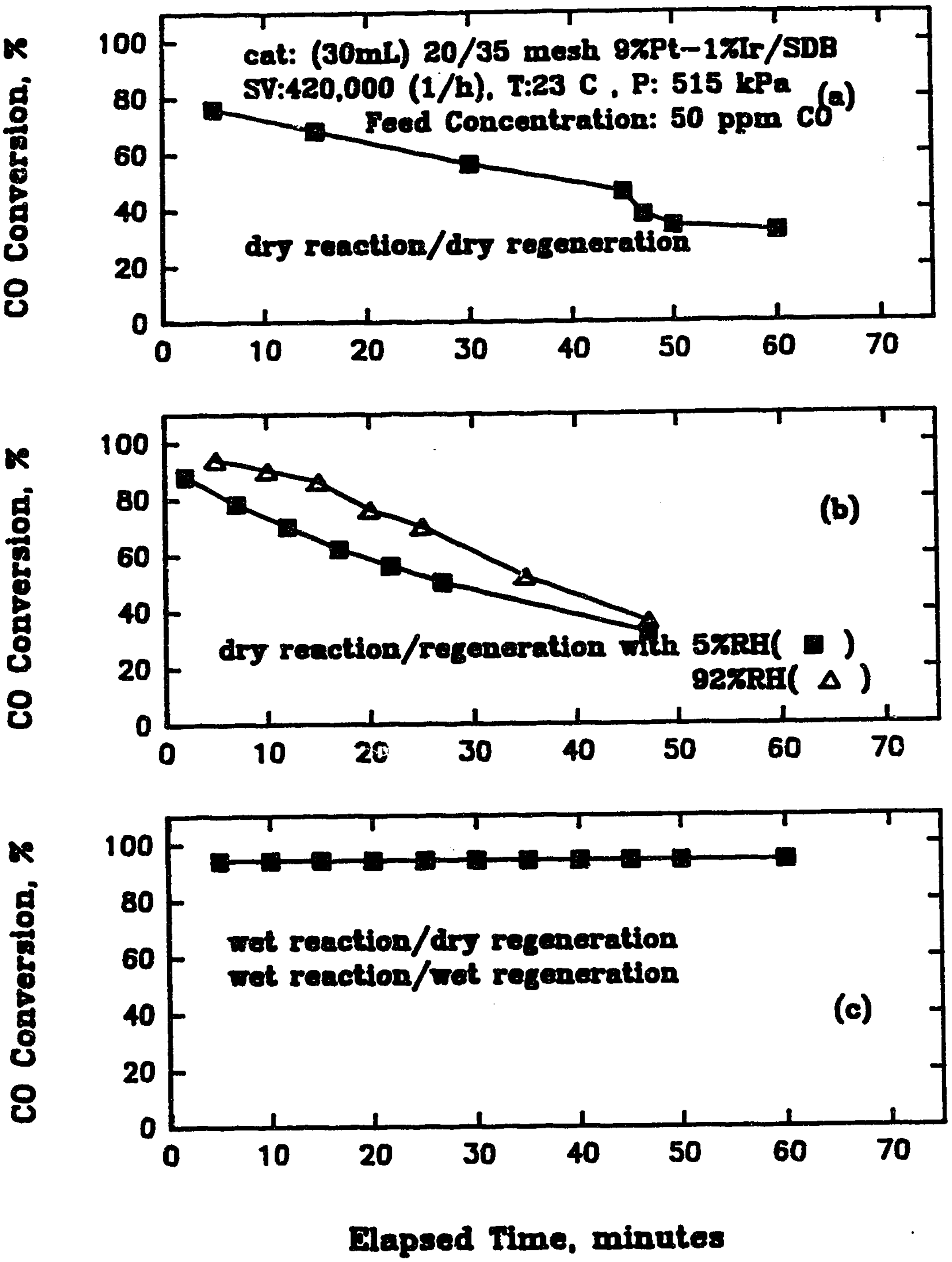


Figure 5.11: Catalyst regeneration/reaction results

under wet conditions.The results further emphasize the importance of water vapor in order to maintain catalyst activity at the high flow rates employed in the present investigation.

Chapter 6

Summary and Conclusions

A **hydrophobic** catalyst process for the effective removal of low (ppm) levels of carbon monoxide from air was developed. Several catalysts containing various ingredients on different supports were examined for their ability to oxidize CO at room temperature. Platinum-iridium-metal supported on styrene-divinyl benzene(SDB) exhibited the highest activity and is suitable for commercial applications.

In the course of process development, the behavior of the catalyst during CO oxidation was studied. Contrary to conventional noble metal supported catalysts, water vapor was found to enhance catalyst activity. In the absence of water vapor and at the conditions involved in this study, adsorbed CO inhibited the dissociative adsorption of oxygen and resulted in low activity of the catalyst. However, using a CO-free air the Pt-Ir catalyst was readily regenerable at room temperature and hence eliminated the need for a high temperature regeneration step. This suggests that active ingredient and/or support may play an important role in the catalyst regeneration. The oxidation of CO by nitrous oxide(N_2O) was also carried out to compare the results obtained from using O_2 (air) as the oxidation agent. From the similarity of the results in both cases, it was concluded that the adsorption of oxidant on the catalyst surface is the rate controlling step at high feed

CO concentrations.

Similar to CO oxidation at high CO concentrations and high temperatures, multiplicity and kinetic oscillations were also observed.

Bibliography

Alnot, M., Cassuto, A., Fusy, J. and Pentenero, A., 1974, *Comparative Adsorption of Oxygen and Nitrous oxide on Platinum recrystallized Ribbons, Jpn. J. Appl. Phys. Suppl. 2. Part 2.* 79-84.

Avery, N.R., 1983, *An EELS Study of Nitrous Oxide Adsorption on Pt(111), Surf. Sci.* **131**, 501-510.

Benton, A.F., 1923, *Manganese Oxide in the Catalytic oxidation of Carbon monoxide. J. Am. Chem. Soc.* **45**, 900-907.

Benton, A.F. and Bell, R.I., 1934, *The Oxidation of Carbon monoxide with a Silver Catalyst. J. Am. Chem. Soc.* **56**, 501-505.

Benton, A.F. and Elgen, J.C., 1927, *The Catalytic synthesis of Water vapor in contact with Metallic Gold. J. Am. Chem. Soc.* **49**, 2426-2438.

Beusch, H., Fieguth, P. and Wicke,E., 1972, *Thermisch und Kinetisch verursachte Instabilitaeten im Reaktionverhalten einzelner Katalysatorkorner. Chem.-Ing.-Tech,* **44**, 445-451.

Bond, G.C., 1972, *Catalytic Properties of Gold. Potential Applications in the Chemical Industry, Gold Bull.* **5**(1), 11-13.

Bond, G.C., Fuller, M.J. and Molloy, L.R., 1976, *Oxidation of Carbon Monoxide Catalysed by Palldium on Tin(IV) Oxide: An Example of Spill over Catalysis. Proceedings Sixth International Congr. on Catalysis, London.* **1**, 356-364.

Bond, G.C., Molloy, L.R. and Fuller, M.J., 1975, *Oxidation of Carbon Monoxide over Palldium on Tin(IV) Oxide Catalysts: Example of Spill over Catalysis, J. Chem. Soc. Chem. Commun.* **19**, 796-797.

Bond, G.C. and Sermon, P.A., 1973, *Gold Catalysts for Olefin Hydrogenation, Gold Bull.* **6**(4), 102-105.

Bone, W.A., 1926, *Studies upon Catalytic Combustion - pt III. The Influence of Steam upon Combustion of Carbonic oxide, Proc. Roy. Soc. London.* **A112**, 474-499.

Bonzel, H.P. and Burton, J.J., 1975, *CO Oxidation on a Pt(110) Surface, Surface Sci.*,**52**, 223-229.

Bonzel, H.P. and Ku, R., 1972, *Mechanisms of the Catalytic CO Oxidation on Pt(110), Surface Sci.* **33**, 91-106.

Brown, M.L., Green, A.W., Gohn, G. and Andersen, H.C., 1960, *Selective Oxidation of CO, Ind. Eng. Chem.* **52**, 841-844.

Campbell, C.T., Ertl, G., Kueppers, H. and Segner, J., 1981, *A Molecular beam Investigation of the Interactions of CO with a Pt(111) Surface, Surface Sci.* **107**, 207-219.

Canada EPS Report 7/UP/3, 1990, *National Urban Air Quality Trends - 1978 to 1987.*

Cant, N.W. and Fredrickson, P.W., 1975, *Silver and Gold Catalyzed Reactions of Carbon Monoxide with Nitric oxide and with Oxygen, J. Catal.* **37**, 531-539.

Cant, N.W., Hicks, P.C. and Lennon, B.S., 1978, *Steady-State Oxidation of Carbon monoxide over Supported Noble Metals with Particular Reference to Platinum. J. Catal.* **54**, 372-383.

Chauvin, Y., Commereuc, D. and Dawans, F., 1977, *Polymer Supported Catalysts. Prog. Polym. Sci.* **5**, 95-216.

Chuang, K.T., Quaiattini, R.J., Thatcher, D.R.P. and Puissant, L.J., 1987, *Development of a Wetproofed Catalyst Recombiner for Removal of Airborne Tritium, Appl. Catal.* **30**, 215-224.

Conrad, H., Ertl, G. and Kueppers, J., 1978, *Interactions between Oxygen and Carbon Monoxide on a Pt(111) Surface, Surface Sci.* **76**, 323-342.

bibitem Cortes, J. and Droguett, S., 1975, *Temperature Programmed Desorption of CO from Supported Cobalt. J. Catal.* **38**, 477-481.

Cox, M.P., Ertl, G., Imbihl, R. and Rustig, J., 1983, *Non-equilibrium Surface Phase Transitions during the Catalytic Oxidation of CO on Pt(100), Surface Sci.* **134**, L517-L523.

Cutlip, M. and Kenney, C.N., 1978, *Limit Cycle Phenomena During Catalytic Oxidation Reactions Over a Supported Platinum Catalyst. 5th Intern. Sympos. Chem. Reaction Eng., Houston, ACS Sympos. Ser.* **65**, 475-486.

Daglish, A.G. and Eley, D.D., 1961, *The Carbon Monoxide - Oxygen Reaction on Palladium Gold Alloys, Actes 2^{me} Congr. Intern. Catalyse, Vol I. Ed. Technip, Paris.* 1615-1624.

Desai, M.N., Butt, J.B. and Dranoff, J.S., 1983, *Low-Temperature Oxidation of CO by a Heterogenized Wacker Catalyst, J. Catal.* **79**, 95-103.

Dorling, T.A. and Moss, R.L., 1967, *The Structure and Activity of Supported Metal Catalysts II: Crystallite Size and Carbon monoxide Chemisorption on Platinum/Silica Catalysts, J. Catal.* **7**, 378-385.

Eigenberger, G., 1978, *Kinetic Instabilities in Heterogeneously Catalyzed Reactions-II, Chem. Eng. Sci.* **33**, 1263-1268.

Engel, T. and Ertl, G., 1978, *A Molecular Beam Investigation of the Catalytic Oxidatiion of CO on Pd(111), J. Chem. Phys.* **69**, 1267-1280.

Engel, T. and Ertl, G., 1979, *Catalytic Oxidation of CO on Platinum Metals, Adv. Catal.* **28**, 1-78.

Engel, T. and Ertl, G., 1982, *The Chemical Physics of Solid Surfaces and Heterogenious Catalysis. Edited by King, D.A. and Woodruff, D.P., Elsevier Publishing Company. Amsterdam.* 72-93.

Engelder, C.J. and Blumer, M., 1932, *Catalysts for Oxidation of Carbon Monoxide-II, J. Phys. Chem.* **36**, 1353-1358.

Ertl, G. and Koch, J., 1973, *The Catalytic Oxidation of CO on Palladium Surfaces, Proc. 5th Int. Congr. Catal. (1972).* 969-979.

Fieguth, P. and Wicke, E., 1971, *Der Uebergang vom Zund/Losch-verhalten zu stabilen Reaktionzustanden bei einem adiabatischen Rohrreaktor, Chem. -Ing. Tech.* **43**, 604-608.

Ford, R.R., 1970, *Carbon Monoxide Adsorption on The Transition Metals, Adv. Catal.* **21**, 51-145.

Freel, J., 1972, *Chemisorption on Supported Platinum II: Stoichiometry for Hydrogen, Oxygen and Carbon Monoxide, J. Catal.* **25**, 149-160.

Golodets, G.I., 1983, *The Oxidation of Carbon Monoxide, Heterogeneous Catalytic Reactions Involving Molecular Oxygen. Elsevier Scientific Publishing Company, Amsterdam.* 280-311.

Greek, W. P. and Dorweiler, V. P., 1990, *Regulation of Carbon monoxide : Are current standards Safe?, Environ. Sci. Technol.*,**24** (1), 32-33.

Griffiths, K., Jackman, T.E., Davies, J.A. and Norton, P.R., 1984, *Interaction of* O_2 *with Pt(100): I. Equilibrium Measurements, Surface Sci.* **138**, 113-124.

Haruta, M., Kobayashi, T., Sano, H. and Yamada, N., 1987, *Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature far below* $0\,^{\circ}C$*, Chem. Lett.* 405-408.

Haruta, M., Yamada, N., Kobayashi, T. and Iijima, S., 1989, *Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide, J. Catal.* **115**(2), 301-309.

Hawkins, C.J., 1978, *Ph.D Thesis, U. of Cambridge*

Hegedus, L.L., Oh, S.H. and Baron, K., 1977, *Multiple Steady-states in an Isothermal, Integral Reactor: The Catalytic Oxidation over Platinum-Alumina, AICHE J.* **23**, 632-642.

Hodges, C.N. and Roselaar, L.C., 1975, *Gold and Platinum Catalyzed Oxidation of Methanol, J. Appl. Chem. BioTechnol.* **25(8)**, 609-614.

Holliday, R., 1981, *Ph.D Thesis, U. of Cambridge*

Imbihl, R., 1989, *The Study of Kinetic Oscillations in the Catalytic CO-Oxidation on Single Crystal Surfaces, Dechema Monographs, Papers of the 27th Tutzing Symposium, March 6-9* **120**, 405-441.

Jensen, K.F. and Ray, W.H., 1980, *A Microscopic Model for Catalytic Surfaces - I. Catalytic Wires and Gauges, Chem. Eng. Sci.* **35**, 2439-2457.

Jensen, K.F. and Ray, W.H., 1982, *A Microscopic Model for Catalytic Surfaces - II. Supported Catalysts, Chem. Eng. Sci.* **37**, 1387-1410.

Katz, M., 1953, *The Heterogeneous Catalytic Oxidation of Carbon Monoxide, Adv. Catal.* **5**, 177-216.

Kisliuk, P.J., 1957, *The Sticking Probabilities of Gases Chemisorbed on the Surfaces of Solids, Phys. and Chem. Solids.* **3**, 95-101.

Kisliuk, P.J., 1958, *The Sticking Probabilities of Gases Chemisorbed on the Surfaces of Solids II, Phys. and Chem. Solids.* **5**, 78-84.

Lamb, A.B., Bray, W.C. and Frazer, J.C.W., 1920, *The Removal of Carbon Monoxide from Air, Ind. Eng. Chem.* **12**, 213-223.

Langmuir, I., 1922, *The Mechanism of the Catalytic Action of Pt in the Reactions* $2CO + O_2 = 2CO_2$ *and* $2H_2 + O_2 = 2H_2O$, *Trans. Faraday Soc.* **17**, 621-.

Leder, F. and Butt, J.B., 1966, *Surface Catalysis of the Hydrogen-Oxygen Reaction on Platinum At Low Temperatures, A.I.Ch.E.J* **12(4)**, 718-721.

Lieto J., D. Milstein, R.L. Albright, J.V. Minkiewicz and Gates, B.C., 1983, *Polymeric Supports for Catalysts, J. CHEMTECH*, January, 46-53.

Lintz, H.G., 1981, *The Oxidation of CO by* O_2, *NO and* N_2O *on Polycrystalline Platinum Under Knudsen Conditions: A Comparison, Surf. Sci.* **108**, L486-L489.

Lorimer, D. and Bell, A.T., 1979, *Reduction of NO by CO Over a Silica-Supported Platinum Catalyst: Infrared and Kinetic Studies, J. Catal.* **59**, 223-238.

Matsushima, T., 1978, *Trace Studies on the Reaction Paths of CO Oxidation over Platinum, J. catal.* **55**, 337-347.

McCarthy, E., Zahradnik, J., Kuczynski, G.C. and Carberry, J.J., 1975, *Some Unique Aspects of CO Oxidation on Supported Pt, J. Catal.* **39**, 29-35.

Nishiyama, Y. and Wise, H. *Surface Interaction between Chemical Species on Platinum: Carbon monoxide, Hydrogen, Oxygen and Methanol, J. Catal.* **32**, 50-62.

Norman, J.D.V, Brown, K.G., Schryer, J., Schryer, D.R., Upchurch, B.T. and Sidney, B.D., 1990, *The Effect of H_2O and Pretreatment on the Activity of a Pt/SnO_2 Catalyst, NASA Conference Publication 3076.* 181-191.

Norton, P.R., 1974, *Surface Analysis of Platinum by X-Ray Photo Electron Spectroscopy (XPS), Surface Sci.* **44**, 624-628.

Norton, P.R., 1975, *An Investigation of the Adsorption of Oxygen and Oxygen Containing Species on Pt by Photoelectron Spectroscopy, Surface Sci.* **47**, 98-114.

Norton, P.R., Griffiths, K. and Bindner, P.E., 1984, *Interaction of O_2 with Pt(100): II. Kinetics and Energetics, Surface Sci.* **138**, 125-147.

Oh, S.H., Baron, K., Cavendish, J.C. and Hegedus, L.L., 1978, *Carbon Monoxide Oxidation in an Integral Reactor: Transient Response to Concentration Pulses in the Regime of Isothermal Multiplicities, Amer. Chem. Soc. Sympos. Ser.* **65**, 462-474.

Oh, S.H., Baron, K., Sloan, E.M. and Hegedus, L.L., 1979, *Effects of Catalyst Particle Size on Multiple Steady States, J. Catal.* **59**, 272-277.

Padberg, G. and Wicke, E., 1967, *Stabiles und Instabiles verhalten eines Adiabatischen Rohrreaktors am Beispiel der katalytischen CO-Oxydation, Chem. Eng. Sci.* **22**, 1035-1051.

Papp, H. and Kamp, P., 1988, *Characterization of Supported Pd Catalysts, Surface and Interface Analysis.* **12**, 253-256.

Razon, L.F. and Schmitz, R.A., 1986, *Intrinsically Unstable Behavior during the Oxidation of CO on Platinum, Catal. Rev. -Sci. Eng.* **28**(1), 89-164.

Sales, B.C., turner, J.E. and Maple, M.B., 1982, *Oscillatory Oxidation of CO over Pt, Pd and Ir Catalysts: Theory, Surface Sci.* **114**, 381-.

Schmitz, R.A., 1975, *Multiplicity, Stability and Sensitivity of States in Chemically Reacting Systems, Adv. Chem. Ser.* **148**, 156-211.

Schryer, D.R. and Hoflund, G.B., Editors, 1990, *Low-Temperature CO Oxidation Catalysts for Long Life CO_2 Lasers, NASA Conference Publication 3076.*

Schryer, D.R., Upchurch, B.T., Hess, R.V., Wood, G.M., Sidney, B.D., Miller, I.M., Brown, K.G., Norman, J.D.V., Schryer, J., Brown, D.R., Hoflund, G.B., Herz, R.K., 1990, *Pt/SnO_2 - Based CO-Oxidation Catalysts for Long-Life Closed-Cycle CO_2 Lasers, NASA Conference Publication 3076.*

Schwab, G.M. and Gossner, K., 1958, *Die Kohlenoxydverbrenung an Silber, Palladium und deren Legierung, Z. Phys. Chem. NF.* **16**, 39-63.

Schwank, J., 1983, *Catalytic Gold: Applications of Elemental Gold in Heterogeneous Catalysis, Gold Bull.* **16**(4), 103-110.

Sheintuch, M. and Schmitz, R.A., 1977, *Oscillations in Catalytic Reactions, Catal. Rev. -Sci. Eng.* **15**, 107-172.

Sheintuch, M., Schmidt, J., and Lecthman, Y., 1989, *Modelling Catalyst - Support Interactions in CO oxidation Catalyzed by Pd/SnO$_2$, Appl. Catal.* **49**, 55-65.

Sherwood, A.E., 1981, *Kinetics of Catalysed Oxidation in Air at Ambient Temperature, Am. Chem. Soc. Natl. Top. Meet.*, Dayton, Ohio, April 29 - May 1.

Sklyarov, A.V., Tretyakov, I.I., Shub, B.R. and Roginskii, 1969, *Oxidation of Carbon Monoxide by Oxygen on Platinum Cleaned in Ultravacuum, Dokl. AN SSSR.* **189**(6), 1302-1305.

Slin'ko, M.G. and Slin'ko, M.M., 1978, *Self Oscillations of Heterogeneous Catalytic Reactions, Catal. Rev. -Sci. Eng.* **17**, 119-153.

Smith, T.G., Zahradnik, J., Kuczynski, G.C. and Carberry, J.J., 1975, *Non-Isothermal Inter-Intraphase Effectiveness Factors for Negative order Kinetics - CO Oxidation over Pt, Chem. Eng. Sci.* **30**, 763-767.

Sokoloskii, D.V., Popova, N.M. and Sizbikbayeva, M.B., 1965, *Trudy Inst. Khim. Nauk An Kaz. SSR.* **13**, 118.

Stark, D.S. and Harris, M.R., 1983, *J. Phys. E: Sci. Instr.* **16**, 492-.

Stewart, R., 1975, *Ann. Rev. of Pharmacol.: Annual Reviews:* Palo Alto, CA.

Stiles, A.B., 1983, *Catalyst Manufacture - Laboratory and Commercial Preparations, Chemical Industries/14, Marcel Dekker, Inc. New York.*

Tajbl, D.G., Simmons, J.B. and Carberry, J.J., 1966, *Heterogeneous Catalysis in a Continuous Stirred Tank Reactor, Ind. Eng. Chem. Fundam.* **5**, 171-175.

Tamhankar, S.S. and LaCava, A.I., 1989, *Catalytic Oxidation of traces of CO and H$_2$ in the ultra-purification of inert gases, Gas Sepn. and Purn.* **3**, 128-132.

Taylor, J.L., Ibbotson, D.E. and Weinberg, W.H., 1979, *The Chemisorption of Oxygen on the (110) Surface of Iridium, Surface Sci.* **79**, 349-384.

Thiel, P.A. and Madey, T.E., 1987, *The interaction of Water with Solid Surfaces : Fundamental Aspects, Surface Sci. Rept.* **7**, 211- 385.

Tretyakov, I.I., Sklyarov, A.V. and Shub, B.R., 1970, *Kinetics and Mechansims of the Oxidation of Carbon Monoxide on Ultravacuum-Purified Platinum, Kinetics and Catalysis* **11**, 133-139.

Tretyakov, I.I., Sklyarov, A.V. and Shub, B.R., 1970, *Catalysis by Metals Purified under Ultrahigh Vacuum, Kinetics and Catalysis* **11**, 397-405.

Tretyakov, I.I., Sklyarov, A.V. and Shub, B.R., 1971, *Kinetics and Mechanism of the oxidation of CO on Pure Palladium, Kinetics and Catalysis* **12**, 884-889.

Tucker Jr., C.W., 1964, *Low-Energy diffraction study of CO adsorption on the (100) face of Platinum, Surface Sci.* **2**, 516-521.

Votruba, J. and Hlavacek, V., 1974, *Experimental Study of Multiple States in a Tubular Adiabatic Reactor, Intern. Chem. Eng.* **14**, 461-469.

Wagner, F.T., Moylan, T.E. and Schmieg, S.J., 1988, *Hydrophilic Versus Hydrophobic Coadsorption: Carbon Monoxide and Water on Rh(111) Versus Pt(111), Surface Sci.* **195**, 403-428.

Wei, J. and Becker, E.R., 1975, *The Optimum distribution of Catalytic Material on Support Layers in Automotive Catalysis, Adv. Chem. Ser.* **143**, 116-132.

Weinberg, W.H., 1973, *A Model Description of the Adsorption and Decomposition of Nitrous Oxide on Clean and Carbon Covered Platinum Surfaces. J. Catal.* **28**, 459-470.

Weinberg, W.H., Comrie, C.M. and Lambert, R.M., 1976, *The Kinetics of Adsorption of CO on Group VIII Transition Metals, J. Catal.* **41**, 483-493.

Whitesell, W.A. and Frazer, J.C.W., 1923, *Manganese dioxide in the Catalytic Oxidation of CO, J. Am. Chem. Soc.* **45**, 2841-2851.

Wilf, M. and Dawson, P.T., 1975, *The Adsorption and Desorption of Oxygen on the Pt(110) surface: A thermal desorption and LEED/AES study, Surface Sci.* **65**, 399-418.

Winter, E.R.S., 1969, *The Decomposition of Nitrous Oxide on the Rare Earth Sesquioxides and Related Oxides, J. Catal.* **15**, 144-152.

Wright, C.R.A. and Luff, A.P., 1878, *On Some Points in Chemical Dynamics, J. Chem. Soc.* **33**, 535.

Yao, H.C., Sieg, M. and Plummer Jr., H.K., 1979, *Surface Interactions in the Pt/γ-Al_2O_3 System, J. Catal.* **59**, 365-374.

Yates, D.J., 1969, *J. Colloid Interface Sci.* **29**, 144.

Zhdan, P.A., Boreskov, G.K., Egelhoff, W.F. and Weinberg, W.H., 1976, *The Application of XPS to the Determination of the Kinetics of the CO oxidation reaction over the Ir(111) Surface, Surface Sci.* **61**, 377-390.