

## **CHAPTER II**

### **HISTORICAL REVIEW**

#### **2.1 Background**

Catalytic reduction of nitric oxide by carbon monoxide is an important process in air pollution control. This redox reaction has been investigated by a number of researchers using 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 catalyst for NO reduction and CO oxidation and have been studied in detailed (both transient and steady-state conditions). 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 cheaper and more readily available (Heck and Farrauto, 1995).

The roles of the various noble metals (platinum, palladium and rhodium) used for automotive emission control were defined from research in the 1970s.

Platinum and palladium were necessary to control HC and CO emissions while rhodium was considered in controlling NO<sub>x</sub> emissions. Furthermore, platinum was preferred to palladium because it had high poisoning resistance to gasoline and motor oil contaminants. However, palladium was more resistant to thermal sintering than platinum (Summers and Williamson, 1993).

Nieuwenbuys et al. (1993) found that rhodium (Rh) was much better than platinum (Pt) as the catalyst for the NO reduction by CO. Furthermore, CO inhibited the dissociate adsorption of NO on the Pt surface. NO dissociation required more than one vacant Pt atom. In the reduction of NO with N<sub>2</sub>, Pt was more active than Rh. For on both Pt and Rh catalysts, the reaction temperature for 50% NO conversion was lower when H<sub>2</sub> was used as the reactant instead of CO.

Cu ion exchanged ZSM-5 zeolites were used for the catalytic decomposition of nitric oxides. The treatment, manifested under a specific mode of ion exchange, enhanced the catalytic activity at high temperatures (450-600 °C) due to the stability of the active copper sites (Zhang and Maria, 1993).

Jen and Gandhi (1993) developed Cu/ZSM-5, Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pd/ZSM-5, and Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which were used as catalysts for the reduction of NO by C<sub>3</sub>H<sub>6</sub> in excess O<sub>2</sub>. The catalyst with higher activity of C<sub>3</sub>H<sub>6</sub> oxidation incurred the reduction of NO at lower temperatures.

Haruta and Sano (1983) studied the active oxide catalysts for the low-temperature catalytic combustion of hydrogen and carbon monoxide. They

found that the activity of the reaction depended strongly on the ratio of Ag-Mn-Co. In addition, the oxides enhanced activity and thermal stability remarkably.

The mechanism of the oxidation of CO by nitrous oxide and oxygen over a silver catalyst was studied by Kobashi and Takegam (1984). They found that half of the total surface sites were active for the adsorption of oxygen and one third of the active sites were employed for the decomposition of N<sub>2</sub>O, indicating the heterogeneity of the silver surface. At a steady-state of CO oxidation in the N<sub>2</sub>O+CO and O<sub>2</sub>+CO systems, the surface for the N<sub>2</sub>O+CO reaction was less than that for the O<sub>2</sub>+CO oxidation. The activation energy of 10 kcal/mole for the N<sub>2</sub>O+CO reaction suggested different rate-controlling steps.

Felter and Weinberg (1982) studied the oxidation of carbon monoxide by active oxygen pre-adsorbed on Ag(111) using photoelectron spectroscopy. They had found that the rate of reaction increased with the decrease of temperature which corresponded to a negative activation energy,  $E_a = -1.7$  kcal/mole. It might be clarified as the difference between the activation energy for CO desorption and that for reaction with oxygen active surface led to CO<sub>2</sub> desorption.

Cant and Freddrickson (1975) reported that the reactions of carbon monoxide with oxygen and with nitric oxide over gold catalyst had similar characteristics for the temperature range of -30°C to 100°C and their activation energies were close to zero. Oxidation by oxygen was about 40 times faster than that by nitric oxide and the latter poisoned readily above 40 °C due to the interactions of nitric oxide with the surface. For the CO+NO reaction, the rate passed through its maximum as the NO pressure was increased, eventually, tending to be the inverse first order. Its activation energies were 14

kcal/mole and 4 kcal/mole for the temperature below and above 118 °C respectively.

The chemical reactivity of gold catalysts was studied for the oxidation by oxygen, the reduction of nitrogen oxides by CO, and H<sub>2</sub>, and the selective oxidation of organic compounds by nitrogen dioxide, hydrogenation of alkenes and so on (Haruta et al., 1989).

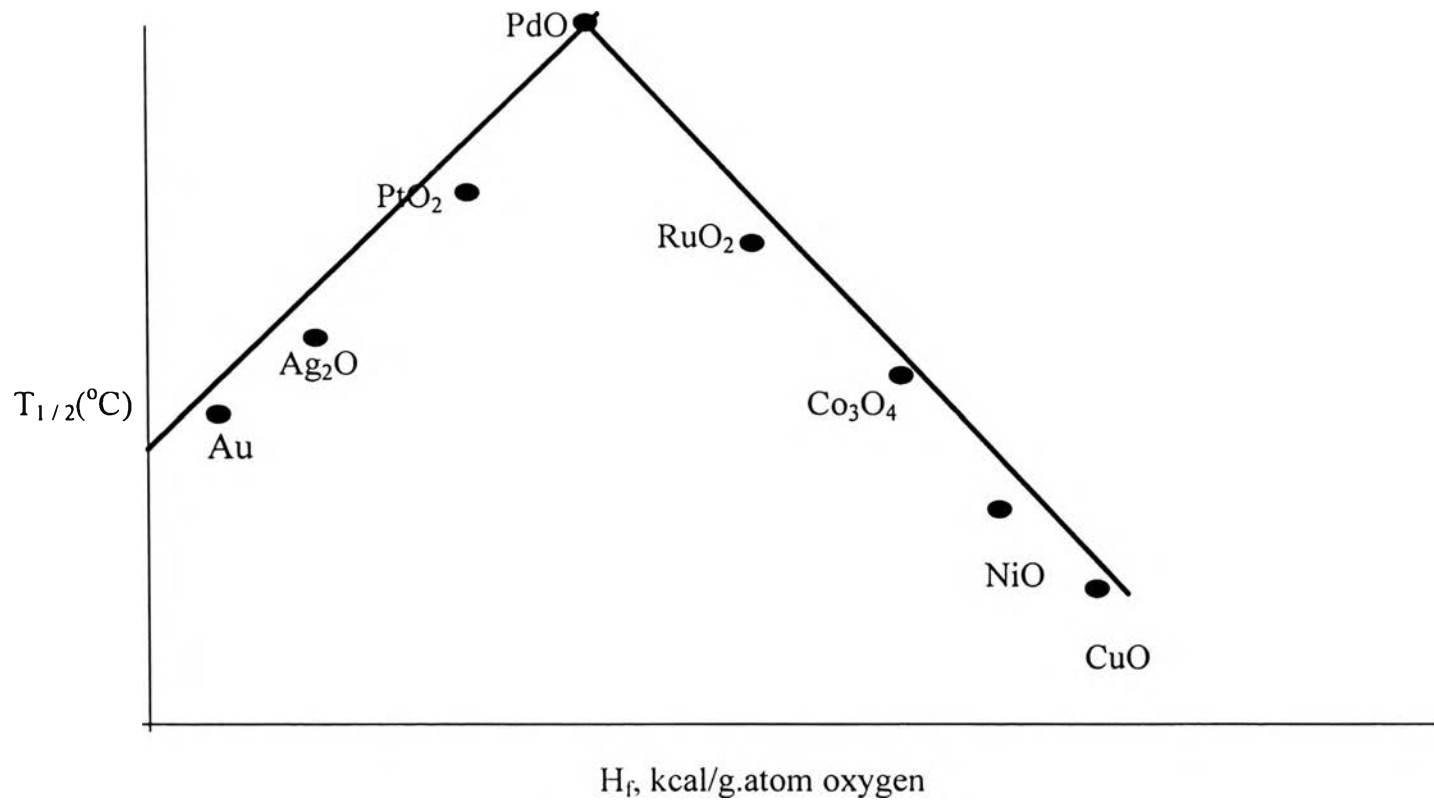
Silver and gold were chosen in this study since these adsorbed less oxygen than other metals (Cant and Fredrickson, 1975).

Figure 2.1 shows the dependence of hydrogen oxidation activities of metal oxides on the heat of formation per gram-atom of oxygen. The catalytic oxidation activity of hydrogen had a volcano-like relation with the heat of formation of oxides per-gram of atom of oxygen. This indicates that the formation of metal oxygen (M-O) bonds is rate-determining for the oxides of Ag and Au, which are located on the left of the plot. Therefore, an attempt was to develop composite oxides of Ag with Au for the NO reduction and CO oxidation catalysts (Haruta et al., 1989).

## 2.2 Research objectives

The objectives of this study were:

- i) to prepare silver/gold catalyst from silver/gold on gamma aluminum by using impregnation and coprecipitation techniques;
- ii) to examine the effect of the calcination temperature and the silver/gold ratio in 5% loading on the catalytic activity;
- iii) to compare the activity from impregnation and coprecipitation method;
- iv) to characterize the catalyst by using BET, XRD, and TEM;
- v) to study the kinetic expression of the NO reduction and CO oxidation.



**Figure 2.1** Dependence of hydrogen oxidation activities of metal oxides on the heat of formation per gram-atom of oxygen.