

CHAPTER II

LITERATURE SURVEY

2.1 Epoxidation

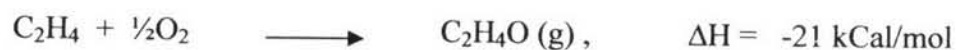
2.1.1 General

Ethylene oxide is mainly used as chemical intermediate to produce various consumer products. Almost 60% of ethylene oxide is converted to ethylene glycol which is used as anti-freeze reagent and in the manufacture of polyesters. Additionally, ethylene oxide is used for the production of ethoxylates, which are surface-active agents used in the detergent, textile, and paint industries (Wells, 1991).

Other derivatives are glycol ethers, which are widely used in brake fluids; ethoxylates in detergent formulations; as a solvent for paints and lacquers; an extractant of sulphur compounds from refinery gases, and ethanolamines used in textiles finishing and detergents. Di and triethylene glycols, polyols and choline chloride are also synthesized from ethylene oxide. Ethylene oxide is also an excellent disinfectant, fumigant and sterilizing agent (Wells, 1991).

In 1859, Wultz developed the chlorohydrin process involving the addition of hypochlorous acid to ethylene followed by dehydrochlorination. In 1931 a patent was issued to Lefort for direct oxidation of ethylene to ethylene oxide using a silver catalyst. Currently, around 98% of ethylene oxide capacity in the world is based on this route. In many plants, oxygen is favored over air because it is more economic and allows higher productivity and pollution problems caused by vent gases such as dichloroethane are markedly reduced.

The primary and secondary reactions which take place during the oxidation of ethylene are (Dumas and Bulani, 1974):



Both reactions are exothermic reactions and carbon dioxide and water are the undesired products formed from the complete oxidation of both ethylene oxide and ethylene. The deep oxidation reaction releases a large amount of heat. Thus, attempts have been made to minimize the deep oxidation reaction (Dumas and Bulani, 1974 and Matar *et al.*, 1989).

Pena *et al.* (1998) studied the ethylene oxidation in different membrane reactors which were PBMR-O (oxygen as permeate with ethylene flowing over the catalyst bed) and PBMR-E (ethylene as permeate with oxygen flowing over the catalyst bed), and compared the performance of the membrane reactors with that of fixed bed reactors (FBR). The study of FBR showed that a high oxygen/ethylene ratio increased the ethylene oxide selectivity. The behavior of the membrane reactors was different depending on the configuration, with the PBMR-O exhibiting smaller and the PBMR-E gave larger ethylene oxide selectivity, as compared to the FBR. The selectivity of EO also increased with residence time of both reactants. It was found that a high oxygen/ethylene ratio favored ethylene oxide selectivity for all different levels of adding dichloroethane in the feed and the performance was in the order PBMR-E>FBR>PBMR-O. An increase in dichloroethane concentration in the inlet stream increased the ethylene oxide selectivity to values exceeding 80% for low ethylene conversions. The addition of ethane was found to govern the amount of chlorine adsorbed on the catalyst surface. High levels of dichloroethane resulted in detectable catalyst deactivation after a few hours on stream. The optimum level of dichloroethane was found to be 1-2 ppm (Lafarga and Varma, 2000).

The model of the intrinsic reaction kinetics in plug flow behavior over the packed bed catalyst and the dusty gas model (DGM) for membrane transport were used to show that the imposed pressure gradient resulted in predominantly flow through the membrane, which inhibits back diffusion of components from the catalyst bed. The variables studied included reaction temperature and inlet reactant concentrations. The model results, as also demonstrated experimentally, confirmed that the PBMR-E was the best configuration, followed by the conventional fixed-bed reactor (FBR) and the

PBMR-O, respectively (Al-Juaied *et al.*, 2001).

2.1.2 Oxygen Adsorption

In the late 1980s, Campbell (1985) studied the kinetics of selective ethylene oxidation catalyzed by a clean Ag (111) surface compared to Ag (110) and supported Ag catalyst. The results showed that the activity of Ag (111) in epoxidation was about half that of Ag (110), but about 50 times higher than the reported results for the high surface area Ag catalysts. The reason is that Ag (111) is close surface structure, while Ag (110) is open surface structure. Therefore, more open surface structure is typically more active in bond breaking reaction. The steady-state coverage of atomically adsorbed oxygen was a factor of about 18 lower on Ag (111) than on Ag (110). These results are consistent with a mechanism whereby molecularly adsorbed O₂ and ethylene are combined to form an intermediate in the rate-determining step. This intermediate then rapidly branches into ethylene epoxide or CO₂ pathways.

In contrast, there are three groups suggesting that atomically adsorbed oxygen is the active species for epoxidation. Grant *et al.* (1985) proposed that in the absence of promoters and moderators, chemisorbed atomic oxygen reacts with adsorbed ethylene to yield both ethylene oxide and CO₂ and H₂O. Chemisorbed dioxygen appears to play no direct role in either of these reactions; the presence of subsurface oxygen is necessary for selective oxidation but not for total oxidation. van Santen *et al.* (1986) studied the reaction mechanism of ethylene epoxidation using ¹⁶O₂ and ¹⁸O₂. The results showed that under the conditions where ¹⁸O₂ equilibration in the gas phase was slow, ethylene initially reacted more rapidly with preadsorbed atomic oxygen than with molecular oxygen adsorbed in the precursor state if O_{ads}/Ag_s was unity. Nevertheless, with oxygen preadsorbed with O_{ads}/Ag_s < 0.5 and pretreated such that the oxygen atoms resided below the surface, it was concluded that subsurface oxygen atoms became incorporated in to the epoxide upon exchange with adsorbed oxygen surface atoms. Thus oxygen atoms that have been dissociated during adsorption of oxygen are incorporated into the epoxide. Carterand *et al.* (1988) theoretically explained the mechanism using ab initio

theoretical estimates. This mechanism proposed that a *surface atomic oxyradical anion* was the active oxygen species for forming epoxide.

Nakatsuji *et al.* (1997) studied the partial oxidation of ethylene to ethylene oxide catalyzed by silver by ab initio Hartee-Fock and MP2 methods using the dipped adcluster model (DAM). They explained that the active species was the superoxide O_2^- which is molecularly adsorbed in the bend end-on geometry on the silver surface. Ethylene reacted with the terminal oxygen atom and the reaction proceeded smoothly without a large energy barrier to yield ethylene oxide.

Bukhtiyarov *et al.* (1994) showed that the treatment with a mixture of C_2H_4 and O_2 could activate a clean silver foil surface for ethylene oxide formation. They proposed that the catalytic surface center to be active for ethylene epoxidation must contain two adsorbed oxygen states with different ionicities of the Ag-O bond. The "ionic" oxygen [Eb(O 1s) = 528.4 eV] produces the sites of Ag^+ ions for ethylene adsorption, while the "covalent" oxygen [Eb(O 1s) = 530.5 eV] incorporates in the ethylene molecule, forming ethylene oxide.

Oxygen adsorption on supported silver depending on the cluster sizes was studied by XPS and TPD using a model carbon-supported silver catalyst (Bukhtiyarov and Kaichev, 2000). It was shown that the electrophilic oxygen active in ethylene epoxidation was produced on the small silver clusters ($\leq 100 \text{ \AA}$) more effectively than on the bulk metal due to formation of subsurface oxygen. Enlargement of the silver particles decreased the amount of subsurface oxygen and results in the appearance of nucleophilic oxygen. These results were used in an attempt to explain the particle size effect in ethylene epoxidation over Ag/Al_2O_3 catalysts.

In temperature-programmed desorption (TPD) experiments, there were three adsorbed oxygen species observed (Kondarides and Verykios, 1993). First, a weakly adsorbed species (desorbed below $150^\circ C$) was related to the 10.5 kCal/mol adsorption process and assigned to molecularly adsorbed oxygen. Second, the desorption peak at $285^\circ C$ was related to a nearby nonactivated process and is ascribed to atomic oxygen, probably multicoordinated on the

surface. Third, high temperature (300-400°C) feature, desorbing above 400°C is related to the highly activated process of 24 kcal/mol and attributed to desorption of subsurface oxygen.

2.1.3 Effect of Promoters

Presently, the catalysts used in commercial processes for ethylene oxide are metallic silver on the low surface area inert supports. Electronegative moderators have been found to be necessary for improving the selectivity of ethylene oxide. A large amount of moderators, however, can destroy the catalyst activity. The moderators, which are known to improve the selectivity of silver are Cl, Br, I, S, Se, Te, P and Bi. Chlorine is the most commonly used moderator added in the form of organic chlorides such as 1, 2-ethylene dichloride with a low concentration of a few parts per million. The role of the moderator is thought to change not only the relative concentrations of atomic and molecular oxygen, but also to increase the probability for molecular oxygen to react with ethylene to form ethylene oxide. Moreover, the role of promoters is also significant to stabilize silver against sintering (Matar *et al.*, 1989).

Campbell *et al.* (1985) studied the selectivity of ethylene oxide as a function of chlorinated hydrocarbons added to the reactant feeds. The results showed that the activation energies were varied with chlorine coverage (θ_{Cl}) and correlated with the electronic effects of θ_{Cl} upon desorption energies for molecularly adsorbed O_2 and ethylene. However, these reaction rates had no relationship to the large increase in selectivity appearing when $\theta_{Cl} > 0.4$. It was concluded that an increase in selectivity was governed by the ensemble effect, while CO_2 production required more free Ag atoms than epoxide production did.

Yeung *et al.* (1998) studied the ethylene epoxidation reaction network on a $Ag/\alpha-Al_2O_3$ catalyst in the presence of 1,2-dichloroethane (DCE) using a single-pellet reactor. The results showed that the selectivity of ethylene oxide and the ethylene conversion decreased with increasing the width of the active layer and placing the Dirac-type active layer which was a thin layer of catalyst at the external surface or subsurface of pellet. Nevertheless, addition of

DCE promoted the catalyst selectivity for ethylene oxidation reaction, but inhibited the overall reaction.

Yong *et al.* (1990) studied the epoxidation of ethylene over silver catalysts in the presence of added carbon monoxide and hydrogen. The addition of carbon monoxide and hydrogen in the feed stream led to incomplete oxidation and inhibited ethylene oxidation by direct competition for the silver surface. Ethylene conversion and ethylene oxide selectivity were reduced under the ethylene-rich condition. Moreover, for long periods (more than 10 h) and the presence of carbon monoxide in the feed stream, it was observed that ethylene conversion fell steadily while the ethylene oxide selectivity rose. The effect was very similar to the case of 1, 2-dichloroethane at the ppm level in the feed stream. In addition, comparing oxygen and nitrous oxide as oxidants, it was found that the ethylene oxide selectivity was declined to 14% at 240°C with nitrous oxide. Activation energies for ethylene conversion to all products were similar for the two oxidants but the rate was found to be approximately six times higher with oxygen than nitrous oxide (Yong and Cant, 1989).

Rhenium has also been used as promoter for ethylene epoxidation over silver catalysts (Jun *et al.*, 1992). It was found that both the conversion of ethylene and the selectivity of ethylene oxide could be improved by the use of a rhenium-modified silver catalyst. The effect of rhenium is to weaken the silver-oxygen bond, and to reduce the electron density of the adsorbed oxygen, which could be the reason for the enhancement of the selectivity of ethylene oxide.

Cesium is another metal used as a promoter. It has been found that the fresh catalyst with Cs promoter has fairly uniform coating of Ag over the planar α -alumina surface (Minahan and Hoflund, 1996a, 1996b, 1996c). For high surface area α -alumina, addition of cesium contributes to the neutralization of surface acidity which promotes complete combustion (Mao and Vannice, 1995). Moreover, Cs likely stabilizes the defects on the Ag surface, where electrophilic oxygen is probably localized. On the other hand, it can decrease the concentration of nucleophilic oxygen (surface Ag_2O), which is responsible for the deep oxidation of C_2H_4 (Goncharova *et al.*, 1995).

Various Cs oxides formed on the Ag (111) and Ag(110) single crystals depending on cesium coverage and oxygen pressure have been identified by XPS and TPD. The results were shown the existence of few Cs oxides with various stoichiometry: from suboxide, Cs_{2+x} , to superoxide, Cs_2O_4 . The spectroscopic characteristics of two of them (suboxide and peroxide) are also observed for Cs-promoted Ag/ Al_2O_3 catalysts suggesting their existence in real catalytic conditions. Their roles in silver-catalyzed ethylene epoxidation are different: peroxide seems to suppress the total oxidation, while promotion of ethylene epoxidation can be suggested for the suboxide comparison (Podgornov *et al.*, 2000).

The effect of non-Faradaic electrochemical modification in catalytic activity was investigated during ethylene epoxidation on Ag films deposited on β - Al_2O_3 , a Na^+ conductor (Dumas and Bulani, 1974). It was found that sodium coverage (θ_{Na}) up to 0.03 could enhance the rate of epoxidation without a significant effect on the rate of complete oxidation. The maximum selectivity of ethylene oxide (88%) was obtained for $\theta_{Na} = 0.03$ and 1 ppm dichloroethane. The results indicate that the chlorine atoms can replace strongly adsorbed oxygen atoms, and that chlorine adsorption consequently weakens the bond strength of the coadsorbed oxygen by withdrawal of electrons from the silver atoms and by creation of sites for the adsorption of weakly bound electrophilic oxygen which interacts with the double bond of ethylene molecules producing C_2H_2O . In contrast, the presence of sodium on the silver surface seems to stabilize the adsorbed chlorine via the formation of a silver-oxychloride surface complex (Karavasilis *et al.*, 1996).

Kondarides and Verykios (1996) conducted a study to investigate the effect of alloying silver with gold on the oxygen adsorption characteristics of silver using microgravimetric and temperature desorption techniques. Gold was chosen due to its ability to form solid solutions with silver at any composition and because of its inertness toward oxygen adsorption and ethylene oxidation. The results confirmed the presence of three adsorbed species of oxygen at elevated temperatures, namely molecular, atomic and subsurface. They also concluded that alloying Ag with Au influenced the bond strengths of oxygen with the silver surface, which resulted in modifying the relative population of the adsorbed species. In the oxidation of ethylene, Geenen

et al. (1982) exhibited that the selectivity to ethylene oxide decreased sharply with increasing gold content of Ag-Au alloy on α -alumina support. On gold rich alloys no ethylene oxide was formed, the only products being carbon dioxide and water. The reason is that the reaction of ethylene with O_2^- results only in ethylene oxide if the adsorbed complex is sterically hindered by adjacent adsorbed species, such as O^{2-} or Cl^- , such that abstraction of hydrogen from the ethylene molecule in the way depicted above cannot occur. In the case of the alloys, the O_2^- species are separated from one another and hence the adsorbed ethylene complex will react to form carbon dioxide and water.

2.2 Support Materials

2.2.1 Alumina Support

The effect of support materials such as Ag/ η - Al_2O_3 , Ag/ TiO_2 , Ag/ α - Al_2O_3 and Ag/ SiO_2 was investigated by Seyedmonir *et al.*(1990). Commercial α -alumina is a unique support material for silver because it facilitates the highly selective ethylene epoxidation. This is attributed to its inertness for isomerization of ethylene oxide to acetaldehyde. High silver loadings on the low surface area α -alumina (surface area $<1\text{ m}^2\text{g}^{-1}$) are typically used for commercial ethylene oxidation catalysts, in which silver is in poor dispersion. Mao *et al.* (1995) used high surface area (HSA) α -alumina (about $100\text{ m}^2\text{g}^{-1}$) as support. The results showed that (HAS) α -alumina was a poor support for ethylene epoxidation due to the formation of small nanoparticles of Ag. The reaction rate increased with increasing surface area but the selectivity was poor. Therefore, it is interesting to prepare Ag catalysts on a high surface area alumina that permit to stabilize Ag in form of larger particles. In this study, fumed alumina of Degussa C having a surface area of $98\text{ m}^2/\text{g}$ was used as support for Ag. This support is a nonporous material, and it was hoped that it should be provided a large particle size of Ag on this support which is believed to be good for the epoxidation reaction of ethylene.

2.2.2 Titania and Ceria Supports

Supported metal catalysts are undoubtedly one of the major areas of research in heterogeneous catalysis. The study of well-known strong metal-support interaction (SMSIs) when the support is a reducible oxide has received a lot of attention. The reason is the ability of the oxygen migration of reduced support particles onto the surface of metallic particles. The formation of a suboxide of the support was facilitated by the reduction being induced by the metallic particles (Holgado *et al.*, 1998). It has been known that group VIII noble metals supported on TiO_2 exhibits a strong metal-support interaction effect. Shastri *et al.* (1984) studied the behavior of gold supported on TiO_2 . The results showed that TiO_2 played a special role compared to other typical catalyst support materials. It could stabilize high dispersion of Au up to 700°C . It was explained that this phenomenon did not appear to be due to the SMSI effect. While a temperature of 700°C was sufficient to accomplish the complete phase transformation of anatase to rutile in the blank TiO_2 , no transformation occurred under the identical conditions on TiO_2 impregnated with Au. Seyedmonir (1990) found that in the presence of 0.5 ppm EDC, ethylene oxide selectivity over Ag/TiO_2 was low about 10% as compared to 60% over the $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalyst. The low ethylene oxide selectivity of the Ag/TiO_2 catalyst was attributed to the secondary oxidation reaction in which ethylene oxide was further oxidized on this reactive support. In addition, the average crystallite size of the Ag/TiO_2 catalyst was in the range of 3.5 to 7.0 nm. Moreover, Yong (1991) found that silver supported on TiO_2 showed zero ethylene oxide selectivity. They explained that ethylene oxide formed was further oxidized over the TiO_2 support. In situ infrared measurements with TiO_2 showed that ethylene oxide reacted instantaneously with surface hydroxyl groups to form a glycol like species. Reaction of acetaldehyde over TiO_2 occurred at a much slower rate than that of ethylene oxide. It was concluded that the zero selectivity of silver supported on TiO_2 for ethylene epoxidation was due to isomerization of ethylene oxide to acetaldehyde on the support followed by complete oxidation on the silver.

Ceria has an important role in most commercial catalytic processes in terms of economic relevance and tonnage: three-way catalysis (TWC) and fluid catalytic cracking (FCC). In addition, ceria can stabilize supports and keep high

surface area, prevent the sintering of precious metal, and thus, stabilize their disperse state, promote CO oxidation and water-gas shift reaction, and act as oxygen reservoir (Kaspar *et al.*, 1999 and Imamura *et al.*, 2000).

Halgado *et al.* (2000) found that reduction of CeO_2 by preference removal of oxygen by sputtering led to the formation of Ce^{3+} species and the development of a new peak at the O1s spectrum at around 532.4 eV. This lateral component of oxygen peak had been attributed to oxide ions at the surface of the film with an unusual low coordination. Exposure of the reduced CeO_x film to O_2 produced a progressive reoxidation at each equilibrium pressure, to rather homogeneous compositions which indicates fast electron and oxide ions diffusion processes between the inner zones of the altered layer and its surface. After a deep oxidation, highly stable Ce^{3+} species still remain face and interfaces together with part of the low coordinated lateral oxygen ions. The lateral O1s component is tentatively attributed to oxygen ions with unusual coordination in a defective CeO_x ($x < 2$) structure, while the remaining Ce^{3+} ions might be due to fully coordinated species. Enrichment of the surface of the defective cerium oxide with these oxygen species seems to be a result of the same structural rearrangements that favor the observed stabilization of Ce^{3+} species at the surface.

2.3 Silver Catalysts

Silver is a uniquely effective catalyst for the industrial important epoxidation of ethylene. The ethylene epoxidation over silver catalyst has been intensively investigated due to two main reasons. First, there is no thermodynamic limit for further increasing selectivity to ethylene oxide and, second, there are still some fundamental questions concerning the mechanism of the reaction that remain unanswered. It has been proposed that the mechanistic steps may involve oxygen adsorption on the Ag surface, reaction of the adsorbed oxygen species with ethylene, and formation of intermediates on the surface (Minahan and Hoflund, 1996c).

The effect of crystallite size of silver on the activity and selectivity was studied by Wu *et al.* (1975). The activities per unit surface area for ethylene oxide

formation and for carbon dioxide formation decreased with increasing crystallite size, but not at the same rate. The ethylene oxide selectivity was nearly zero for 20 Å silver particles and gradually increased to 60% for 500 Å silver particles. Two types of active site are believed to be formed by adsorption of oxygen at steps and faces of the silver crystals, and reaction occurs between ethylene and atomic or molecular oxygen competitively adsorbed on these sites.

Verykios *et al.* (1980) studied the kinetic effect of total surface, average silver crystallite size, and silver crystallite morphology of supported silver catalysts on the epoxidation reaction. They found that the specific activity and selectivity of the catalysts were a strong function of the total surface area. The specific rates to ethylene oxide and to carbon dioxide and water formation exhibited strong structure sensitivity with minimum rates at silver crystallite sizes in the range of 500-700 Å. The changes in specific activity and selectivity appeared to be related to changes in the morphology as well as the size of the silver crystallites. Furthermore, they explained that crystallite size effects can be significant in small crystallites in which the surface atoms constitute a significant fraction of the total number of atoms in the crystal. Otherwise, edge and corner atoms constitute a significant fraction of the total number of surface atoms in small crystal (Smeltzer *et al.*, 1956). It is expected that edge and corner atoms exert different catalytic activities because they have a different coordination number than other surface atoms. Binding energies between surface atoms and between bulk atoms are different; for small crystallites such differences can be expected to depend on the size of the crystallites. These differences can influence the bonding energy with an adsorbed molecule and affect the specific catalytic activity.

Lee *et al.* (1989) proposed that the influence of metal crystallite size on the kinetic parameters was also found to depend on the carrier employed. Thus, the specific activity of Ag/ α -Al₂O₃ was found to exhibit a maximum ethylene oxide selectivity at an average crystallite size of approximately 400 Å while that of Ag/SiO₂ increased with crystallite size and appeared to level off at an average crystallite size of approximately 500 Å.

Comparably high selectivity can be attained over both large and small Ag crystallites in the presence of ethylene dichloride. The optimum levels of ethylene

dichloride appear to differ, with larger crystallites requiring higher ethylene dichloride concentrations. The lower TOF values on the Ag/SiO₂ catalysts are compensated by their much higher dispersions and these SiO₂ supported catalysts also show much greater resistance to sintering. A comparison with literature results indicates that in the absence of moderators a 1000-fold decrease in TOF occurs as Ag crystallite size decreases to 3 nm from that in bulk samples; however, structure sensitivity cannot be unequivocally claimed because of the unknown role of adsorbed oxygen on these small particles (Seyedmonir *et al.*, 1990).

2.4 Gold Catalyst

Gold is unique among metallic elements because of its resistance to oxidation and corrosion. In addition to its inert property to any chemical reactions, gold has very low affinity for gas adsorption. Moreover, it was found that molecular oxygen was chemisorbed on gold powder over the wide temperature range, with two distinct maxima at -50°C and at 200°C (MacDonald and Hayes, 1970 and Schwank, 1983).

Kondarides *et al.* (1996) studied the effect of adding gold into silver catalysts on oxygen adsorption. The results confirmed the presence of three adsorbed oxygen species: atomic oxygen, molecular oxygen and subsurface oxygen at elevated temperatures and showed that alloying Ag with Au influenced the bond strengths with silver surface and, thus, modified the relative population of the adsorbed species.

Regarding to literature survey articles, attempts have been focused on the advances in the catalysis research of Au catalyst for many reactions such as propylene epoxidation, CO oxidation, photocatalytic reaction and other reactions.

2.4.1 Epoxidation of Propylene

Hayashi and co-workers (1998) studied the vapor phase epoxidation of propylene over Au/TiO₂ in the presence of oxygen and hydrogen. They found that propylene oxide was produced with a high selectivity greater than 90% and the propylene conversions of 1-2% at temperatures of 303-393 K when gold was

deposited on TiO_2 by deposition-precipitation techniques as hemispherical particles with diameters smaller than 4.0 nm. Moreover, the reaction rate was independent on the concentration of propylene and increased linearly with increasing concentration of O_2 and H_2 . Therefore, the results suggested that propylene adsorbed on gold surface might 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. In addition, it was observed that gold particles larger than 2.0 nm in diameter produced propylene oxide, whereas smaller gold particles yielded propane.

Due to the deactivation of Au/TiO_2 catalysts, adding silica to the titania support can induce a longer life time of the catalyst. In 1999, Nijhuis *et al.* modified the titania support by dispersing SiO_2 on TiO_2 (TS-1). It was found that Au on TS-1 was more resistant to deactivation and able to give slightly higher yields of propylene oxide. The maximum propylene oxide yield obtained with this type of catalyst remained low (less than 2%). These low yields might be a result of oligomerization of propene oxide occurring on the catalyst when the propylene oxide partial pressure becomes too high.

The presence of hydrogen was crucial for the activity of the catalyst, most likely because the hydroperoxide-like compound formed on the gold particles is transferred via a spillover mechanism to the titanium atoms. This hydroperoxide on titanium was expected to be the species reacting with propene to produce propylene oxide (Nijhuis *et al.*, 1999).

Furthermore, Uphade and co-workers (2000) employed Au/Ti-MCM-41 ($\text{Ti/Si} = 3/100$) to study the effect of an addition of CsCl onto these catalysts on the gas phase epoxidation of propane using H_2 and O_2 . They obtained 92% propylene oxide selectivity at the reaction temperature of 100°C after 60 min of reaction. The presence of CsCl with this catalyst reduced H_2 consumption by about 90% and improved the propylene oxide selectivity up to 97% at a propene conversion of 1.7%. It was reported that agglomeration of gold particles was caused by Cl^- anion. The mean diameter of Au particles, 2.2 nm, in Au/Ti-MCM-41 increased to about 10 – 20 nm and some clusters were even larger than 50 nm in size due to the direct contact between chloride and Au particles.

Mul and co-workers (2001) reported that irreversible adsorption of propylene oxide was observed on both 1 wt% Au/TiO₂ and 1 wt% Au/TiO₂/SiO₂, and the reaction yielded bidentate propoxy moieties. The spectroscopic evidence for oligomerization or dimerization of propylene oxide was not found. Similar propoxy species were observed after prolonged exposure of the catalysts to a propene/oxygen/hydrogen mixture. Additionally, formate and acetate species were formed exclusively on the Au/TiO₂ catalyst after exposure to the reacting mixture at 400 K or decomposition of the adsorbed bidentate propoxy species in a hydrogen/oxygen mixture. Supporting Au and TiO₂ on SiO₂ apparently reduced the activity toward C-C bond breaking. Based on the spectroscopic results, deactivation of Au/TiO₂ catalyst likely related to the irreversible adsorption of a propoxy species on the activation of Ti site. On the TiO₂/SiO₂ catalyst, the acidic Ti sites that cause ring opening of propylene oxide are apparently not located near the active epoxidation center. Thus, no deactivation of dispersed Ti catalyst was observed. Analysis of the Au/TiO₂/SiO₂ catalyst showed the formation of acetone and propanal. However these side products initially remained adsorbed on the catalyst surface under reaction conditions, maintaining a gas phase selectivity of 99%.

Stangland *et al.* (2000) characterized the two most effective propylene oxide catalysts, which were deposition-precipitation of gold onto titania-modified silica and silica-supported Au-Ti nanoclusters with a 200:1 gold to titanium ratio. The propylene oxide TOFs (turnover frequency) for Au/TiO₂ catalysts exhibited a relatively small spread at 373 K, but varied over 4 orders of magnitude as the temperature approached 473 K. The amount and phase of titania in contact with gold, influencing the number and type of Au-Ti contacts, is important in maximizing PO formation and limiting both oxidative cracking of PO to ethanal and CO₂ and propylene oxide isomerization reaction. A D₂ kinetic isotope effect observed for propylene oxide formation supports the idea that hydroperoxy intermediates are produced from H₂ and O₂ over catalyst's surface.

Zwijnenburg *et al.* (2002) prepared bimetallic Au catalyst by adding Pt or Pd on Au/TiO₂/SiO₂ with deposition-precipitation techniques. The results for Pd-Au catalysts indicated that although Pd seems well dispersed over support, hydrogenation of propene to unwanted propane occurred. This is probably due to the

presence of monometallic Pd particles. Moreover, results for Pt showed an increase in the hydrogen and oxygen efficiency, combined with a stable yield in propylene oxide. Hydrogenation of propene occurs at higher temperatures, but can be prevented by operating below 373 K.

2.4.2 CO Oxidation

The oxidation of CO is a typical reaction for which Au catalysts are extraordinarily active at room temperature and more active than other noble metal catalysts at temperature below 400 K. For this oxidation reaction, Au/TiO₂ has been intensively studied. This is because neither Au nor TiO₂ alone is active for CO oxidation but their combination generates surprisingly high catalyst activity. The following are literature articles relating to Au catalysts.

Haruta and co-workers (1993) prepared highly dispersed gold catalysts via co-precipitation and deposition-precipitation. They proposed that the small gold particles were hemispherical in shape and stabilized by epitaxial contact, dislocations, or contact with amorphous oxide layer. Among the gold catalysts supported on TiO₂, α -Fe₂O₃, and Co₃O₄, the turnover frequencies for CO oxidation per surface gold atom were almost independent on the kind of support oxides used and they increased sharply with a decrease in diameter of gold particles below 4 nm. Small gold particles not only provide the sites for the reversible adsorption of CO but also appreciably increase the amount of oxygen adsorbed on the support oxide. Based on the TPD and FT-IR data, the mechanism was proposed in which CO adsorbed on gold particles migrated toward the perimeter on support oxides and then it reacts with adsorbed oxygen to form bidentate carbonate species (Haruta *et al.*, 1993).

Adsorption of CO on pre-oxidized Au/TiO₂ at 253-303 K took place mainly as reversible Langmuir-type chemisorption. A large portion of CO was found to be adsorbed on TiO₂ support, which contributed to the reversible part of chemisorption. The irreversible part of CO adsorption, which was about 10% of the total amount of adsorbed CO, was related to CO₂ formation on the surface of gold particles and the accumulation of carbonate-like species on the surface of TiO₂ (Iizuka *et al.*, 1997). Adsorption of CO and CO₂ occurred almost instantaneously and

reversibly on preoxidized Au/TiO₂, where a slow increase in the O₂ pressure was observed at 273 K in the absence of evacuation. A similar increase of O₂ pressure was observed from oxidized TiO₂ but Au powder did not show any increase. The increase was ascribed to the desorption of weakly adsorbed O₂ on the support surface of Au/TiO₂. The rate of the reduction of preoxidized Au/TiO₂ with CO almost corresponded to the increase in the O₂ pressure and was far smaller than the rate of the catalytic oxidation of CO with O₂ on the catalyst, indicating that molecular oxygen weakly adsorbed on the support surface of Au/TiO₂ contributes only partly to the catalytic oxidation of CO. During the oxidation, O₂ in the gas phase may be directly activated on the surface of deposited gold particles and/or on the very narrow perimeter interface between the gold and the support (Iizuka *et al.*, 1999).

Furthermore, Boccuzzi and co-workers (2001a, 2001b) studied the effect of calcinations for three Au/TiO₂ catalysts prepared by the deposition-precipitation technique. The different calcination temperatures were 473, 573 and 873 K giving the mean diameters of Au particles of 2.4, 2.5 and 10.6 nm, respectively. The first two catalysts exhibited 100% conversion of CO at temperature below 240 K, whereas the third catalyst exhibited 100% conversion at temperature above 300 K. From the FT-IR data at 90 K, the large majority gold terrace sites did not adsorb CO.

2.4.3 Photocatalytic Reaction

Bamwenda and coworkers (1995) compared Au/TiO₂ and Pt/TiO₂ catalysts used for photo-assisted hydrogen production from a water-ethanol solution. They found that the activity of Au catalysts for H₂ production strongly depended on the method of catalyst preparation, but the activity of Pt catalysts was less sensitive to the preparation method. In addition, the yield of H₂ depended on the pretreatment conditions. Both gold and platinum catalysts calcined in air at 573 K had the highest activities towards H₂ generation. The maximum H₂ yield was observed for 0.3-1 wt% Pt and 1-2 wt% Au. The rate of H₂ production was strongly governed by the initial pH (4-7) of the suspension. The roles of Au and Pt on TiO₂ seem to involve the attraction and trapping of photogenerated electrons, the reduction of protons and the formation and desorption of hydrogen. The higher overall activity of Pt catalysts

samples is probably a result of the more effective trapping and pooling of photogenerated electrons by Pt and/or because platinum sites have a higher capability for the reduction reaction.