

# CHAPTER I

## INTRODUCTION

### 1.1 Introduction

Carbon monoxide is an especially dangerous gas as it reduces the flow of oxygen in the bloodstream to vital organs in the body. The removal of carbon monoxide from air has been acquiring immense practical importance in environmental protection.

The removal of CO as CO<sub>2</sub> from automotive exhaust is accomplished by a catalytic converter utilizing the supported noble metals, Pt, Pd, and Rh, but they work well at high temperature. Therefore, a catalyst for the purification of air containing low levels of carbon monoxide at room temperature has been developed.

Because of the range of possible uses of carbon monoxide oxidation catalysts which can operate at temperature below 100°C, the catalysts for these purposes should have performance and stability. The requirements are for a material which has good carbon monoxide oxidation performance, maintains this performance over a long time period, can tolerate the presence of moisture and must be stable during non-working periods.

Although the Hopcalite catalysts, a mixture of predominantly manganese and copper oxides (CuO-MnO<sub>2</sub>), are known since 1920's as high activity at ambient temperature, they are quickly deactivated by moisture due to vapor poisoning of the oxides (Haruta et al, 1991). On the other hand,

platinum-group metal catalysts are water tolerant, are less active at low temperatures.

Gold highly dispersed on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, or NiO has been found to be active at a temperature as low as -70°C and in water tolerant (Haruta et al., 1989); however, gold is too expensive for practical use. We have attempted to develop pure transition metal oxide catalysts (Ag, Mn, and Co) and composite catalysts of transition metal oxide (Mn-Co, Ag-Mn, Ag-Co, and Ag-Mn-Co) by coprecipitation method for low temperature CO oxidation.

## 1.2 Background

It is postulated by Schryer et al. (1990) that OH groups on the surface of SnO<sub>2</sub> phase participate in the oxidation of CO chemisorbed on adjacent Pt sites. It has been proposed that the cause of the activity dip is dehydration, and no activity loss has been found when the reaction occurs at an elevated humidity.

Based on the results obtained from FTIR, TPD, and kinetic studies, carbon monoxide is reversibly adsorbed on gold particles and partly migrates toward support oxides and it reacts with adsorbed oxygen to form bidentate carbonate species. The decomposition of the carbonate intermediate appears to be rate determining step (Tsubota et al., 1994).

Sze et al. (1993) have prepared coprecipitated gold/iron oxide catalysts and tested the long term stability in an excess oxygen environment. It has indicated the crucial role of the calcination temperature as an important parameter in influencing catalytic performance since the calcination temperature results in structure of the catalyst.

Gardner and Hoflund (1991) have developed noble metal reductive oxides (NMRO),  $\text{MnO}_x$ ,  $\text{Ru/MnO}_x$ ,  $\text{Ag/MnO}_x$ ,  $\text{Pd/MnO}_x$ ,  $\text{Cu/MnO}_x$ ,  $\text{Au/MnO}_x$ ,  $\text{Au/CeO}_x$  and  $\text{Au/Fe}_2\text{O}_3$ , for  $\text{CO}_2$  laser applications. They found that gold supported on manganese oxide performs better than  $\text{Pt/SnO}_x$  with respect to activity and decay characteristics for CO oxidation at 30 to 45°C.

Silver is relatively abundant and cheap compared to precious metals of the VIII group and gold, is used as an oxidation catalyst in reactions of epoxidation of ethylene and oxidation of methanol to formaldehyde. It is not used at high temperatures because of its thermal instability with respect to sintering upon reaction (Imamura et al., 1988). Recently, Haruta and Sano (1983) have prepared reducible metal oxide supported silver (Mn/Ag) catalysts which are highly active for CO oxidation. The combination of these two elements seems to be an important factor to enhance the thermal stability and activity. Moreover, they claimed that composite (Mn/Co/Ag) catalysts are the most preferable in a viewpoint of both catalytic activity and economics. It is not only as active as Ag-Mn oxide but also thermally more stable.

Hurata and Sano (1983) summarized catalytic hydrogen oxidation catalysts by a volcano-like relation with the heat of formation of oxides per gram-atom of oxygen as shown in Figure 1.1.

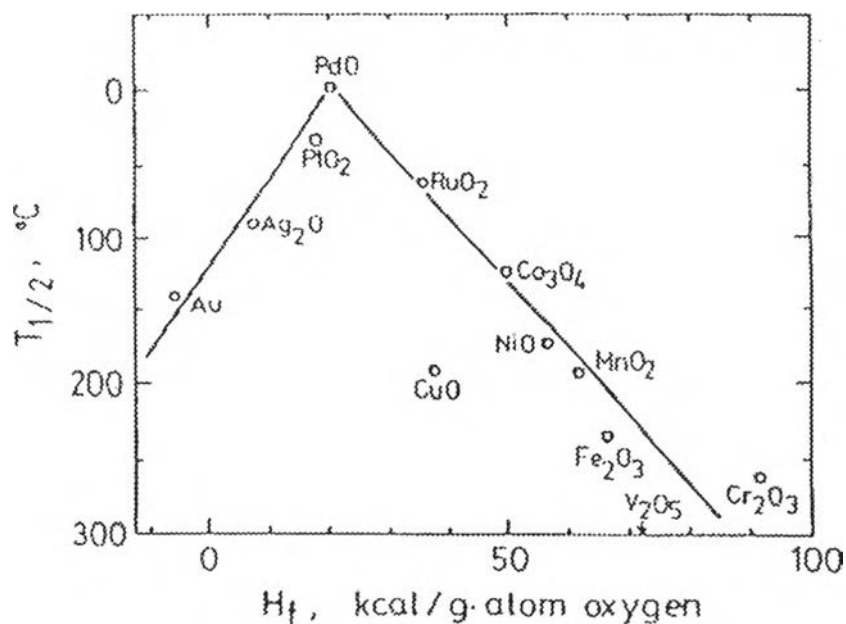


Figure 1.1 Dependence of hydrogen oxidation activities of metal oxides on their heat of formation per gram-atom of oxygen (Haruta and Sano, 1983).

The volcano-plot indicates that the breaking of metal-oxygen (M-O) bond is the slowest step in hydrogen oxidation over the oxides located on the right arm and thus the catalytic activity decreases with increasing bond energy. In contrast, over silver oxide, the formation of M-O bond may be slower than bond breaking and therefore it is more active than gold. Based on the above generally accepted interpretation of the volcano-shaped curve, an attempt was made to develop composite oxides of silver with the transition metal oxides located on the opposite arm of the curve expecting a remarkable enhancement in catalytic activity. In fact, the mixture effect was not so appreciable among the 3d transition metal oxides, for examples, in Co-Mn, Co-Cu, Mn-Ni, Mn-Cu, and Ni-Co oxides (Sze, 1995).

### 1.3 Research Objectives

Silver oxide prepared by coprecipitation method was thought to be active catalyst for low temperature CO oxidation. Based on the volcano curve of catalytic oxidation of hydrogen (See Figure 1.1), we attempted to synthesize the composite catalysts of reducible metal oxides located on the opposite arm of the curve with silver oxide by coprecipitation method to improve thermal stability. Therefore, this work focused on pure transition metal oxide catalysts (Ag, Mn, and Co) and composite catalysts of transition metal oxide (Mn-Co, Ag-Mn, Ag-Co, and Ag-Mn-Co) prepared by coprecipitation method.

In this study, XRD, BET, TGA, and temperature for 50% CO conversion tests under various environmental conditions were used to identify structural properties with catalytic performance. To understand the deactivation scenarios, phase and surface area changes of catalyst were examined by XRD and BET methods, respectively.