

CHAPTER II

LITERATURE SURVEY

2.1 Chemical and Physical Properties of Gold

Gold is unique among metallic elements because of its highly resistance to oxidation and corrosion. It has a long history of usage in coinage and in jewelry. Gold ($Z = 79$) has the atomic configuration $[\text{Xe}]4f^{14}5d^{10}6s^1$, and lies in Group 11(IB) of the periodic classification of the elements with copper and silver. The three metals are often being referred to as the “coinage metals,” and gold lies between platinum in group 10 and mercury in Group 12. Gold exhibits all the expected properties of a metal in terms of luster, hardness, ductility (ability to be drawn into wire), malleability (ability to be beaten or rolled into sheets), high thermal and electrical conductance, having the highest electronegativity especially when compared to selenium, and being only slightly more electropositive than sulfur and iodine. The high electronegativity of gold gives rise to another unique feature of its chemistry. Gold does not react directly with other electronegative elements such as sulfur or oxygen, and it is only dissolved in hydrochloric acid when a strong oxidizing agent such as nitrate ion is present (Bond and Thompson, 1999).

The reason that gold is the most noble metal can be explained by the electronic configuration. Beneath the outer shell, each of the alkali metal atoms has a noble-gas core whereas each of the coinage metal atoms has an 18-electron shell, a pseudo-noble-gas configuration. The 18-electron shell does not screen the positive nucleus charge as effectively as the 8-electron shell does. Thus the positive charge of nucleus's coinage metal atom is more attractive to the outer shell electron than that of alkaline metals. Gold has only

one electron at the outer shell. So the valence electron of gold is hard to be removed from outer shell to become ionized gold (Au^{+1}) or to be shared with other elements to form compounds (Douglas *et al.*, 1982).

2.2 Preparation of Active Gold Catalysts

Although many great different methods for preparing supported metal catalysts have been reported in the literatures, three of them are predominated as described below.

2.2.1 Impregnation

Impregnation method is to deposit gold particles on a preformed support by soaking the support in a solution of gold salt, followed by aging, drying, and calcination. This may be done either by just filling the pores of the support with the solution or by suspending the support in a larger volume of solution, from which the solvent is then removed. Impregnation is the simplest classical method to make supported gold catalysts. The generally used salt is either chloroauric acid (Bamwenda *et al.*, 1997) or hydrogen tetrachloroaurate (Okumura *et al.*, 1998). The traditional supports for gold catalysts, namely titania and magnesia, were studied frequently in many research works (Schwank *et al.*, 1986). Other supports which have been used with gold, prepared by impregnation method, are silica (Choi *et al.*, 1998) and ferric oxide ($\alpha\text{-Fe}_2\text{O}_3$) (Haruta *et al.*, 1996).

2.2.2 Coprecipitation

In this technique the solution containing the gold salt and the salt of a component that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxide or carbonate. After

washing, the precipitate can be transformed to oxide by heating. Ammonium carbonate or bicarbonate have often been used to raise the pH because they are completely decomposed during calcination (Haruta, 1997).

There has been no detailed examination of the physical chemistry associated with the precipitation of gold and other precursors from the solution. In addition the chemical identity of the first-formed gold species does not seem to be established. By adding a solution containing chloroauric acid and a metal nitrate to a solution of sodium carbonate, the two hydroxides (or hydrated oxides) will be precipitated simultaneously. The coprecipitation route, devised by Haruta *et al.* (1993), has been widely imitated (Waters *et al.*, 1995 and Chen *et al.*, 1996). The product after being dried can be calcined at a variety of temperatures in the range 473-873 K (Haruta *et al.*, 1993 and Vogel, 1996).

2.2.3 Deposition-Precipitation

This procedure is, in principle, similar to the coprecipitation method previously described. The precipitation of a metal hydroxide or carbonate is formed on the particles of a powder support through the reaction of a base with the gold precursor. After that, the material is filtered, washed, dried, and calcined, as described in the coprecipitation procedure.

Deposition-precipitation has the advantage over coprecipitation in that all active components remain on the surface of the support and none is buried within it. This procedure has been preferentially used to prepare a number of supported gold catalysts because it provides a narrower particle size distribution (Haruta *et al.*, 1993).

2.3 Chemisorption on Gold Surfaces and Gold Catalysts

Considering chemisorption on gold, it is necessary to distinguish between gold's macroscopic forms (single crystals, polycrystalline materials such as wires, foils, films, and coarse powders) and microscopic gold particles which are usually supported on any materials and contain at most a few thousand atoms. The chemisorption on the surface of macroscopic gold was hardly occurred based on many reports. Small particles can much better chemisorb simple molecules probably because the large fraction of low coordination number (CN) atoms at the surface negates metallic behavior (Bond and Thompson, 1999).

Molecular oxygen is not adsorbed on clean planes of gold, however, it can be adsorbed on a disordered layer of gold (Bond and Thompson, 1999). It was found that molecular oxygen chemisorbed on gold powder over a wide temperature range with two distinct maximum adsorption at 223 K and 473 K (Schwank, 1983). Upon investigating the adsorption of carbon monoxide on gold supported on titania catalyst, Iizuka *et al.* (1997) found that the "active oxygen species" were formed on the surface of small gold particles with pre-adsorbed carbon monoxide.

There is an evidence from Haruta's work (1997) that carbon monoxide and oxygen atom can both be adsorbed on a single gold atom; this entity could be an intermediate in forming carbon dioxide. The importance of pretreating supported gold catalysts under oxidizing conditions (Haruta *et al.*, 1993) and of selecting the proper choice of calcination temperature suggests that the interaction mode of oxygen be vitally relevant to securing high activity for carbon monoxide oxidation, however, the reason has not been understood yet.

2.4 Oxidation of Carbon Monoxide

In Schwank's work (1983), it was known that gold surface was capable of catalyzing the oxidation of carbon monoxide to carbon dioxide. Recently, various aspects of this reaction have been studied. Results from one of recent studies (Iizuka *et al.*, 1997) indicated that carbon monoxide and oxygen were adsorbed onto the gold surface.

Throughout the renewed interest in gold catalysis during the past decade, it has been apparent that the method of preparation has a significant effect in the properties of supported gold catalysts. When they are prepared using conventional impregnation, generally thought to be the best preparation method for metals of Groups 8-10, the supported gold catalysts are considerably less active than the platinum group metals catalysts prepared by this method. For example, 1% Au/TiO₂ prepared by impregnation method that gave carbon monoxide oxidation at a rate of 1.7×10^{-10} mol/g_{cat}s at 300 K, considerably much lower than that given by 1% Pt/TiO₂ at a rate of 1.9×10^{-7} mol/g_{cat}s (Bamwenda *et al.*, 1997). However, 1% Au/TiO₂ prepared by deposition-precipitation method gave a rate of 5.5×10^{-6} mol/g_{cat}s under the same conditions (Bamwenda *et al.*, 1997).

Apart from preparation methods, the type of support materials and calcination temperature also effect the catalytic activity of gold catalysts. It was reported that even at a temperature as low as 197 K, 5% Au/ α -Fe₂O₃ was still active for carbon monoxide oxidation (Haruta *et al.*, 1989). In addition, the calcination temperature has a significant influence on the catalyst performance (Haruta *et al.*, 1993). Haruta's method involves washing the coprecipitated catalyst (to remove chloride ions), followed by vacuum drying and calcination in air at 673 K.

The studies conducted by Gardner *et al.* (1991) demonstrated the high activity of Au/MnO_x catalysts, obtained from coprecipitation, for carbon monoxide oxidation. These catalysts were five times more active than Pt/SnO_x catalysts prepared by deposition-precipitation and showed that the rate of Au/MnO_x increased as the oxygen content of the reacting gas increased.

Interestingly, Haruta and co-workers (1993) confirmed that gold catalysts could be effective at or below ambient temperatures. A number of attempts have been made to demonstrate how to obtain the high activity of gold catalysts in many laboratories, using various preparation and activation procedures together with a variety of high-surface-area oxide supports. Three important major factors towards the activity of the catalysts are the type of metal oxide supports, the size of the gold particles, and the strength of the interaction between the gold particles and the supports (Haruta, 1997).

Haruta and co-workers (1989) demonstrated that the nature of the support had a decisive role in the activity of gold catalysts. Although both gold and pure NiO, used as catalysts, were inactive for carbon monoxide oxidation below 500 K, 1%Au/NiO was found to be active at 203 K.

Yuan and co-workers (1997) studied the effect of supports on the activity of catalysts derived from a phosphine-stabilized mononuclear gold complex [Au(PPh₃)(NO₃)] and a phosphine-stabilized gold cluster [Au₉(PPh₃)₈](NO₃)₂. The catalysts derived from both complexes showed low activities for carbon monoxide oxidation when supported on oxides such as α-Fe₂O₃ and TiO₂ by impregnation. However, when gold catalysts were prepared by forming precipitated metal hydroxides, M(OH)_x, and then followed by temperature-programmed calcination, they had higher activities. For example, the rates obtained from 3% Au/Fe(OH)₃ and coprecipitated 4.1% Au/Fe₂O₃ were 9.7×10⁻⁷ mol/g_{cat}s at 203 K and 4.1×10⁻⁸ mol/g_{cat}s at 234 K, respectively.

For coprecipitated sample of Au/Fe₂O₃ (Minicò *et al.*, 1997), the maximum activity was obtained with gold content of 5%, and the activity was inversely proportional to the calcination temperature.

It was recognized that, for the oxidation of carbon monoxide catalyzed by gold, the activity increased as the particle size decreased (Haruta, 1989). The optimum size of gold particles on both oxides and molecular sieve supports was less than 5 nm, and their size could be made within this range by careful control of the conditions used in catalyst preparation. It was also demonstrated that high activities were obtained with crystallites of 4-5 nm (Okumura *et al.*, 1998).

Arrhenius parameters have already been published for carbon monoxide oxidation on Au/TiO₂ and Pt/TiO₂ catalysts prepared by various methods (Haruta, 1997). Activation energies of Pt/TiO₂ catalysts did lie between 49 and 60 kJ/mol, as well as those of Au/TiO₂ catalysts prepared by impregnation or photo-decomposition, where the particle sizes were relatively large. However, the deposition-precipitation route resulted in much lower values (18-27 kJ/mol). In addition, Tsubota and co-workers (1998) reported somewhat lower activation energies of Au/TiO₂ (10-18 kJ/mol).

2.5 Oxidation of Methanol

For the catalytic combustion of methanol, Haruta *et al.* (1996) reported that gold supported on α -Fe₂O₃ was as active as Al₂O₃-supported Pd and Pt catalysts at below 393 K. Recently, 8.2% Au/Fe₂O₃ prepared by coprecipitation has been found to be active at 313-353 K (Minicò *et al.*, 2000).

2.6 Yttrium Oxide Catalyst

The phase transfer of yttrium oxide was studied by Kuroda *et al.* (2000). The TPD data showed that three desorption peaks occurred at 370, 420, and 650 K respectively, corresponding to three distinct desorption processes in the molecular forms of $Y(OH)_3$ to $YOOH$, and Y_2O_3 respectively. The exchange of $^{16}O_2/^{18}O_2$ isotopes on various types of metal oxide surfaces has been extensively studied by Hutchings and Taylor (1999). A ranking order for oxygen activation is:



Moreover, a ranking order of the temperature for 30% methanol conversion to carbon dioxide was demonstrated that the activities felt in the following order:



In recent study on the selective catalytic reduction of nitric oxide with methane using yttrium oxide (Fokema and Ying, 1998), of which nanocrystalline form had a predominate effect, it was suggested that the activity of yttrium oxide be 75% of that of Co-ZSM-5 at 873 K. Yttrium oxide was also found to have excellent hydrothermal stability, with only a small inhibition of activity in the presence of water vapor.