CHAPTER II
BACKGROUND

It has been widely recognized that catalysis plays a major role in improving our atmosphere and reducing pollution. Catalytic oxidation is one of the effective ways to control air pollution. In recent years, the use of catalytic combustion has been intensively found for a variety of applications, such as the control or removals of CO, NO, volatile organic compounds (VOCs), automobile exhaust emission control, and controls of by-products from chemical's production, odour and toxic organics in wastewaters (Luo *et al.*, 1998).

The oxidation of carbon monoxide is an important step in many relevant processes, such as methanol synthesis, water gas shift reaction and automobile exhaust controls. In the past, gold catalysts were considered not to be catalytically competitive in compared to platinum group in terms of activity. Until a few years ago, gold has attracted little attention in the development of heterogeneous catalysis, because of chemical inert character, high sensitivity towards the preparation methods, and low melting point (1063°C) which causes difficulties in depositing gold on supports with high dispersion as classical impregnation methods. However, it was recently shown that gold exhibited remarkably high activity at low temperatures when highly dispersed on as fine particles over suitable support by co-precipitation or deposition-precipitation methods (Boccuzzi *et al.*, 1996; Haruta, 1997a; and Kalvachev *et al.*, 1997).

Haruta *et al.* (1989) studied the low temperature oxidation of hydrogen and of CO using gold catalysts prepared by coprecipitaiton from an aqueous solution of $HAuCl_4$ and nitrates of various transition metals. It was found that Au/α-Fe_2O_3, Au/Co_3O_4, and Au/NiO were highly active for H_2 and

CO oxidation. Additionally, these catalysts markedly enhanced the catalytic activities due to the combination effect of gold and transition metal oxides. For the oxidation of CO, they were active even at a temperature as low as $-70°$ C. In addition, CO oxidation activity increased with decreasing the size of Au particles, where the size of Au particles depended on the type of the supports due to the different Au-support interaction. In addition, they showed that coprecipitation is an effective method to prepare small gold particles with good thermal stability and possibly to avoid contamination from chloride ions and Pt group metals.

Haruta *et al.* (1993) concluded that small gold particles not only provided the sites for the reversible adsorption of CO, but also appreciably increased the amount of oxygen adsorbed on the support oxides.

Tsubota *et al.* (1995) showed that gold doposited on TiO_2 as hemispherical fine particles with diameters smaller than 4 nm could be prepared by deposition-precipitation method. It was also reported that Au / TiO_2 by this preparation method exhibited very highly catalytic activity for low temperature CO oxidation and it had a stronger interaction between the Au particles and the TiO_2 support. In addition, it was found that it was more resistive against coagulation.

Chen *et al.* (1996) studied the effect of small gold particles added to the Co_3O_4 using coprecipitation method on the catalytic activity for oxidative destruction of dichloromethane. The activity was essentially independent of gold loading at gold loading between 0.2 and 10.0 wt.%. In addition to this, the Au/Co_3O_4 catalysts were also significantly more active than other noble metal catalysts, and exhibited the activities 10 times higher than Cr_2O_3 / Al_2O_3, 70 times higher than 0.5 % Pt / Al_2O_3, and 560 times higher than 0.5 % Pd / Al_2O_3 at 300 °C.

Bamwenda *et al.* (1996) found that deposition-precipitation method produced small gold particles where as impregnation method yielded much larger particles and with a poor dispersion.

Haruta *et al.* (1996) showed that deposition-precipitation method could produce Au catalysts for more active than Pt catalysts. However, impregnation method resulted in much lower activity for Au than Pt. Deposition-precipitation method yielded smaller Au particles than the impregnation. It was also revealed that the catalytic activity of gold supported catalysts was markedly dependent on both type of metal oxide support and the particle size of Au. The turnover frequency for CO oxidation increased with a decrease in the diameter of gold particles, especially in the range below 4 nm.

Sakurai and Haruta (1996) showed that both coprecipitation and deposition-precipitation methods gave very fine gold particles with diameter smaller than 5 nm in the case of loading less than 5 % while impregnation method gave much large gold particles. However, gold particles became larger even though coprecipitation method was used, when gold loading increased above a level of 33 %. They also showed that the activity for methanol synthesis from CO_2 oxidation over supported gold catalysts strongly depended on the nature of support oxides and required high dispersion of gold.

Sakurai *et al.* (1997) found that gold exhibited very high catalytic activities, compared with that of a conventional $Cu/ZnO/Al_2O_3$ catalyst, for both forward and reverse water-gas shift reactions when supported on titanium oxide by deposition-precipitation method.

Haruta (1997b) showed that when gold deposited on selected metal oxides as hemispherical ultrafine particles with diameters smaller than 5 nm , it exhibited surprisingly high activities and/or selectivities in the combustion of CO and saturated hydrocarbons, the oxidation-decomposition of amines and organic halogenated compounds, the partial oxidation of hydrocarbons, the

hydrogenation of carbon oxides, unsaturated carbonyl compounds, alkynes and alkadienes, and the reduction of nitrogen oxides.

Haruta (1997a) studied the factor controlling activity and selectivity of gold catalyst. He found that the three factors affecting the catalytic properties of gold were the type of metal oxide support, the minimization of the size of gold particles, and the interaction of the gold particles with the metal oxide support. It was also found that coprecipitation, deposition-precipitation, and chemical vapor deposition methods were especially effective for depositing gold as nanoparticles with diameters smaller than 5 nm and with strong interaction with supports. In addition, by using over highly dispersed gold catalysts, CO oxidation could take place even at -77°C when the supports of 3d metal oxides of group VIII and coprecipitation were used.

Sanchez *et al.* (1997) used gold supported on manganese oxides for selective oxidation of CO in hydrogen. They found that even in H_2 streams, CO could be selectively oxidized over the Au/MnO_x catalyst with 1/50 Au/Mn loading. The gold catalyst was also found to resistive to both CO_2 and H_2O containing in the feed stream with a wide range of their concentrations. It offered numerous advantages over Pt-based catalysts in that CO conversion is larger, readily exceeding 95%, and that the selectivity for hydrogen conversion is smaller than that for CO.

From the study conducted by Haruta *et al.* (1998), only gold supported on titanium-based oxides by deposition-precipitation method exhibited selectivity for the production of propylene oxide or propanal. In contrast, impregnation and CVD methods resulted in having poorly selective catalysts which produced CO_2 as main product.

Haruta and Ueda *et al.* (1998) showed that Au/Al_2O_3 prepared by deposition-precipitation method and mixed mechanically with Mn_2O_3 could enhance the catalytic reduction of NO with propene in the presence of excess oxygen and moisture.

As all mentioned above, the catalytic nature of gold is newly created or tuned by metal oxide supports and has been found a wide variety of applications for example, in the oxidation of CO and H_2. Gold supported on metal oxides is much more active for CO oxidation while unsupported gold powder is more active for H_2 oxidation (Haruta, 1997b).

Recently, a wide range of applications of gold catalysts can be summarized in Table 2.1. Conclusively, the main point is that the type of metal oxide supports results in the variety of catalytic performance of gold catalyst due to the different interaction between the gold and metal oxide supports. Therefore, it is interesting to investigate the characteristics of gold catalysts supported on various types of metal oxides. In this research, the metal oxides chosen as supports were NiO, MnO_2, and Y_2O_3.

Table 2.1 Gold catalysts on different support materials for various reactions (Haruta, 1997b)

Reactions	Supports	Notes
Complete oxidation		
-CO	TiO_2, Fe_2O_3,	active even at $-70°C$
	Co_3O_4, NiO,	active even at $-70°C$
	$Be(OH)_2$,$Mg(OH)_2$	active even at $-70°C$
	Mn_2O_3	selective in H_2 at$80°C$
-CH_4	Co_3O_4	as active as Pd
-$(CH_3)_3N$	$NiFe_2O_4$	selective to N_2
Partial oxidation		
-$CH_3CH=CH_2 \rightarrow CHOCH=CH_2$	$Bi_2Mo_3O_{12}$	enhanced catalytic. activity with selectivity unchanged

Table 2.1 continued

Partial oxidation		
$-CH_3CH=CH_2 \rightarrow CH_3CH\!\!-\!\!-\!\!CH_2$ (epoxide, O)	TiO_2	highly selective in the presence of H_2
$-C_3H_8 \rightarrow (CH_3)_2CO$	TiO_2	selective in the presence of H_2
$-i\text{-}C_4H_{10} \rightarrow (CH_3)_3COH$	TiO_2	selective in the presence of H_2
$-C_5H_{11}OH \rightarrow C_4H_9CHO$	Borosilicate glass	$NO_2 \rightarrow NO$
Hydrogenation		
$-CO_2, CO \rightarrow CH_3OH$	ZnO, Fe_2O_3, ZrO_2	as active as Cu
$-H_2C=CH\text{-}CH=CH_2 \rightarrow$ $H_3C\text{-}CH_2CH=CH_2$	Al_2O_3	highly selective
Environmental		
$-NO + C_3H_6 + O_2 \rightarrow N_2$	ZnO, TiO_2, Al_2O_3	less selective to N_2O
Others		
$-CH=CH + HCl \rightarrow CH_2CHCl$	$HAuCl_4/C$	highest catalytic activity