

CHAPTER I

INTRODUCTION

1.1 Introduction

The uses of fossil fuels for heating and cooling, transportation, industry and energy conservation, and the incineration of various forms of industrial wastes all contribute to air pollution released to the atmosphere. Sources of these pollutants are varied in that they have been categorized into four main groups: i) mobile transportation (i.e., motors, vehicles, and aircraft), ii) stationary combustion (i.e., residential, commercial, and industrial power), iii) industrial processes (i.e., chemical, metallurgical industries, and petroleum refineries), and iv) solid waste disposal (i.e., household, commercial refuse, and agricultural burning).

Transportation was noted to be the largest source of air pollution consisting of five major types of air pollutants, carbon monoxide, hydrocarbons, oxides of nitrogen, sulfur dioxide, and particulates. Carbon monoxide is predominantly produced from the exhaust gas emission. This colorless, tasteless, odorless toxic gas is chemically inert under normal conditions; however, at high concentrations, it can seriously affect human aerobic metabolism, owing to its high affinity for hemoglobin (Hb) as it reacts with hemoglobin in the blood 300 times stronger than oxygen to give carboxyhemoglobin (COHb). Exposure to carbon monoxide affects the human's ability to use oxygen because carbon monoxide limits red blood cells ability to carry oxygen. Adverse effects upon long term exposure to carbon monoxide, as levels increase, result in headaches, loss of balance and irregular

heart beat. Higher levels result of exposure in nausea, weakness, confusion, loss of memory, numbness of senses and ultimately death.

Oxidation of carbon monoxide is an important issue in industry, environments and domestic sectors (Haruta et al., 1987). In our environment, emission of carbon monoxide from gasoline and diesel engines is seriously concerned. The most efficient and commercially employed combustion catalysts are supported by noble metals like platinum, palladium, and rhodium. They will operate well at high temperatures and their catalytic behaviors have been investigated extensively. In addition, attempts have also been made to use base metal catalysts for the oxidation of carbon monoxide because of the limited availability of these precious metals, but so far low activities are achieved which made them non competitive with platinum group.

Although base metal oxide catalysts were highly active, they demonstrated a significant deactivation in long term tests. Highly active carbon monoxide oxidation catalysts with good low temperature activity are essential and valuable for numerous environmental applications including chemical CO gas sensors (either the semiconductor or optical types) (Kobayashi et al., 1990), gas masks (Yang et al., 1991), long-life sealed carbon dioxide lasers (Gardner et al., 1991), air purification devices and cigarette filters (Yang et al., 1991). Hopcalite catalysts, mixed oxides mainly composed of manganese and copper (CuO-MnO_2), have been most frequently used. However, they are not water tolerant and are not sufficiently active at ambient temperature (Haruta et al., 1987). This has limited their utilities since water is usually present in the fuel gas. In contrast, the heterogenized Wacker catalyst ($\text{PdCl}_2\text{-CuCl}_2$) has high activity for carbon monoxide oxidation at temperature around 60°C but it works only in the presence of water vapor (Desai et al., 1983). The commercially employed precious metals for combustion such as platinum, palladium, and rhodium are active catalysts but only for very dilute concentrations of carbon monoxide, i.e., part per million (ppm) concentrations

near ambient temperature and are typically used at temperature above 100 °C to optimize their activities.

Gold has long been regarded as catalytically far less active than platinum metal group. However, recent publications have clearly disclosed that gold can be remarkably active for low temperature oxidation of carbon monoxide when it is highly dispersed and deposited on reducible semiconductor metals or hydroxides of alkaline earth metals. Furthermore, it has been discovered that by selecting suitable metal oxides as supports, gold becomes active for catalytic combustion of hydrocarbons, reduction of NO with CO to N₂ (Haruta et al., 1993). However, gold is expensive for practical use; therefore, we have to develop the composites of transition metal oxides like silver, cobalt, manganese, nickel, and so on for low temperature carbon monoxide oxidation.

Silver, relatively abundant and cheap compared to precious metals of the VIII group and gold, is used as an oxidation catalysts in reactions of exoxidation of ethylene and oxidation of methanol to formaldehyde. It is not used as a combustion catalyst because of its thermal instability with respect to sintering during reaction at high temperature. Recently, Haruta and Sano prepared Mn/Co/Ag composite catalysts which are highly active for combustion of carbon monoxide and hydrogen. As these catalysts contain manganese as well as silver, a combination of these two elements seems to be an important factor contributing to their activities, but details of the action of silver and manganese in these catalysts are not understood (Imamura et al., 1988).

Haruta and Sano summarized the activities of 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.

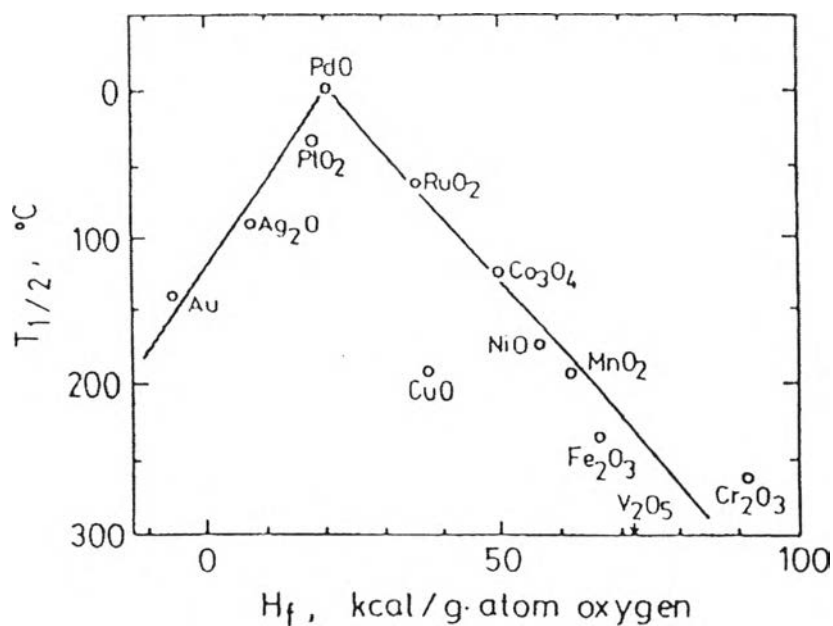


Figure 1.1 Dependence of Hydrogen Oxidation Activities of Metal Oxides on Their Heat of Formation per Gram-Atom of Oxygen (Haruta and Sano, 1983).

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 volcano-shaped curve, an attempt was made to develop the composite oxides of silver with the transition metal oxides located on the opposite arm of the curve expecting an enhancement in catalytic activity.

1.2 Research Objectives

This thesis focuses on the long term ambient temperature carbon monoxide oxidation activities of the numerous composite oxides supported silver catalysts (Ag-Mn-Co) using 0.1, 1, and 5% atom silver.

Based on Figure 1.1, the catalytic oxidation activity of hydrogen, it was attempted to develop the composite oxide catalysts using metal oxides located on opposite arms of the curve for enhancement the catalyst activity, a *synergistic effect*, by co-precipitation technique.

Also in this study, the activities of a number of composite oxide catalysts subjected to various environmental conditions were investigated. Temperature for 50% conversion ($T_{1/2}$) tests was used to identify the most active catalysts for further investigation to long term activity tests. In addition, the effect of pretreatment on the unreacted catalysts and regeneration of the deactivated catalysts were also determined. Characterizations of these catalysts by X-ray diffraction, BET surface area analyser, Transmission electron microscopy and Thermogravimetry was carried out for structural analysis of active and deactivated catalysts.