

## CHAPTER II

### LITERATURE SURVEY

The catalytic oxidation of carbon monoxide has been one of the most extensively studied reactions due to its utility. Low temperature catalysis as a means of removing carbon monoxide, hydrocarbons and oxidizable compounds from the indoor atmosphere has been acquiring immense practical importance in the environment : protection of air from smoking, gas fueled space heaters, in the protection of high purity nitrogen and oxygen gases from air and in safety gas masks for mine industries. Advances in oxidation catalyst technology have resulted in the noble metal/metal oxide catalysts that are highly efficient, durable and stable at near room temperature as well as water tolerant.

Consequently, the development of low temperature carbon monoxide oxidation catalysts has received attention. Although significant progress has been made with regard to understanding the reaction mechanism, there remains a need for development of catalysts which exhibit higher activities for prolonged periods at low temperatures (typically less than 100°C) and the diverse ranges of oxidation environment which is encountered. Factors determining oxygen availability and gaseous impurities often have pronounced effect on catalyst performance. Carbon monoxide oxidation in ambient air takes the advantage of excess oxygen and low carbon dioxide concentration which facilitates the reaction considerably. Therefore, numerous materials are known to oxidize carbon monoxide in excess oxygen at low temperatures but complications due to the presence of humidity and air pollutants are often detrimental to their activities. In CO<sub>2</sub> laser, carbon monoxide and oxygen are

present in small stoichiometric quantities in a large amount of carbon dioxide. Although the catalytic reaction benefits from the fact that the lasers normally operate at temperatures somewhat above 25-100°C, catalytic oxidation of carbon monoxide is difficult under these conditions.

Noble metals, notably platinum and palladium, have been shown to be particularly well suited for the catalyzing oxidation reactions in the auto exhaust environment. Typically, all noble metal based catalysts examined are supported on inert and highly porous materials such as  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$ . However, the high cost and relatively short supply of these metals encourage the search to continue for oxidation catalysts which are less costly, plentiful and also as effective as the metals of the platinum metal groups. Single component transition metal cannot rival these precious metals; accordingly, the catalytic activity has been improved by combining more than two elements such as Hopcalite, Perovskite catalysts. Recently, a new class of catalysts has been developed consisting of a noble metal on an active reducible oxide catalysts such as platinized tin oxide ( $\text{Pt}/\text{SnO}_2$ ) and gold/manganese dioxide ( $\text{Au}/\text{MnO}_2$ ) have shown to demonstrate high activity for carbon monoxide oxidation at room temperature, even with low stoichiometric amounts of carbon monoxide and oxygen.

Haruta et al. (1983) reported that an appreciable enhancement in catalytic activity was achieved in some composite oxide of silver with 3d transition metals prepared by coprecipitation technique. Specifically, mixed oxides composed of cobalt, manganese, and silver (20:4:1 in atomic ratio) was the optimum composition which exhibited remarkably both enhanced activity and good thermal stability for oxidation of hydrogen and carbon monoxide.

Gardner and Hoflund (1991) have developed a number of other materials catalytically term noble metal reducible oxide for  $\text{CO}_2$  laser applications.  $\text{MnO}_x$ ,  $\text{Ru}/\text{MnO}_x$ ,  $\text{Pt}/\text{MnO}_x$ ,  $\text{Ag}/\text{MnO}_x$ ,  $\text{Pd}/\text{MnO}_x$ ,  $\text{Cu}/\text{MnO}_x$ ,

Au/MnO<sub>x</sub>, Au/CeO<sub>x</sub>, and Au/Fe<sub>2</sub>O<sub>3</sub> were synthesized by using impregnation, and coprecipitation technique and exposed to various environments as well as screened for carbon monoxide oxidation activity in low concentration of stoichiometric carbon monoxide and oxygen and the temperature between 30 and 75°C. They also found that Au/MnO<sub>x</sub> and Au/CeO<sub>x</sub> performed better than Pt/SnO<sub>x</sub> with regard to both activity and decay characteristics.

Novel gold catalysts prepared by the coprecipitation technique and calcined in air at 400°C produced ultrafine gold particles smaller than 10 nm and dispersed uniformly on the transition metals e.g., Fe<sub>2</sub>O<sub>3</sub>, NiO, Co<sub>3</sub>O<sub>4</sub>, and MnO<sub>x</sub> were highly active for hydrogen and carbon monoxide oxidation and showed markedly enhanced catalytic activities even at a temperature of -70°C (Haruta et al., 1989). Haruta et al. (1991) also synthesized gold in highly dispersed state on TiO<sub>2</sub>, MnO, and Al<sub>2</sub>O<sub>3</sub> powder by depositon-precipitation and calcined the catalysts under air and vacuum environment which resulted in a large difference in catalytic behavior.

Manganese-silver composite oxides have higher activities than manganese over the whole ranges in the oxidation of carbon monoxide and the results show that the oxidized states of silver are stabilized in the presence of manganese if its content is not large. In addition, the total lattice oxygen of Ag<sub>2</sub>O is eliminated between 100 and 300°C and metallic silver crystallizes above 300°C. Their high activities are caused by differences in their affinities toward oxygen (Imamura et al., 1988).

Yang et al. (1991) have studied mixed oxides of copper, cobalt, and manganese used as catalysts for carbon monoxide oxidation using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) for surface characterization of the composite oxides and the results of X-ray diffraction showed that single and mixed oxides of CuO and Co<sub>3</sub>O<sub>4</sub> were the most active

while the activity of  $\text{MnO}_2$  was one order of magnitude lower. Moreover, it clearly demonstrated by XPS results that manganese tended to migrate to the surface resulting in a lowering of the overall activities and cobalt and copper ions at the surface are partially reduced by manganese ions.

The extraordinary high activity for low temperature carbon monoxide oxidation can be generated by controlling the size of gold particles and choosing a suitable oxide support ( $\alpha\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{Be}(\text{OH})_2$ , and  $\text{Mg}(\text{OH})_2$ ) on which the oxidation can occur as low as  $-70^\circ\text{C}$  (Haruta et al., 1989).

Apart from the atmosphere, the heat treatment temperature during calcination also plays a crucial role in activating these carbon monoxide oxidation catalysts. Tanielyan, and Augustine (1992) have observed that an increase in calcination temperature leads to a significant decrease in activity over gold or silver supported catalysts (i.e., Au and Ag supported on  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CuO}$  prepared by coprecipitation technique) and that most active catalysts are those that undergo an oxygen treatment prior to reaction studies. It is noticed that the relative reactivities of these catalysts are influenced not only by the environment in which heat treatment is carried out, but also by the degree of heating and oxygen exposure before usage.

Lin et al. (1993) have studied  $\text{Au}/\text{SiO}_2$  and  $\text{Au}/\text{TiO}_2$  catalysts for low temperature carbon monoxide oxidation in three different pretreatments; low temperature reduction (473 K), high temperature reduction (773 K), and high temperature reduction followed by calcination at 673 K and by low-temperature reduction followed by calcination at 673 K and by low-temperature reduction respectively. For low-temperature reduction, the activity was inhibited by the residual chloride content (50%) on the surface of the catalysts. On the other hand, the other catalysts retained less chlorine content.

The most active Au/TiO<sub>2</sub> was obtained from high temperature reduction followed by calcination and then low temperature reduction.

Sze et al. (1993) have studied catalysts consisting of ultra-fine gold particle supported on iron oxides (Fe<sub>2</sub>O<sub>3</sub>) synthesized by coprecipitation technique and have found that atomic ratio Au/Fe = 1/19 is the most active. The long term stability of the catalysts was studied in on excess oxygen environment. It also demonstrated that the heat pretreatment temperature affected changes in the material properties of the catalysts. Crystallite size was found to increase with calcination temperature whereas the activity was found to decrease.