

CHAPTER II

LITERATURE SURVEY

2.1 Partial Oxidation of Propylene over Gold Catalyst

Gold has long been thought to be chemically inert, however, it has recently been proven that its catalytic performance is dramatically tunable by control of particle size and by careful selection of the support metal oxide. A typical example is the selective oxidation of propylene in the gas containing oxygen and hydrogen. When gold is deposited on TiO_2 by deposition-precipitation technique as hemispherical particle with diameter smaller than 4 nm. It produced propylene oxide with selectivity higher than 90 % and conversion of 1-2 % at 303-393 K. The oxidation of hydrogen to form water is depressed by propylene, whereas propylene oxidation was not only enhanced but also restricted to partial oxidation by hydrogen. The depression of hydrogen combustion by the presence of propylene and a new peak due to gold deposition in TPD spectra have indicated that propylene was adsorbed on the surface of both gold particle and the TiO_2 support. The propylene adsorbed on a gold surface may react with oxygen species formed at the perimeter interface between the gold particles and the TiO_2 support through the reaction of oxygen with hydrogen. When gold loading decreased to 0.1 wt%, the reaction product switched from propylene oxide to propane. TEM observed indicated that gold particles larger than 2.0 nm in diameter produced propylene oxide, whereas smaller gold particles produced propane. Oxygen molecules on small Au particles behaved as a peroxo-like adsorbed species, which enhanced the dissociation of hydrogen molecules. The active oxygen species were a similar peroxo-like species formed on a Ti cation site at the boundary between the Au particles and the TiO_2 support. The larger Au

particles that were prepared by impregnation method had much weaker interactions and much shorter perimeter interface with the TiO_2 on which the peroxy-like species were produced Hayashi *et al.* (1998).

Haruta (1997a) studied over factors controlling activity and selectivity of gold catalyst, which were types of metal oxide supports, size of the gold particles and control of the contact structure of the gold particles with the supports. These factors are influenced by the preparation method. They found that in the presence of both oxygen and hydrogen, propylene was converted to PO with selectivity above 90 % over Au/TiO_2 . The Au/TiO_2 prepared by impregnation was poorly active and produced almost exclusively CO_2 . The presence of hydrogen not only enhanced the oxidation of propylene but also led to the selective partial oxidation to epoxide. It was found that there was a critical particle size of gold around 1-2 nm where the catalytic nature of the supported gold changed dramatically.

Haruta *et al.* (1998) found that gold supported on titanium-based metal oxides can assist the selective partial oxidation of propylene at temperatures from 313 K to 573 K in the gas containing both H_2 and O_2 . The preparation method was found to be crucial in controlling the selectivity. In general, impregnation and chemical vapor deposition methods do not produce selective catalysts. Only the deposition-precipitation method made gold selective to propylene oxide or propanol, suggesting that a strong contact between the gold particles and the titanium ion site on the support is important. The effect of changing the support was also dramatic. The use of the anatase form of TiO_2 results in propylene oxide production, while the rutile structure of TiO_2 caused complete oxidation to CO_2 . These results indicated that the oxidation of propylene in the co-presence of H_2 must involve the surface of the supports and that the reaction took place at the interface perimeter around the gold particles.

Tanaka *et al.* (1996) have proven that the catalytic performance of gold can be finely tuned by changing the size of metal particles and by the selection of metal oxide support. The structure sensitive catalytic properties of gold supported on titanium oxide have been investigated. In the reaction of propylene in the gas phase containing oxygen and hydrogen, Au/TiO₂ catalysts with Au loading higher than 0.2 % catalyzed partial oxidation to produce propylene oxide selectively, while they catalyzed hydrogenation only to produce propane when Au loading is lower than 0.1 %. It was found that 2 nm might be a critical size for the reaction of propylene. It was also found that Au/TiO₂ could selectively produce propylene oxide from propylene in coexistence with hydrogen and oxygen, while many other metal catalysts produced propane. The formation of PO from propylene (partial oxidation) and the formation of propane (hydrogenation) depending on Au loading. Gold particles smaller than 2 nm gave an electronic state that the presence of oxygen could dissociate hydrogen molecules into atomic species. This led to hydrogenation. But at higher Au loading, charge transfer had little effect on the electronic state of Au atom at the surface.

Gas phase selective oxidation of propylene to propylene oxide (PO) or propionaldehyde (PA) in the presence of H₂ and O₂ has been carried out with a propylene conversion in the range of 0.5-3.7 % over gold deposited on titanosilicates by deposition-precipitation (DP) method. PO was obtained with a selectivity above 90% at the temperature in range of 50°C-120°C whereas PA was obtained at temperatures higher than 200°C with a selectivity above 70 % over thoroughly washed catalysts with low Au loading (Uphade *et al.*, 1998).

2.2 Catalyst Preparation Method

Heterogeneous catalysts are often prepared by wet chemistry methods such as precipitation, co-precipitation, deposition-precipitation, hydrothermal synthesis or sol-gel process (Livage, 1998). The catalytic properties are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also depended on the choice of the base materials and experience shows that several ways of preparation can be considered, even for a given selection of the base material (Perego and Villa, 1997). In this work, catalysts were prepared by deposition-precipitation and sol-gel methods.

2.2.1 Deposition-precipitation Method

The procedure consists of the precipitation of a metal hydroxide or carbonate on the particles of powder support through the reaction of the base with the precursor of the metal. The main problem is to allow the precipitation of the metal hydroxide particles inside the pores of the support. Therefore the nucleation and growth on the support surface will result in a uniform distribution of small particles on the support. On the contrary, rapid nucleation and growth in the solution bulk will lead to large crystallites and inhomogeneous distribution, since the last particles will be unable to enter into the pores, but will deposit only on the external surface. In order to obtain the best results, an efficient mixing should be used together with a slow addition of the alkali solution in order to avoid the build up of local concentration. It has been found that the best base is urea, which is usually added at room temperature: by raising the temperature at 90°C, urea slowly hydrolyzed generating ammonium hydroxide homogeneously through the solution. The pH of the solution remained practically constant at the rate of precipitation, which was higher than that of hydrolysis. Best results in terms of homogenous

distribution were also obtained when an interaction between the support and the active precursor took place (Pinna, 1998).

Gold exhibited a unique catalytic nature and action when it was deposited as nanoparticles on a variety of metal oxides. Most reactions were noticeably structure sensitive over such supported gold catalysts. Deposition-precipitation was effective to deposit gold with high dispersion on TiO_2 and Al_2O_3 . This method was applicable to any forms of support including beads, honeycombs, and thin films. An important requirement was that the support materials should have high specific surface areas, preferably larger than $50 \text{ m}^2/\text{g}$. Since gold hydroxide could not be deposited at low pH, this method was useless for metal oxides having low points of zero charge, for example, SiO_2 - Al_2O_3 support (Haruta, 1997b).

2.2.2 Sol-gel Method

Sol-gel method has several promising advantages over precipitation. In general, sol-gel synthesis offers better control over surface area, pore volume and pore size distribution. Moreover, sol-gel method allows the formulation of quite a number of gel with high uniformity and stability (Perego and Villa, 1997).

One of the features of sol-gel method is the formation of liquid phase precursors consisting of $\text{M}_1\text{-O-M}_2$ bonding during mixing the metal alkoxides dissolved in the organic solvent, where M_1 is the host metal ions and M_2 the doped and/or mixed metal ions. Thus the homogeneous distributions of metal ions are expected in the gel prepared by hydrolysis of the liquid phase precursors and, consequently, in the dried powders. High purity of the products is also the great feature of sol-gel method. Therefore, it has often been applied to the preparation of catalysts in order to avoid some inconveniences derived from impurities in the catalysts (Ueno, 1992).

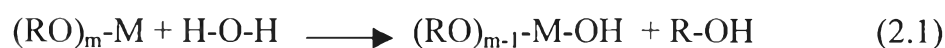
Since catalytic reactions take place on the surface of metal particles in a supported metal catalyst. Not only the activities but also the product selectivity are improved on small size metal particles. The sol-gel method is one of the promising techniques to control metal particle sizes in the supported metal catalysts (Ueno, 1992). The control of pore size is significant because the rate of sintering can be reduced when the size of the metal particle is matched to the size of the pore (Gonzalez *et al.*, 1997).

One can tailor make catalyst to fit particular application by using this method. Other advantages include higher BET surface area, improved thermal stability of the supported metals, well-defined pore sizes distributions, and the ease with which additional elements can be added (Gonzalez and Lambert, 1997).

According to the synthesis of sol-gel, it occurs in two distinct steps as following (Gonzalez *et al.*, 1997):

1. Pregelation, which occur when the reactants (alkoxides and metal precursors) hydrolyze and condense to form a gel.

The hydrolysis can be obtained as followed, when metal alkoxides reacts with water to form hydroxyl group of metal.



Where

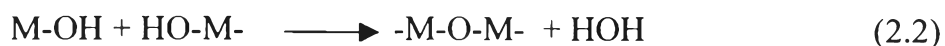
M = metal corresponding to the alkoxide

m = metal valence

R = alkyl group (CH₃, C₂H₅, C₃H₇, etc.)

After that, the condensation or polymerization can be achieved when alkoxide groups (M-OR) react with hydroxyl groups (M-OH) formed

during the hydrolysis to the form metaloxanes (M-O-M). The reactions that take place are as given below.



2. Postgelation, the second stage in the sol gel synthesis, changes that occur during the drying and calcination of the gel include desorption of water, the evaporation of the solvent, the desorption of organic residues, and the dehydroxylation reactions and structural changes.

There are many variables, which influence the sol-gel products such as water/alkoxide ratio, reaction pH, the influence of the solvent, time, temperature of reaction, the different alkyl groups, and the metallic precursor used.

2.3 Silver Catalyst for Epoxidation

Bowman (1989) found that by using a mixed silver-promoter metal silicate catalyst. The epoxidation of propylene produced a conversion greater than 0.2 mole percent and a selectivity to propylene oxide greater than about 28 mole percent. Silver-containing salt was any water-soluble silver salt that will not adversely react with the silicate-containing salt to form an undesirable precipitate.

Ranney *et al.* (1997) have studied on the role of water in partial oxidation of propylene over silver catalyst. They found that water could enhance selectivity by blocking of combustion sites occupied with water/hydroxyl on the Ag surface. Additionally, water decreased the desorption activation energy for propylene and PO which would lead to lower concentration on the catalyst surface under steady state operations. The lower surface concentration would be an increase in turnover of sites active for PO

production. A lower concentration of propylene on the surface could enhance the selectivity if the lower concentration was primarily realized at deep oxidation sites.

The Ag/ α -Al₂O₃ catalysts are well known as commercial catalysts, which is currently used in direct oxidation of ethylene to ethylene oxide by molecular oxygen. However, that catalysts and reaction conditions which are best suited for ethylene oxide production do not give comparable results in the direct oxidation of propylene. The study over silver catalyst that was comprised of promoting amount of an inorganic chloride and a potassium promoter was done to improve the catalytic activity (Cooke *et al.*, 1998).

Lu and Zuo (1999) found that by using silver catalyst modified with alkali or alkali earth chloride salts could produce PO with 33.4% selectivity and 18.6% propylene conversion. The catalyst preparation factors and the operating conditions could effect obviously the catalytic epoxidation property of silver catalyst. It was shown that, as a promoter of the silver catalyst, NaCl was more suitable than LiCl and NH₄Cl.