

CHAPTER II

BACKGROUND

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 production 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.

Ambient temperature catalytic oxidation of carbon monoxide is being examined in the joint study by the National Aeronautics and Space Administration (NASA) and Rochester Gas and Electric Corporation (RGE). Initiated in October 1992, in order to develop one or more economically feasible catalysts which can be incorporated into heating and cooling systems or into stand-alone systems for localized control, phase I of the study will evaluate promoted noble-metal/metal oxide catalysts developed by NASA for low temperature oxidation of carbon monoxide and then phase II will address modifications to the NASA catalysts or the development of other materials to meet the specific needs of RGE. Finally, phase III will entail the long-term field testing and subsequent technology transfer to industry for commercialization.

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 CO₂ lasers, 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 metals based catalysts examined are supported on inert and highly porous materials such as SiO₂, and Al₂O₃. 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 metal oxide supports. A number of these noble metal reducible oxide catalysts such as platinumized tin oxide (Pt/SnO₂) and gold/manganese dioxide (Au/MnO₂) have shown to demonstrate high activity for carbon monoxide oxidation at room temperature, even with low stoichiometric of carbon monoxide and oxygen.

Pt/SnO₂ and Pd/SnO₂ catalysts have been researched extensively for use in CO₂ lasers. It is found that plantinized tin oxide has significantly higher catalytic activity for CO oxidation at low temperatures than does either Pt or SnO_x alone (Brown et al., 1986). Increase in their activities results from the synergistic effect (Sheintuch et al., 1989 and Schryer et al., 1990). The synergistic effect has been explained by the hypothesis that oxygen species may spill over onto the metal and react there with chemisorbed carbon monoxide (Lintz, 1989 and Boulahouache, 1992). A mechanism for Pt/SnO_x catalyzed CO oxidation was proposed by Schryer et al. (1991).

Haruta et al., (1983) reported that an appreciable enhancement in catalytic activity was achieved in some composite oxides of silver with 3d transition metals prepared by co-precipitation 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 termed noble metal reducible oxide for CO₂ laser applications. MnO_x, Ru/MnO_x, Pt/MnO_x, Ag/MnO_x, Pd/MnO_x, Cu/MnO_x, Au/MnO_x, Au/CeO_x, and Au/Fe₂O₃ were synthesized by using impregnation, and co-precipitation 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_x and Au/CeO_x performed better than Pt/SnO_x with regard to both activity and decay characteristics.

Novel gold catalysts prepared by the co-precipitation 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., Fe₂O₃, NiO, Co₃O₄, and MnO_x 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_2 , MgO , and Al_2O_3 powder by deposition-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_2O 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_3O_4 were the most active while the activity of 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.

Cunningham et al. (1992) have noticed that a marked difference in catalytic low temperature carbon monoxide oxidation behavior of Au/TiO_2 samples calcined under vacuum and air. The extraordinary high activity for low temperature carbon monoxide oxidation can be generated by controlling the size of gold particles and choosing the suitable oxide supported ($\alpha\text{-Fe}_2\text{O}_3$, Co_3O_4 , NiO , Be(OH)_2 , and Mg(OH)_2) which the oxidation can occur as low as -70 °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 Co_3O_4 , Fe_2O_3 , and CuO prepared by co-precipitation technique) and that most active catalysts are those that undergone 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 Au/SiO_2 and Au/TiO_2 catalysts for low temperature carbon monoxide 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 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_2 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_2O_3) synthesized by co-precipitation technique and have found that atomic ratio $\text{Au}/\text{Fe}=1/19$ 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 and the activity was found to decrease.