CHAPTER II
LITERATURE SURVEY

2.1 Partial Oxidation of Propylene

The epoxidation, or partial oxidation, of ethylene over silver catalysts has had significant industrial application for many years. Silver has been extensively tried by various workers to produce PO. Unfortunately, the attempts to produce PO with the same catalysts has failed, due to very low activity and selectivity to PO. One reason is that the epoxidation of propylene over the silver catalyst found to have very low selectivity to PO (usually less than 10%) and the rate constant for the complete oxidation of PO is extremely low and negligible. The low selectivity of PO is primarily caused by the high rate of complete oxidation of propylene, which is almost a factor of 10 faster than the complete combustion of ethylene. On the other hand, the epoxidation reaction of propylene is almost a factor of 10 slower than epoxidation reaction of ethylene (Nijhuis, 1997).

Duma and Hönicke (2000) have summarized that the epoxidation reaction of propylene on silver catalysts gave selectivity and conversion less than 15%, while ethylene gave a high conversion and selectivity, because propylene has allylic hydrogen atoms, which ethylene does not have. The interaction between molecular oxygen and metals or metal oxides will produce electrophilic and nucleophilic oxygen species. For the transformation of the vinyl group of an alkene in an oxirane ring, a mild electrophilic oxygen species will be necessary. However, the molecular oxygen produces a strong electrophilic oxygen species over noble metals and nucleophilic species over transition metal oxides.

Generally, the reaction between oxygen species and the propylene molecule will occur, depending on the electronic properties of the oxygen species, following one of three possible reactions:
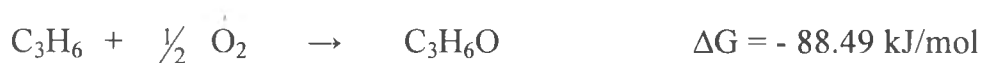
1. The reaction between mild electrophilic oxygen species and propylene will take place at the π-bond of propylene. In this pathway will emerge PO, propanal and acetone. High temperatures and acidic or basic conditions will favor, directly or by isomerization of PO, the formation of propanal and acetone. Therefore, those circumstances have to be avoided in order to improve the selectivity to PO.

2. Strong electrophilic oxygen species will attack all C-C bonds. Thus, the reaction products will be carbon oxides and organic molecules having one or two carbon atoms.
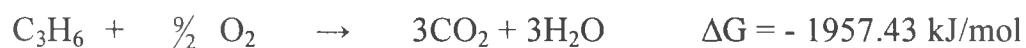
3. Nucleophilic oxygen species will attack preferentially H atoms in the allylic hydrogen position. This reaction path will lead to products like allyl alcohol, acrolein, and acrylic acid paths (Duma and Hönicke, 2000).

There are two major competitive reactions in the oxidation of propylene:

1. Partial oxidation:

$$C_3H_6 + \tfrac{1}{2} O_2 \longrightarrow C_3H_6O \qquad \Delta G = -88.49 \text{ kJ/mol}$$

2. Total oxidation:

$$C_3H_6 + \tfrac{9}{2} O_2 \longrightarrow 3CO_2 + 3H_2O \qquad \Delta G = -1957.43 \text{ kJ/mol}$$

It can be seen that the total oxidation is more exothermic than partial oxidation (Lu and Zuo, 1999).

Yamanaka *et al.* (1998) has tried to epoxidize propylene to PO with oxygen catalyzed by the EuCl$_3$-system. They studied this system at atmospheric pressure and under pressure at 30°C. Active oxygen species, generated in the EuCl$_3$-catalytic system, is an oxidant powerful enough to be able to epoxidize simple alkenes, propylene and hexenes. The results stated that the high yield and the selectivity to PO (17.1 TON, 3.3% yield, and 94%

selectivity) were obtained under pressure conditions (C_3H_6 10 atm and O_2 4 atm) at $30^{\circ}C$.

Lu and Zuo (1999) studied PO formation by using air over a silver catalyst modified with alkali or alkaline earth chloride salts. The catalyst preparation factors and the operational conditions could affect obviously the catalytic epoxidation property of the silver catalyst. It was shown that, as a promoter of silver catalyst, NaCl or $BaCl_2$ is more suitable than LiCl or NH_4Cl. The loading of NaCl should be controlled at about 3.8 wt%.

The epoxidation of propylene using molten salts has been investigated by Nijhuis *et al.* (2000). They compared the epoxidation results in the molten salts with experiments using the same, but empty reactors, an attempt was made to clarify the mode of operation of the salt. The salt acts as a catalyst in the formation of free radicals, necessary for the homogeneous gas-phase oxidation that is taking place in the gas bubbles present in the molten salt medium. The effect of the molten salts is a significant enhancement of the reaction rate. Therefore, salts does not actually take part in the oxidation reaction, but only acts as an initiator to the radical reaction process allowing for either shorter times or lower pressures.

Laufer *et al.* (1999) has investigated the epoxidation of propylene to PO with H_2O_2 over palladium impregnated, reduced titanium silicalite, merely impregnated titanium silicalite, and untreated titanium silicalite. The use of such catalytic systems in the epoxidation of propylene with H_2-O_2 mixture to assess the influence of operating conditions and the effect of the Pd loading on the epoxidation capability of the titanium silicate catalystTitanium silicalite was found to be very active even at temperature as low as $10^{\circ}C$. Lowering the H_2O_2 concentrations to only 2 wt% of H_2O_2 caused the PO yield to increase slightly over titanium silicalite and 1% Pd/titanium silicalite.

Chen *et al.* (1998) has tried to epoxidize propylene with hydrogen peroxide catalyzed by molecular sieves containing framework titanium. They

investigated four Ti-containing silicalites, namely titanium silicalite (TS-1), TiO_2-SiO_2 xerogel, Ti-MCM-41, and $TiCl_4$ modified HZSM-5 zeolite. It was found that only the crystalline molecular TS-1 and the $TiCl_4$ modified HZSM-5 zeolite were active, whereas the TiO_2-SiO_2 xerogel and the mesoporous Ti-MCM-41were almost inactive. The structure of these Ti-containing silica materials plays an important role in determining their catalytic performances. Shape-selectivity and hydrophobic nature of the material are the two most important factors.

2.2 Reactions Using Gold Catalysts

Gold is almost never used as a catalyst, since it is the least reactive metal, it has been regarded as poorly active as a heterogeneous catalyst. However, it has recently been proven that its catalytic performance is dramatically changed by control of the particle size by careful selection of support metal oxide. In the CO-oxidation reaction gold by itself is inactive, while it is deposited in the form of small particles (typically < 20 nm) on a number of metal oxide support materials, for examples, Co_3O_4, NiO, ZrO_2, or TiO_2, a very active CO-oxidation catalyst is created. This activity is caused by a phase-cooperation mechanism (Kozlov et al., 1999).

Haruta (1997[a]) had summarized the adsorption properties and reactivities of gold in terms of their size dependency from bulk to fine particles, clusters and atoms. The catalytic performances of gold remarkably depend on dispersion, supports, and preparation methods. When gold is deposited on select metal oxides as hemispherical ultra fine particles, it exhibits surprisingly high activities and 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. The unique catalytic nature of supported gold can be explained by assuming that the gold metal oxide perimeter interface acts as a site for activating at least one of the reactants, for examples, oxygen.

Haruta *et al.* (1996) have reported gold can be used as catalyst in combustion of CH_3OH, $HCHO$, and $HCOOH$ when it was deposited on some reducible metal oxides. They found that gold supported on $\alpha\text{-}Fe_2O_3$ is active as Al_2O_3-supported Pd and Pt catalysts in the oxidation of CH_3OH, $HCHO$, and $HCOOH$. While gold catalysts are less active in H_2 oxidation, they are remarkably more active in CO oxidation at low temperature.

Sakurai and Haruta (1996) have investigated the methanol synthesis by hydrogenation of CO_2 over supported gold catalysts. They found that gold catalysts strongly depended on the nature of supported oxides and required high dispersion of gold at calcination temperature between 150 and 400°C. Acidic oxides like TiO_2 gave high CO_2 conversion but low methanol yields. Zinc oxide component was indispensable for selective methanol synthesis. Significantly, the smaller gold particles, the higher methanol productivity per exposed surface area of gold. Furthermore, zinc oxide was also used in many reactions, such as partial oxidation of methanol supported palladium (Cubeiro and Fierro, 1998).

The catalytic nature of gold can be widely tuned by the three factors; type of support, size of the gold particles, and the structure of the contact interface between gold and the support. These factors are markedly influenced by the preparation method. Surprisingly, high activities for CO-oxidation at temperature as low as − 77°C (Haruta, 1997[b]).

2.3 Gold Catalysts for Epoxidation

A typical example is the selective oxidation of propylene in a gas phase containing oxygen and hydrogen. When gold is deposited on TiO_2 by deposition-precipitation technique as hemispherical fine particles, with diameters smaller than 4 nm. It produces PO with selectivities higher than 90% and conversions of 1-2% at temperatures of 303-393 K (Hayashi et al., 1998).

The oxidation of hydrogen to form water is depressed by propylene, where as PO is 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 is adsorbed on both surfaces of gold particles and TiO_2 support. The reaction rate is almost independent of the concentration of propylene and increases linearly with increasing concentration of oxygen and hydrogen.

The catalytic nature of gold can be tuned by the preparation method. Surprisingly, it gave excellent selectivities to PO in the partial oxidation of propylene. It is found that there is a critical particle size of gold around 1-2 nm where the catalytic nature of the supported gold changes dramatically to enhance this reaction (Haruta, 1997[c]).

Gold supported on titanium-based metal oxides can assist the selective partial oxidation of propylene at temperature from 313 to 573 K in a gas containing both hydrogen and oxygen. The preparation method was found to be crucial in controlling the selectivities. In general, impregnation and chemical vapor deposition methods do not produce selective catalysts.

Haruta et al. (1998) have claimed that only the deposition-precipitation method makes gold selective to PO or propanal, suggesting that a strong contact between gold particles and the titanium ion sites in the supports

is important. The change of supports dramatically effected the selectivity to the PO production.

The effects of gold loading in epoxidation of propylene is surprising in that the reaction product switches from PO to propane when gold loading is decreased to 0.1 wt% (Hayashi *et al.*, 1998).

Catalysts with gold particles smaller than 2 nm almost exclusively hydrogenate propylene to propane. This hydrogenation to propane was only observed in the presence of oxygen. It was explained by oxygen being able to make the very small gold particles electron-deficient making it act more like a hydrogenating metal such as platinum or palladium (Nijhuis *et al.*, 1999[c]).

2.4 Catalyst Preparation

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

2.4.1 Deposition-precipitation Method

The procedure consists of the precipitation of 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 induce the precipitation of the metal hydroxide particles in side 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 large particle will be unable to enter to 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 to $90^{\circ}C$, urea is slowly hydrolyzed to generate 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. The best result in term of homogeneous distribution was 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. This method was applicable to any forms of support including beads, honeycombs, and thin films. An important requirement was the support materials should have high surface areas, preferably higher than 50 m^2/g . Since gold hydroxide could not be deposited at low pH, this method was useless for metal oxides having low point of zero charge, for example, SiO_2-Al_2O_3 support (Haruta, 1997[c]).

Gold hydroxide precipitates with high homogeneous dispersion on TiO_2, most probably on specific surface sites, in the pH range 6 to 10. The calcination of TiO_2 with $Au(OH)_3$ in reducing gas atmosphere, such as H_2 and CO led to smaller gold particles than in air. Physically mixed Au/TiO_2 samples had been thought of much lower catalytic activity. An increase in

calcination temperature not only caused particle coagulation but also brought about stronger interaction with the TiO_2 support (Tsubota et al., 1995).

The catalytic activity of supported gold catalysts has been investigated by Haruta *et al.* (1996), especially Au/TiO_2, strongly depended on the pH of a starting solution, metal loading, the addition of magnesium citrate and calcination atmosphere. The unique role of Mg citrate might be, firstly, to prevent coagulation during calcination due to blockage by citrate anions sticking on TiO_2 surface. The second role can be assumed to suppress earthquake effect caused by crystallization of $Ti(OH)_4$ to TiO_2 because Mg^{2+} ion was found to retard the crystallization of amorphous titanium oxide, and finally, it can be effected to reduce the particle size of gold for the preparation of Au/TiO_2 (Sakurai and Haruta, 1996).

2.4.2 Co-precipitation Method

In this procedure the solutions containing the metal salt and salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate as hydroxide and/or carbonate. After washing, this can be transformed to oxides by heating. Typical examples of industrial catalysts prepared by this procedure are Ni/Al_2O_3 and Cu-Zn oxide/alumina, both are used in large scale productions. The first in the stream reforming process and the second in the methanol synthesis and in low temperature shift. The choice of the salts and/or alkali depends mainly on availability at a moderate cost, the solubility in the solvent (water), and, most important on avoiding the introduction of compounds that can cause negative effects in the final catalyst. For instance, except in particular cases, chlorine ions are known as common poisons and their presence has to be avoided as well as sulfate that can be reduced to sulfide during the last step of activation. Therefore, nitrate salts or organic compounds, such as formate, oxalate are preferred although some problems can arise with them too. In fact, the latter

are expensive and during the calcination may not completely decompose. Nitrate is inexpensive and particularly soluble in water, but calcination has to be controlled because of the exothermic evolution of nitrogen oxides. As to the alkali, Na^+, K^+, NH_4^+ hydroxides, carbonates, and bicarbonates can be used as precipitating agents, although ammonium hydroxide is often preferred because of absence of cation residue.

By co-precipitation a uniform distribution on a molecular scale of the different active species in the final catalyst could be attained, at least in principle. Many variables have to be controlled: the very important one is an efficient mixing, the procedure and order of addition of different solutions, the temperature, the aging time of precipitate, that may help filtration by transferring a gelatinous precipitate in a more crystallite one. Since this process is dealing with multicomponent system, the pH (value and variation) has to be carefully controlled in order to avoid precipitate of the component at a different sequence, thus affecting the final structure of the solid (Pinna, 1998).

2.4.3 Sol-gel Method

Sol-gel method has several promising advantages over precipitation method. In general, sol-gel synthesis offers better control over surface area, pore volume, and pore size distribution. More over, 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 precursor consisting of M_1-O-M_2 bonding during mixing the metal alkoxides dissolve in the organic solvent. Where M_1 is the host metal ions and M_2 is the dope and/or mixed metal ions. Thus, the homogeneous distribution of metal ions was expected in the gel prepared by hydrolysis of the liquid phase precursor and, consequently, in the dried powder. 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 the catalytic reactions take place on the surface of metal particles in a supported metal catalyst. Not only, the activity but also the product selectivity is improved on small-size metal particles. The sol-gel method is one of the techniques to control metal particle size 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 (Gonsalez *et al.*, 1997).

One can tailor make catalyst to fit particular application by using this method. The other advantages included higher BET surface area, improved thermal stability of the supported metal, well defined pore size distribution, and the ease with which additional elements can be added (Gonsalez and Lambert, 1997).

According to the synthesis of sol-gel, it occurs in two distinct steps as following:

1. Pregelation, this occurs when the reactants (alkoxides and metal precursors) hydrolyze and condense to form gel. The hydrolysis can be obtained as followed, when metal alkoxides reacts with water to form hydroxides to react with water to form hydroxyl group metal.

$$(RO)_m\text{-}M + H\text{-}O\text{-}H \longrightarrow (RO)_{m-1}\text{-}M\text{-}OH + R\text{-}OH$$
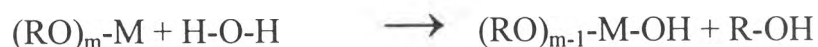
where

M = metal corresponding to the alkoxide

m = metal valence

R = alkyl group (CH_3, C_2H_5, 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 reaction that take place are as given:

$$M\text{-}OH + HO\text{-}M\text{-} \longrightarrow \text{-}M\text{-}O\text{-}M\text{-} + HOH$$

$$M\text{-}OR + HO\text{-}M\text{-} \longrightarrow \text{-}M\text{-}O\text{-}M\text{-} + ROH$$

2. Postgelation, the second stage in the sol-gel synthesis, there are many changes that take place during the drying and calcining of the gel. For example, desorption of water, evaporation of the solvent, desorption of organic residues, and dehydroxylation reaction and structural changes are occurred.

There are many variables, which influence the sol-gel products such as water/alkoxide ratio, reaction pH, solvent, time, temperature of the reaction, type of alkyl groups, and the metallic precursors, etc (Gonsalez *et al.*, 1997).