

## CHAPTER I

### INTRODUCTION

#### 1.1 Introduction

Air pollution which is defined as the addition to our atmosphere of any material(s) having a deleterious effect on life has recently become a serious problem, especially in the large cities of the world. There are several sources of air pollution that can be generated by six major types of sources:

1. Transportation
2. Domestic heating
3. Electric power plants
4. Refuse burning
5. Forest and agricultural fires
6. Industrial fuel burning and process emissions (Sell, 1992)

The main pollutants are carbonmonoxide (CO), oxides of nitrogen (NO<sub>x</sub>), unburnt hydrocarbon (HC), oxides of sulfurs, heavy metals, soots, polyaromatics, aldehydes, ketones, and nitro-olefins. However, the first four pollutants are produced in significant quantities.

Carbonmonoxide is a by product of combustion caused by incomplete combustion of hydrocarbons. It has a serious effect on human and animal nervous systems even in low concentrations. It can easily combine with hemoglobin, the component of blood responsible for the transport of oxygen, to form carboxyhemoglobin (COHb). CO has an affinity for hemoglobin of the blood by more than 200 times that of oxygen, thus reducing the capability of the blood to carry oxygen (Benitez, 1993). Two percent of carboxyhemoglobin is

enough to generate observable effects. Oxygen transport system is clearly affected at 75 % carboxyhemoglobin, generated at CO levels of 30 ppm or greater (Sell, 1992).

Oxides of nitrogen (NO<sub>x</sub>) include six known gaseous compounds:

1. Nitric oxide (NO)
2. Nitrogen dioxide (NO<sub>2</sub>)
3. Nitrous oxide (N<sub>2</sub>O)
4. Nitrogen sesquioxide (N<sub>2</sub>O<sub>3</sub>)
5. Nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>)
6. Nitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>)

NO<sub>x</sub>, like CO, are mainly formed during combustion, although a few industries also emit these gases from process operations. It is estimated that of the 19.5 million metric tons of NO<sub>x</sub> emitted in 1987, 43 % is produced from mobile sources, the remainder comes mostly from fuel combustors. Consisting primarily of nitric oxide and nitrogen dioxide, NO<sub>x</sub> are formed by the oxidation of fuel-bound nitrogen (fuel NO<sub>x</sub>) and by the fixation of nitrogen in the combustion air at the high temperatures associated with combustion (thermal NO<sub>x</sub>). The formation of fuel NO<sub>x</sub> depends on such factors as the nitrogen content of the fuel, total excess air, and relative distribution of primary and secondary combustion air. Formation of thermal NO<sub>x</sub> is influenced by oxygen availability, temperature, pressure, and residence time in the combustion unit.

However, NO and NO<sub>2</sub> are usually found in much lower concentrations than CO. Their ultimate effect on humans is not clearly understood, but they do act as irritants to breathing, and create discomfort to the eyes. NO<sub>2</sub> can also destroy the cilia in the respiratory system and suppress alveolar macrophage

activity, the lungs' final defense against foreign matter. Nitrogen oxides are also the main cause of acid rain problem. NO is the key starting chemical for all of the other oxides of nitrogen. Once produced, NO is rapidly oxidized by ozone, OH, or HO<sub>2</sub> radicals to form the higher oxides of nitrogen, such as NO<sub>2</sub>, HNO<sub>2</sub>, and HO<sub>2</sub>NO<sub>2</sub>. Thus, if NO is prevented from entering the atmosphere, most of the downstream effects of NO<sub>x</sub> pollution can be eliminated (Armor, 1994).

The control technology of nitrogen oxides is generally divided into two groups. The first group is a technology by which the formation of thermal nitric oxide is greatly suppressed, for example, using catalytic combustion which lowers the combustion temperature below 1300 °C. The second group is a technology by which the emitted nitrogen oxide is removed in various methods for example catalytic reduction, adsorption, electron irradiation, and etc. ( Nakatsuji, 1991).

One of the most efficient technologies used to control nitric oxide emission is catalytic reduction and oxidation by using carbonmonoxide, hydrogen, or hydrocarbon as a reducing agent. Generally, a NO<sub>x</sub> decomposition catalyst is required to have at least 2 characteristics: the stability of catalyst is the first required character. This stability includes thermal resistance, anti-poison and anti-abrasion. The second required character is high activity over a wide range of temperatures. Exhaust gas temperature depends upon the change of load on combustion. So the decomposition of NO<sub>x</sub> catalyst should be possible for wide range of temperatures.

## 1.2 Background

Catalytic reduction of nitric oxide by carbonmonoxide is an important process in air pollution control. This redox reaction has been investigated by a lot of researchers with several metal catalysts. During the early implementation of the clean air act, many catalytic materials have been studied and the area of high temperature stabilization of alumina has been explored. Noble metals (Pt, Pd and Rh) have been shown to be excellent catalysts for NO reduction and CO oxidation and studied in detail (both transient and steady-state condition). Generally, most noble metals based catalyst research have used highly porous inert materials as support ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ). Some researchers have used a combination of more than two noble metals. Many base metal candidates have been investigated, such as Cu, Cr, Ni, Mn, and so on. Non-noble metals are normally less active than the noble metals but are substantially cheaper and more readily available (Heck, et al., 1995 ).

The reduction of nitric oxide on copper-nickel catalysts was examined by Bauerle in 1974. The result was that the catalyst activity was dependent on the nickel:copper ratio. In general, activity increased with increasing copper content. At the higher copper levels, the reaction was first order with respect to NO and the reaction order decreased with decreasing copper content below 24 %.

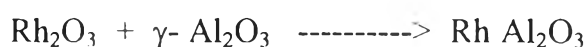
Recently, Iwamoto, et. al. (1991) and Held, et. al. (1990) have independently reported that copper ion-exchanged ZSM-5 zeolite (Cu-Z) was able to reduce NO<sub>x</sub> in the presence of oxygen, with hydrocarbon (HC) as the reducing agent. At the maximum activation temperature of 400 °C, the NO<sub>x</sub> reduction efficiency of about 25 % can be obtained with the unburnt hydrocarbon in the exhaust. Furthermore, if the hydrocarbon concentration is

increased by supplying hydrocarbon from outside the exhaust, the NO<sub>x</sub> reduction efficiency can be improved up to 80 %.

Nitric oxide reduction by hydrocarbons over Cu-ZSM5 monolith catalyst under lean conditions at steady state conditions was also studied by Cho in 1993. The results showed that C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> were individually active for selective reduction of NO over Cu-ZSM5 under lean conditions. However, C<sub>2</sub>H<sub>4</sub> was more efficient than C<sub>3</sub>H<sub>6</sub> due to its superior selectivity.

Although the reduction of nitric oxide was investigated by non-noble metal catalysts, the efficiency and activity were lower than noble metal catalysts (Heck, et al., 1995).

Platinum and palladium addition to supported rhodium catalysts were investigated for automotive emission control (Schlatter and Taylor, 1977). A supported rhodium catalyst with low loading (0.002 wt % Rh) was found to have good activity for converting nitric oxide to nitrogen in a laboratory feedstream, but its oxidation activity was inadequate. Addition of platinum and palladium improved the oxidation activity. However, it was found that this two-metal combination (Pt-Rh or Pd-Rh) formed more ammonia under reducing conditions and decreased nitric oxide conversion under oxidizing conditions, as compared to rhodium alone. In addition, studies have been recently conducted to reduce the reaction of Rh with high surface area carriers, such as stabilized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. At temperature in excess of 800-900 °C, in an oxidizing mode, the Rh reacts with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to form the inactive aluminate (Heck, et al., 1995)



Structure sensitive selectivity of the NO-CO reaction over Rh (110) and Rh (111) was also studied by Peden, et al. in 1995. They found that the NO-CO reaction was very sensitive to the Rh surface structure primarily with regard to the selectivity of the reaction for N<sub>2</sub>O. Furthermore, it was observed that the Rh(110) surface consumed NO with a lower apparent activation energy than Rh(111) over the range of temperatures and pressures that were examined. Qualitatively, the Rh(110) surface showed a much stronger tendency toward N<sub>2</sub> production than the Rh(111) surface, whereas the Rh(111) surface produces greater than 70 % of N<sub>2</sub>O under almost all experimental conditions of study. The Rh(110) surface exhibits a lower apparent activation energy, 27.2 vs. 34.8 kcal/mole, than does the Rh(111) surface.

The activity of supported ruthenium catalysts for reduction of NO to N<sub>2</sub> in an exhaust-like feedstream has been examined in laboratory experiments by Taylor and Klimisch (1973). The rate and temperature of NO removal is largely dependent on the NO inlet concentration and independent of the concentration of reducing agents in the system. Increasing the NO concentration tends to decrease both the rate of NO removal and the extent of ammonia formation. The selectivity for nitrogen formation, however, is dependent on the concentration of the reducing agents, CO and H<sub>2</sub>, as well as the concentration of NO. Increasing CO and H<sub>2</sub> concentrations do not affect the rate of NO removal but both tend to increase ammonia formation. CO tends to affect NH<sub>3</sub> formation at low temperature (below 425 °C), while hydrogen tends to increase ammonia formation at above 425 °C. The primary difference between the noble metal catalysts is that CO strongly inhibits NO reduction over platinum and palladium, but not over ruthenium. These results are consistent with chemisorption studies and provide an explanation for the efficient conversion of nitric oxide to elemental nitrogen over ruthenium catalysts.

Mixtures of noble metal and another base metal have also been used. The reduction of nitric oxide on PdO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was examined by Halasz and Brenner in 1993. The PdO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst containing 2 % Pd and 20 % Mo was examined for the reduction of nitric oxide by CO, by H<sub>2</sub> and by CO+H<sub>2</sub> at temperatures from 300 to 550 °C. Both the activity and the selectivity for N<sub>2</sub> and N<sub>2</sub>O production of PdO-MoO<sub>3</sub>/ γ-Al<sub>2</sub>O<sub>3</sub> were higher than those of the monometallic catalysts, PdO/ γ-Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>/ γ-Al<sub>2</sub>O<sub>3</sub> in the presence of oxygen. Catalytic activity of PdO-MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> under oxygen free conditions up to 400 °C was determined. At higher temperatures the molybdenum improved the performance of the catalyst, especially under slightly oxidizing conditions. In this work, they also reported that under oxygen free conditions, the PdO/ γ-Al<sub>2</sub>O<sub>3</sub> catalyst showed high activity for the reduction of nitric oxide. However, the conversions decreased significantly in presence of O<sub>2</sub>.

A comparative study of the coadsorption of CO and NO on Pd (100) and Pd (111) showed that the equilibrium structure and coverage for the adsorption of a CO and NO mixture on palladium surfaces strongly depended on the surface temperature and crystal orientation (Xu, et al., 1994). On all surfaces of Pd, CO to NO coverage ratio increased with decreasing catalyst temperature when equilibrated with an equimolar CO/NO gas mixture.

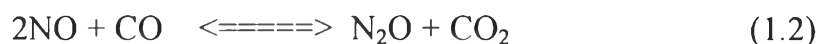
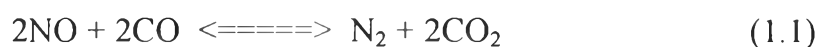
The kinetic rates for CO oxidation by oxygen have been measured on the surface of Pd(100) surface and the c(2 x 2)-Sn/Pd(100) surface alloy in a high pressure/ultra-high vacuum surface analysis chamber over the temperature range of 443-673 K and the pressure range of 0.3 - 108 Torr by Logan and Paffett in 1992. An Arrhenius activation energy of 22 kcal/mole was measured for CO oxidation at the Pd(100) single crystal surface. Furthermore, the reaction order for the CO was found to decrease from -0.2 to

-0.9 as the pressure was lowered from 16 to 1 Torr CO (Pressure of oxygen = 8 Torr), and the O<sub>2</sub> reaction order was found to increase from 0.6 to 1.0 at CO pressures of 16 and 1 Torr, respectively.

### 1.3 Research Objective

The purpose of this work is to find out the rate expression for NO reduction and CO oxidation. The objective can be divided into three parts. The first objective is catalyst preparation. The catalysts is prepared by the impregnation technique. Palladium on alumina is used as the catalyst in this work. Catalyst characterization is the second one. In this research, BET surface area, particle size analyzer and XRD were used to characterize the catalysts.

The final objective is to find the kinetic expression describing the rate of reaction. The possible reactions for nitric oxide reduction and carbonmonoxide oxidation are



It can be seen that the first reaction is a desired reaction because it converts a toxic gas mixture NO and CO into harmless N<sub>2</sub> and CO<sub>2</sub>. From the equation 1.3.1, the rate of N<sub>2</sub> formation is half of the rate of CO oxidation. If the reaction follows the 1.3.2 equation, the rate of CO oxidation will be grater than the double of rate of N<sub>2</sub> formation. Therefore, by observing the nitric oxide reduction selectivity to nitrogen and the rate of carbonmonoxide oxidation, we can determine which one of the reactions is the dominant reaction.