

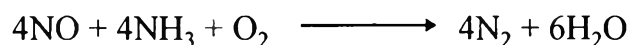
## CHAPTER II

### LITERATURE SURVEY

#### 2.1 NO<sub>x</sub> Removal

There are a number of commercial approaches to NO<sub>x</sub> removal which include, absorption, thermal, and catalytic removal methods. Since the 1960's a great deal of work has been accomplished to control NO<sub>x</sub> emissions. For automotive exhausts, the current three way catalyst use O<sub>2</sub> sensors to control the air/fuel ratio, which permits effective removal of NO<sub>x</sub>, hydrocarbon, and CO. For exhaust gases where excess O<sub>2</sub> is present, the same automotive catalysts are not effective for removing NO<sub>x</sub>. These O<sub>2</sub> rich streams (such in power plants and lean burn engines) represent major sources of NO<sub>x</sub> which must be treated (Armor, 1994).

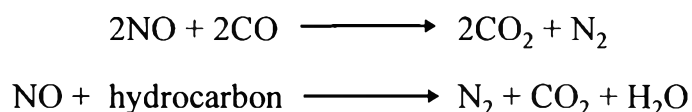
Among the approaches to NO<sub>x</sub> emission from power plants, SCR (selective catalytic reduction) with ammonia is growing in application. SCR uses a catalyst to facilitate reactions between NO<sub>x</sub> and NH<sub>3</sub> in the presence of O<sub>2</sub> which was first discovered in 1962 (Heck and Farrauto, 1995).



Among the advantages of NH<sub>3</sub> as the reducing agent are its high selectivity towards reaction with NO in the presence of O<sub>2</sub> and the promoting effect of O<sub>2</sub> on the rate of the NO-NH<sub>3</sub> reaction. Stoichiometric control of the ammonia must be maintained to avoid emissions of unreacted NH<sub>3</sub>. Additional

problems of the SCR technology include the storage and transportation of ammonia (Amiridis et al., 1996).

Platinum group metals (Pt, Pd, and Rh) have been utilized as three way catalysts (TWC's) in transportation applications for stoichiometric reduction of nitric oxide by carbon monoxide and hydrocarbons



Although these catalysts are able to meet rigorous emission standards in gasoline engines, they are not effective for  $\text{NO}_x$  reduction in lean-burn applications, such as diesel-fueled vehicles. The desire for improved fuel economy and lower emissions of carbon dioxide is projected to increase the demand for diesel engines throughout the world. It is, therefore, of great importance to develop catalyst technologies that will allow  $\text{NO}_x$  reduction in lean environments for truck and passenger car applications (Amiridis et al., 1996).

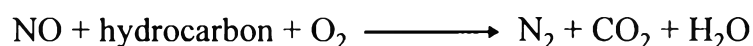
Beyond current SCR technology, the catalytic decomposition of NO to  $\text{N}_2$  and  $\text{O}_2$  is an ideal way to remove NO from the exhaust stream. The direct decomposition of NO to its elements is thermodynamically favorable up to  $\sim 1,000^\circ\text{C}$ , but it had not been demonstrated in any substantial yield until recently by Iwamoto et al. (1990). They found that on a copper ion exchanged zeolite molecular sieve, Cu-ZSM-5, catalyst low but sustained activities were obtained.

Since the Iwamoto paper, Cu ion exchanged ZSM-5 zeolites have been studied by many other investigators for the catalytic decomposition of nitric oxides. The effect is manifested after a specific mode of ion exchange enhanced the catalytic activity at high temperatures ( $450\text{-}600^\circ\text{C}$ ) and appeared

to be due to stabilization of the active copper sites (Zhang and Stephanopoulos, 1993).

Centri et al. (1993), developed Cu-exchanged zeolites (ZSM-5 and Boralite) and Cu-loaded oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) which were used as catalysts for the conversion of NO in the presence and absence of  $\text{O}_2$  studying. The  $\text{O}_2$  can promote the conversion of NO to  $\text{N}_2$ , but at lower reaction temperature and selectivity than those for the anaerobic decomposition. Unfortunately Cu-ZSM-5 has severe problems related to low rates under realistic conditions and poisoning effects by the water and sulfur oxide. The search for the alternative catalysts for this reaction has not yet been successful (Amiridis et al., 1996)

The reduction of  $\text{NO}_x$  with hydrocarbons instead of ammonia, in an oxidizing atmosphere is also a subject of intense research for mobile engine applications. Currently, propane, propylene, and ethylene are the most intensely studied hydrocarbons for the  $\text{NO}_x$  reduction. The presence of  $\text{O}_2$  is essential for the  $\text{NO}_x$  reduction, demonstrating that hydrocarbons readily found in most exhaust emissions can be effective for the selective reduction of lean  $\text{NO}_x$  control (Armor, 1994).



Jen and Gandhi (1993), developed Cu/ZSM-5, Cu/ $\gamma$ - $\text{Al}_2\text{O}_3$ , Pd/ZSM-5, and Au/ $\gamma$ - $\text{Al}_2\text{O}_3$  which were used as catalysts for the reduction of NO by  $\text{C}_3\text{H}_6$  in excess amount of  $\text{O}_2$ . The catalyst with higher activity of  $\text{C}_3\text{H}_6$  oxidation incurred the reduction of NO at lower temperature. For Au/ $\gamma$ - $\text{Al}_2\text{O}_3$ , the conversion of NO was significant only at or above  $450^\circ\text{C}$  with a maximum value of 5%.

It has been reported that the reduction of NO with  $C_3H_8$  occurs over oxides such as alumina ( $Al_2O_3$ ), silica-alumina ( $SiO_2-Al_2O_3$ ), titania ( $TiO_2$ ), and zirconia ( $ZrO_2$ ). The catalytic activity of these oxide catalysts,  $Al_2O_3$  was found to be the most effective.  $Al_2O_3$  is inexpensive and thermally stable. Therefore,  $Al_2O_3$  was an attractive catalyst for removing NO from lean-burn engine exhaust. With alumina, the maximum NO conversion was observed around  $600^\circ C$  at space velocity higher than  $38,570\text{ hr}^{-1}$  when  $C_3H_6$  was used as a reductant and also found that the durability of  $Al_2O_3$  was better than that of zeolite based catalysts for removing NO under oxidizing conditions (Subramanian et al., 1993).

Torokai et al. (1991), found that the loading of Cu on  $Al_2O_3$  can improve the activity for the NO reduction by  $C_3H_6$  on  $Al_2O_3$  at temperature of 573-773 K. The activity was enhanced by adding Cu, Fe, Co, or Cr, while Ni, Mn, Zn, and V little affected the activity and the activity was decreased by adding Ag, Ca, and K.

Burch et al. (1994), prepared the  $Al_2O_3$ -supported Pt catalysts and investigated them for the selective reduction of NO in the presence of a large excess of  $O_2$ . It was demonstrated that the predominant mechanism for selective NO reduction comprised two basic steps : reduction of the platinum sites by the hydrocarbon, followed by the decomposition of NO (to generate  $N_2$  and adsorbed  $O_2$ ) over the reduced platinum sites.

Iwamoto and Hamada (1991), reported that the additional introduction of  $O_2$  into the  $NO+C_3H_6+He$  stream over Cu-ZSM-5 and Ag- $Co_3O_4$  resulted in the great enhancement of catalytic activity for the reduction of NO at temperatures as low as 473-673 K and the increment of concentration of  $C_3H_6$  increased the activity.

Miyadera (1993), studied the effect of water on the selective reduction of NO by C<sub>3</sub>H<sub>6</sub> over several alumina-supported metal catalysts and found that Al<sub>2</sub>O<sub>3</sub>-supported Ag catalysts showed high activities in the presence of water and excess O<sub>2</sub>, while water vapor significantly decrease the activities of Al<sub>2</sub>O<sub>3</sub> and Co/Al<sub>2</sub>O<sub>3</sub> which were highly active in the absence of water.

Bethke and Kung (1997), studied the supported Ag catalysts and found that the 2wt%Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was much more effective than 6wt%Ag/Al<sub>2</sub>O<sub>3</sub>. The difference was attributed to the Ag in the catalysts having different oxidation states under the reaction conditions. The 2wt%Ag/Al<sub>2</sub>O<sub>3</sub> was in oxidized form, while 6wt%Ag/Al<sub>2</sub>O<sub>3</sub> catalyst contained a large number of Ag<sup>0</sup> particles at lower temperature and less at higher temperature. The presence of Ag<sup>0</sup> lead to a high rate of C<sub>3</sub>H<sub>6</sub> combustion at the expense of N<sub>2</sub> formation. The promotional effect of NO<sub>2</sub> on 6wt%Ag/Al<sub>2</sub>O<sub>3</sub> was attributed to the oxidization of Ag<sup>0</sup> to Ag<sup>+</sup> by NO<sub>2</sub> but such a promotion was not seen on 2wt%Ag/Al<sub>2</sub>O<sub>3</sub> as this catalyst was already completely oxidized.

Hoost et al. (1997), also studied the Ag supported on a non porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which was shown to have an optimal metal loading of about 2wt%Ag for NO<sub>x</sub> conversion of simulated lean NO<sub>x</sub>, automotive exhaust and found that Ag was primarily in an oxidized state during reaction.

Ueda et al. (1997), developed gold supported on several metal oxides with high dispersion by deposition precipitation and coprecipitation methods to study the reduction of NO with C<sub>3</sub>H<sub>6</sub> and found that the reaction temperature varied depending on the kind of metal oxide support used and increased in order of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> - ZnO < MgO - TiO<sub>2</sub> < Al<sub>2</sub>O<sub>3</sub>. An amount of O<sub>2</sub> can enhance the reduction of NO by C<sub>3</sub>H<sub>6</sub> and NO<sub>2</sub> reacted with C<sub>3</sub>H<sub>6</sub> at lower temperature than NO indicating that NO reduction could take place through the oxidation of NO to NO<sub>2</sub>, which might then reacted with C<sub>3</sub>H<sub>6</sub>.

## 2.2 Catalyst Preparation

### 2.2.1 Catalyst Preparation Methods

The preparation of catalysts is frequently described as an art, and a catalyst recipe may specify detailed and arcane procedures that appeared to be necessary in order to achieve reproducibility and the desired properties. Most catalysts are either finely divided metal supported on a carrier such as alumina or silica, or a compound, more or less complex, either on a carrier or unsupported (Satterfield, 1993)

#### Impregnation method

This method is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution, usually aqueous, of one or more suitable metal salts. The catalysts that are made in this way may give a low dispersion of the metal on the carrier and can sinter more easily.

#### Precipitation method

In a common procedure, an aqueous metal salt solution is contacted with an aqueous alkali, ammonium hydroxide or ammonium carbonate, to cause the precipitation of an insoluble metal hydroxide or carbonate. These can be readily converted to oxides by heating. The advantages of the precipitation method are that it generally provides more uniform mixing on a molecular scale of the various catalyst ingredients, the distribution of active species through the final catalyst particle is uniform, and the ultimate sizes and shapes are not limited to the forms in which desired carriers are available (Satterfield, 1993). But the precipitates are usually non-stoichiometric and often have an amorphous structure.

### Sol-gel method

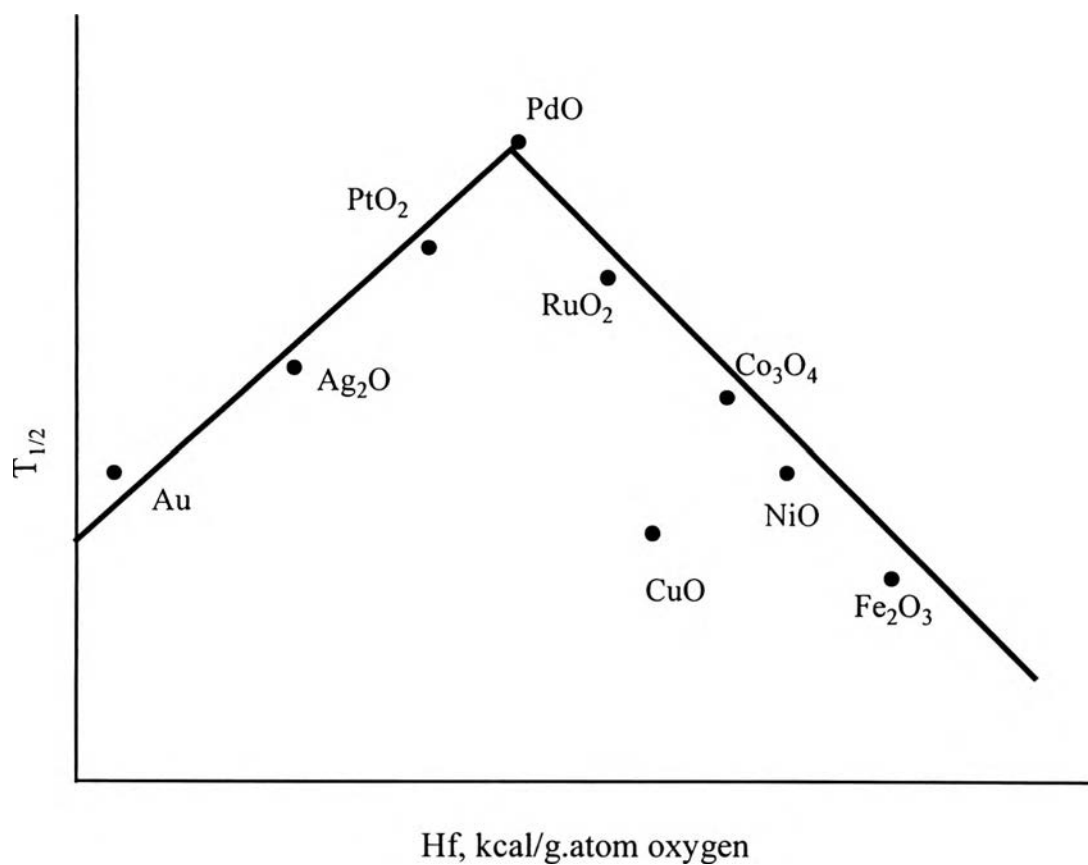
Sol-gel method is the process for the formation of solid from gels. Today, sol-gel methods are recognized as an interesting and promising procedure to prepare catalysts. The features of the method is the formation of liquid phase precursors consisting of  $M_1-O-M_2$  bonding during mixing the metal alkoxides dissolved in the organic solvent, where  $M_i$  means metal atoms of alkoxides employed. The versatility of the sol-gel techniques allow control of the texture, composition, homogeneity, and structural properties of solids, and make possible production of tailored materials dispersed metals, oxidic catalysts, and chemically modified supports (Cauquil and Rodriguez-Izquierdo, 1992).

#### 2.2.2 Active Metal (Gold - Silver)

Gold was regarded catalytically far less active than platinum metal group. However, recent publications clearly disclosed that gold can be remarkably active for the NO reduction by propylene. Furthermore, gold became more active in combination with a suitable metal oxide support. The chemical reactivity of gold catalysts has been studied for the oxidation by  $O_2$  or  $N_2$ , oxides of CO, and  $H_2$ , selective oxidation of organic compounds by nitrogen dioxide, hydrogenation of alkenes (Haruta et al., 1989).

Figure 2.1, shows the “volcano-like” relation of activity with the heat of formation of oxides per gram-atom of oxygen. The volcano relation indicates that the formation of metal-oxide (M-O) bonds was rate determining for the oxides of Ag and Au, which were located on the left hand site, while the breaking of M-O bonds was the slow step for the other metal oxides located on the right side (Haruta et al., 1989). Silver and gold were chosen because, there was evidence to suggest that they adsorb oxygen less readily than most metals (Cant and Fredrickson, 1975). Therefore, an attempt was

made to develop composite oxides of Ag with Au for the catalytic reduction by propylene catalysts.



**Figure 2.1** Dependence of hydrogen oxidation activities of metal oxides on their heat of formation.