CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Ethylene Epoxidation

2.1.1 General

The epoxidation of olefins plays an important role in the industrial production of several commodity compounds, as well as in the synthesis of many intermediates, fine chemicals, and pharmaceuticals. Particularly, the selective oxidation of ethylene to ethylene oxide (C_2H_4O, EO) is one of the most important catalytic processes for the production of high value-added petrochemicals. Almost 60 % of ethylene oxide is converted to ethylene glycol, which is mainly used for the production of antifreeze and polyester fibers. Ethylene oxide not only dissolves in water to produce ethylene glycol, but also reacts with fatty alcohols and the sulfanated compounds to produce surfactants. Therefore, it is extensively used in other various applications, such as washing/dyeing, electronics, pharmaceuticals, pesticides, textiles, papermaking, automobiles, oil recovery, and oil refining. The world consumption of EO in 2002 was 1.47×10^7 metric tons per year, making it the most utilized epoxide species (Lacson, 2003). On the other hand, annual world-wide production of ethylene oxide is about 7-8 million ton, which is a double capacity of propylene oxide production, as shown in Table 2.1.
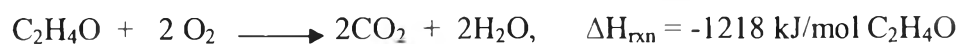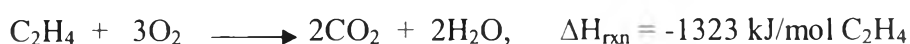
The selective ethylene oxidation, or epoxidation, to produce ethylene oxide takes place between adsorbed ethylene and adsorbed oxygen. Neglecting the form of adsorbed oxygen (molecular or atomic), the basic reaction stoichiometry can be described as (Cassidy and Hodnett, 1998):

$$C_2H_4 \ + \ O_2 \ \longrightarrow \ C_2H_4O$$

Table 2.1 US and worldwide production of oxygenated hydrocarbon monomers and their principal uses (Patterson, 1981; Lyons, 1984)

Oxygenated hydrocarbon monomers	1995 US production (10^6 ton per annum)	1994 world-wide production (10^6 ton per annum)	Principal uses
Ethylene oxide	2.6	7-8	Ethylene glycol for polyester and polyane fibers, antifreeze; di-, tri- and polyols for lubricants, brake and deicing fluids, textile chemicals, plasticizers, cosmetics, ointments
Propylene oxide	1.8	3.5	Propylene glycol for polyester and polyurethane fibers, antifreeze; di-, tri- and polyols for lubricants, brake fluid, textile chemicals, plasticizers, cosmetics, oinments

Apart from the ethylene epoxidation reaction, the direct oxidation of both ethylene and ethylene oxide can easily occur according to the higher changes in enthalpy as compared to that of the ethylene epoxidation reaction.

$$C_2H_4 + O_2 \longrightarrow C_2H_4O, \qquad \Delta H_{rxn} = -105 \text{ kJ/mol } C_2H_4$$

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O, \qquad \Delta H_{rxn} = -1323 \text{ kJ/mol } C_2H_4$$

$$C_2H_4O + 2O_2 \longrightarrow 2CO_2 + 2H_2O, \qquad \Delta H_{rxn} = -1218 \text{ kJ/mol } C_2H_4O$$

Since ethylene oxide is a reactive species due to its highly strained 3-member ring structure, careful control must be taken to stop the direct oxidation after the ethylene oxide is formed and not to further oxidize the product to carbon dioxide and water. Figure 2.1 shows the difference in the surface active structures between the complete combustion and epoxidation. In fact, careful control must also be taken to prevent the total oxidation, or combustion, of ethylene to carbon dioxide and water. The secondary oxidation reaction can be minimized by process control, whereas the

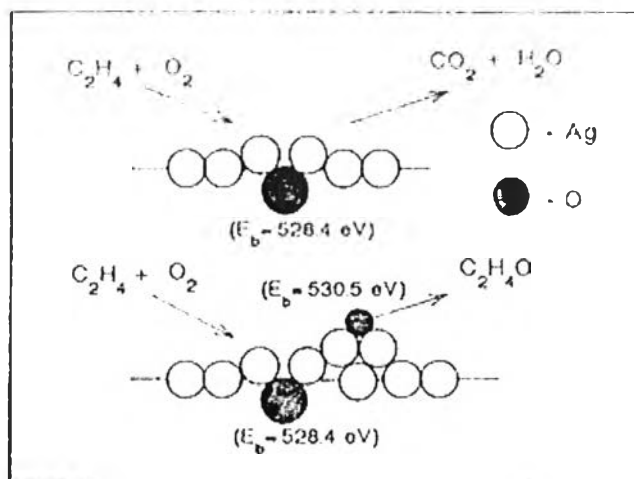total oxidation reaction is primarily catalyst- and process-gas-composition related (Serafin, 1998).

Figure 2.1 Surface structures active in total combustion (top) and epoxidation (bottom) (Bukhtiyarov, 1994).

Lafarga and Varma (2000) compared the performance of 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), with that of a conventional fixed-bed reactor (FBR) for ethylene epoxidation. Figure 2.2 shows how the membrane reactor was set up. The study showed that high oxygen/ethylene ratio enhanced ethylene oxide selectivity. Among three reactors' configuration, the reactor performance was in the order PBMR-E > FBR > PBMR-O. The selectivity for EO also increased with residence time of reactants over the catalyst bed by means of nitrogen partition. An increase in 1,2-dichloroethane (DCE) concentration in the inlet stream entering the catalyst bed increased the EO selectivity to higher than 80 % with low ethylene conversions. Conversely, high levels of dichloroethane showed detectable catalyst deactivation after a few hours under reaction conditions and an optimum level was found to be 1-2 ppm (maximize ethylene oxide yield while maintaining a reasonably high stable catalyst activity). Additionally, ethane was added to control the amount of chlorine adsorbed on the catalyst surface.
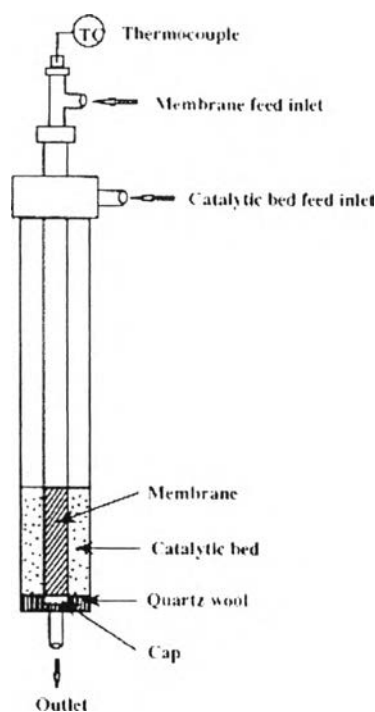
Figure 2.2 Schematic diagram of the membrane reactor setup (Al-Juaied *et al.*, 2001).

The direct epoxidation of ethylene to form ethylene oxide as a product by the oxidative coupling of methane (OCM) is also one of several possible process routes. Liu and Shen (1995) studied direct epoxidation over supported silver catalysts promoted with Ba, K, Cs, and Cl. The results showed that it was possible to epoxidize ethylene directly in the exit gas generated by OCM if carbon dioxide was removed, and an amount of oxygen and ppm levels of 1,2-dichloroethane (DCE) were required. Due to the presence of 2.1 vol.% H_2, the selectivity for ethylene oxide decreased and ethylene conversion increased gradually as a function of time, so addition of DCE in the feed was required to eliminate the effect of hydrogen. This effect was due to a rapid stripping of the chlorine, with which the catalysts were impregnated. When carbon monoxide added to feed was completely oxidized, ethylene epoxidation was not affected. However, when carbon monoxide was not completely oxidized, the conversion of ethylene decreased significantly owing to deposited carbonaceous material. Both hydrogen and carbon monoxide were oxidized much faster than ethylene over the silver catalyst. The inhibiting effect of carbon dioxide on

ethylene epoxidation was observed when carbon dioxide concentration in the feed was higher than 7 vol.%.

2.1.2 Oxygen Species Relating to Ethylene Epoxidation

Viewpoints regarding the mechanism have changed considerably over the past three decades. Three types of oxygen have been observed, namely molecular, atomic, and subsurface oxygen. Silver is an effective catalyst for the epoxidation of ethylene due to its good ability to adsorb oxygen. Furthermore, the roles of chlorine-containing inhibitors and alkali-metal promoters are also explained differently in each mechanism.

In particular, ethylene oxide formation was shown to require adsorbed oxygen in two states: 'ionic' (nucleophilic) oxygen similar to that in Ag_2O (the lowly active oxide, easily forming on small Ag particles which decrease the epoxidation rate) and 'covalent' (electrophilic) oxygen localized at the surface defects. The former (or Ag^+ cations involved) serves for the ethylene adsorption, while the latter reacts with the C_2H_4 molecule, yielding C_2H_4O. So, a pair of active sites is actually required. In the presence of nucleophilic oxygen alone, the adsorbed ethylene reacts to form the products of deep oxidation only (Goncharova *et al.*, 1995).

2.1.2.1 Molecular Oxygen on Silver

The prevailing wisdom until about 1985 was that formation of ethylene oxide proceeds by the reaction of adsorbed ethylene with adsorbed molecular oxygen, whereas the formation of CO_2 occurs via reaction of atomic oxygen with ethylene or ethylene oxide (Campbell, 1985). Molecularly adsorbed oxygen results from non-dissociative adsorption and is more weakly held.

$$O_2 + Ag \rightarrow O_{2ads}^- + Ag^+$$
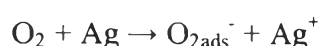
In the molecular (or dioxygen) adsorption model, one molecule of oxygen adsorbs on the silver surface and reacts with one adsorbed ethylene molecule, producing one ethylene oxide molecule and one adsorbed oxygen atom. This remaining oxygen atom participates in a combustion reaction with ethylene. So,

according to this mechanism, it would be advantageous to utilize inhibitors to prevent the adsorption of atomic oxygen. Chlorine inhibitors serve to block active sites from adsorbing atomic oxygen, thereby increasing selectivity. The role of alkali-metal promoters is not fully understood (Santen and Kuipers, 1987).

In 1997, Nakatsuji *et al.* (1997) investigated the oxygen species by dipped adcluster model (DAM). The results were consistent with the mechanism of molecularly adsorbed O_2. For the molecular adsorption, both end-on and side-on geometries were investigated. The ground-state electronic structure of the molecularly adsorbed O_2 species in the end-on form is the superoxide O_2^-, and that in the side-on form is the peroxide O_2^{2-}. The end-on superoxide species is an active species for the partial oxidation of ethylene on an Ag surface. Moreover, they clarified why silver is an effective catalyst for the partial oxidation of ethylene through stabilities and activities of oxygen on Cu, Ag, and Au surfaces. They found that if superoxide species exists on the surface, both Cu and Au surfaces show a reactivity similar to Ag surface, leading smoothly to yield ethylene oxide, and the barriers leading to complete oxidations should be very high. In fact, superoxide species does not exist on Au surface because the molecular adsorption of O_2 does not occur owing to the difficulty of the electron transfer from the clean bulk metal. On Cu surface, the lifetime of the superoxide should be too short to react with ethylene. On Ag surface, however, the superoxide species would have a considerable lifetime on the surface, so Ag is an effective catalyst for epoxidation. Figure 2.3 illustrates the most likely structures for molecular oxygen on Ag(110). They also concluded that the difference in the stability of the end-on superoxide species on Cu, Ag, and Au surfaces is the reason for the observed difference in the catalytic activity of these metals for the partial oxidation of ethylene.
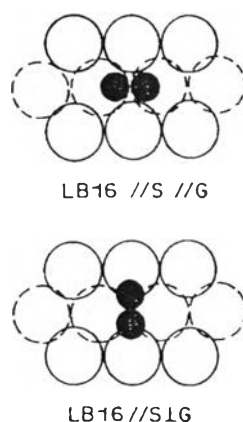
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Figure 2.3 Most likely structures for molecular oxygen on Ag(110) (Selmani *et al.*, 1985).

Since six oxygen atoms are required for the total oxidation of one ethylene molecule, six ethylene oxide molecules are produced for every molecule of ethylene that is combusted. Thus, the selectivity to ethylene oxide is 6/7, or 85.7 % (assuming that neither ethylene nor ethylene oxide are combusted by any other pathways). This mechanism seems to be supported by industrial operations, since the maximum selectivity obtained in an industrial setting is approximately 80 % (Ullman's Encyclopedia, 1987).

2.1.2.2 Atomic Oxygen on Silver

However, a number of studies since about 1985 provided definitive evidence that both ethylene oxide and CO_2 are formed via reactions with atomic oxygen adsorbed either on or in sublayers of the Ag surface, although the selectivity for ethylene oxide versus CO_2 depends on the charge of the oxygen atom, with an atom of lower charge (covalent bonding with Ag) favoring selectivity for ethylene oxide (Bukhtiyarov, 1994). According to this mechanism, it would desirable to use promoters or inhibitors to activate the atomic oxygen towards epoxidation rather than combustion. Atomically adsorbed oxygen results from dissociative oxygen adsorption.

$$O_2 + 4Ag \rightarrow 2O_{ads}^{2-} + 4Ag^+$$
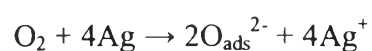
Epoxidation occurs when one oxygen atom reacts with the double bond of one adsorbed molecule of ethylene. Combustion occurs when one oxygen atom abstracts the slightly acidic hydrogen atom of one adsorbed molecule of ethylene, which results in complete oxidation. Similarly, one oxygen atom can react with and completely oxidize a newly produced ethylene oxide molecule.

The presence of inhibitors can increase selectivity by altering the electronic properties of the adsorbed oxygen atom and activating it for epoxidation. Electron-withdrawing species, such as adsorbed chlorine, act to decrease the electron density of the adsorbed oxygen atom. The electron-deficient oxygen favors an attack on the electron-rich double bond of ethylene. Clean silver catalyst samples have been activated by annealing in the presence of oxygen, and this procedure dissolves atomic oxygen in the bulk of the silver. This bulk-dissolved oxygen also acts as an electron-withdrawing species, further activating the surface atomic oxygen (Grant *et al.*, 1985).

Grant *et al.* (1987) proposed a mechanism, in which adsorbed ethylene reacted with chemisorbed atomic oxygen to form either EO or CO_2. They suggested that the competition between the two primary reaction pathways is controlled by the charge on atomic oxygen. When dissolved oxygen or other electron-withdrawing moderators, such as chlorine, are present, the production of EO through electrophilic attack of the olefin double bond by atomic oxygen is favored. Conversely, in the presence of species that contribute valence charge to silver and hence atomic oxygen, the oxygen preferentially attacks a C–H bond in ethylene, leading ultimately to combustion products. In the secondary reaction, EO may undergo further oxidation by adsorbed atomic oxygen to form additional CO_2. Indeed, Haul and Neubauer (1987) proposed ten possible steps for atomically adsorbed O_2 for the formation of ethylene oxidation on silver, as shown in Table 2.2.

Table 2.2   Proposed mechanisms for ethylene oxidation on silver (Haul and Neubauer, 1987)

Step	Elementary reaction	Surface process
1	$O_2 + s \leftrightarrow s\text{-}O_2$	O_2 chemisorption
2	$s\text{-}O_2 + s \leftrightarrow 2s\text{-}O$	O_2 dissociation
3	$C_2H_4 + s\text{-}O \rightarrow s\text{-}O\text{-}C_2H_4$	Ethylene chemisorption (path 1)[a]
4	$s\text{-}O\text{-}C_2H_4 \rightarrow s + C_2H_4O$	Ethylene oxide desorption (path 1)[a]
5	$s\text{-}O\text{-}C_2H_4 \rightarrow s\text{-}O\text{-}CHCH_3$	Isomerization (path 2)[b]
6	$s\text{-}O\text{-}CHCH_3 + 5O\text{-}s \rightarrow 6s + 2CO_2 + 2H_2O$	Total oxidation (path 2)[b]
7	$CO_2 + s\text{-}O \leftrightarrow s\text{-}O\text{-}CO_2$	CO_2 inhibition
8	$H_2O + s\text{-}O \leftrightarrow s\text{-}O\text{-}H_2O$	H_2O inhibition
9	$C_2H_4 + s \leftrightarrow s\text{-}C_2H_4$	Ethylene chemisorption (path 3)[b]
10	$s\text{-}C_2H_4 + O\text{-}s \rightarrow s\text{-}C_2H_4\text{-}O + s$	Form ethylene oxide complex (path 3)[b]

[a] Path 1 is epoxidation.

[b] Paths 2 and 3 are total oxidation. After step 10, path 3 follows steps 5 and 6. Alternatively, after step 10, path 3 follows step 4, causing epoxidation.

Serafin (1998) studied surface science relating to the silver-catalyzed epoxidation of ethylene using Ag(111) and Ag(110) single crystals. The crystals provided evidence for the key role of atomic rather than molecular oxygen in both the epoxidation and combustion reactions. Additionally, scanning tunneling microscope (STM) and in situ Raman studies of oxygen, chlorine, and CO_2 adsorption on Ag surfaces showing dynamic silver restructuring and the identification of reactive surface species were highlighted as an area that could further clarify the understanding of the epoxidation reaction by providing key structural information.

2.1.2.3 Subsurface Oxygen in Silver

Most of the research works cited in this section reported another oxygen species encountered upon high-temperature treatment of silver in the presence of oxygen. This specie is referred to as subsurface oxygen. By its nature, a

detailed characterization by surface science techniques is difficult. An initial systematic single-crystal study of subsurface oxygen was performed by Rovida *et al.* (1972) for Ag(111). They found that the exposure of their crystal to oxygen at temperatures higher than 197 °C resulted in a second very wide, high-temperature desorption peak centered at 507 °C. Exposures above 252 °C resulted in the disappearance of the normal associative oxygen desorption peak, whereas the subsurface oxygen remained.

Backx *et al.* (1981) studied subsurface oxygen in Ag(110) with oxygen-isotope techniques. In line with the findings of Rovida *et al.* (1972) for Ag(111), they found that subsurface oxygen did not involve more dissolution of oxygen in the bulk, since this state could be saturated completely upon moderate exposure. It should be noted that Ag(111) is a close surface structure, while Ag(110) is an open surface structure. Therefore, more open surface structure is typically more active in bond breaking reaction (Campbell, 1985).

In 2002, Michael and Digan showed a possible role of surface carbon during ethylene epoxidation over silver catalysts. The ex situ temperature-programmed oxidation analysis results of the used catalyst samples revealed that carbon surface coverages exceeded one monolayer. Thermodynamic calculations revealed that a strong potential exists for methane and carbon formation from ethylene–oxygen mixtures. The results indicated that the surface carbon formation during ethylene epoxidation over Ag(111) is energetically viable through a mechanism involving hydride abstraction from surface C_2H_x species by adsorbed oxygen. In addition, simple energetic arguments indicate that perturbation of surface Ag–Ag bonds by surface carbon or C_2H_x species is possible. Therefore, it was proposed that some surface sites responsible for ethylene epoxidation over unsupported silver powder and Ag–Cs/α-Al$_2$O$_3$ might deactivate under some experimental conditions as a consequence of carbon deposition and/or mild surface reconstruction facilitated by surface and/or subsurface carbon species.

Quantum mechanical computer simulations were used as a tool to evaluate the catalyst selectivity in the reaction of oxametallacycle (OMC) to form ethylene epoxide (EO). In summary, for ethylene epoxidation to occur, the catalyst had to be sufficiently mild so as to form an OMC rather than to break the C-H bonds

in either ethylene or OMC. In particular, for OMC to transform to EO rather than to acetaldehyde (Ac); (1) its C-metal bond has to be sufficiently weak with respect to its O-metal bond, and (2) the adsorbed EO should be stabilized against the adsorbed Ac. Thus, catalyst selectivity is determined in part by a peculiar electronic effect, which is related to the differential bonding affinity of a catalyst toward the C and O atoms of the OMC. The interplay between O- and C-metal bond strengths is due to the different structures of the two transition states. More generally, they believed that the differential bonding affinity of catalyst toward the various atoms of the molecule to which it binds plays an important role in determining selectivity (Anton *et al.*, 2008).

2.1.3 Catalyst Properties

To assess the catalytic process performance, important characteristics are the space time yield based on the weight of epoxide formed per kilogram of catalyst, and the turnover frequency (TOF) as a measure of the intrinsic activity per active surface metal atom.

2.1.3.1 Particle Size

The silver particle size of silver catalysts is an important parameter, affecting the epoxidation reaction performance. It varies within several dozens Å, depending on preparation method and Ag loading. On the Ag surface, the structure, electron, and other properties of silver (atom environment, electron work function, electric conductance, etc.) can differ considerably from those in the bulk phase. Hence, Ag particles (in particular, the small ones) should be taken into account when considering the size effect because of a weak metal-support interaction.

Goncharova *et al.* (1995) developed a new preparation method for supported silver catalysts with a narrow particle size distribution. They found that the epoxidation pathway did not involve stable intermediates, except for-complexes with Ag^+. Thus, ethylene oxide seemed to form rather quickly, probably via a direct attack of electrophilic oxygen to the activated ethylene molecule. Then, the low activity of small particles resulted from a small concentration of Ag^+ sites or ethylene-complexes. With increasing Ag particle size, the contribution of the regular surface and thus the concentration of π-complexes increased, resulting in the rise of the reac-

tion rate. For particles 300-500 Å in size, the reaction rate was found to increase sharply. The concentration of ethylene π-complexes with Ag^+ cations increased proportionally to the reaction rate. These π-complexes were assumed to be the only intermediates directing the reaction towards epoxidation. The ratio of the reaction rate to the concentration of π-complexes was found to remain constant within a wide range of Ag crystal sizes, including bulk silver samples. The influence of the support (α-Al_2O_3 or SiO_2) on the size effect could relate to the secondary processes of ethylene oxide conversion. Hence, they concluded that the size effect resulted from the change in the ratio of regular and defect regions on silver surfaces. Additionally, the structural changes of the subsurface layers of the silver affected the behavior of its electron properties.

Lu *et al.* (2005) compared the effect of particle size on the epoxidation reactions of ethylene and propylene via O_2 chemisorption. At high loadings of silver, Ag crystals tended to agglomerate. Large particles favored ethylene epoxidation by 3-5 folds at 200-220 °C, whereas Ag particle size did not have a large effect on propylene epoxidation. Moreover, the bulk of the particles consisted of silver in a metallic state, revealed by the X-Ray diffraction measurements, but the results of in situ ultraviolet-visible (UV-vis) spectroscopy showed that in addition to a metallic component, small particles had silver in Ag^+ state. The small particles were probably covered by a layer of Ag_2O, which resulted in lower selectivity for epoxidation for both propylene and ethylene oxidation in the small size regime. Furthermore, transient results indicated that propylene oxidation reached steady state quickly (3–5 h), and parallel UV–vis spectra showed substantial reduction of the oxidic component. In the case of ethylene oxidation, steady state was attained slowly (24–36 h), and UV–vis spectra indicated the retention of the oxidic component (Ag_2O phase), with other spectral changes consistent with the possible presence of adsorbed or subsurface oxygen.

However, sintering processes can lead to changes of the particle size distribution, and thus affect the dependence of the reaction rate on the size of Ag particles. To retard these processes, the support surface or the distance between the silver particles should be increased considerably. This obstacle is most likely the

reason for a high resistance of small silver particles to sintering on Ag/SiO_2 catalyst ($S_{SiO2} \approx 200$ m^2/g) (Seyedmonir *et al.*, 1990).

2.1.3.2 Structure

Xiaofeng and Goodman (2000) used scanning tunneling microscopy (STM) to monitor the morphological changes of oxide-supported metal clusters upon exposure to reactants at elevated pressures. The morphology of the metal clustering induced by O_2 exposure implied the chemisorption of O_2 onto the metal clusters and the TiO_2 substrate at room temperature. Ag and Au clusters exhibited a bimodal size distribution following O_2 exposure due to Ostwald ripening, where certain clusters grew at the expense of other clusters. Volatile oxide species were formed at elevated oxygen pressures and accelerated the intercluster atom transport. The substrate was also found to play an important role in this ripening process in that a surface with enhanced defects or oxygen vacancies facilitated the ripening process.

2.1.3.3 Acidity

The activity of the supports in EO isomerization/oxidation was found to be proportional to their surface acidity. It is generally believed that the selectivity towards EO or CO_2 is strongly affected by the acidic properties of the support. The EO precursors (intermediate species) initially formed on silver sites isomerize to acetaldehyde on Lewis or Brönsted type acid sites of the support. Acetaldehyde is finally oxidized on silver sites, producing CO_2.

Yong *et al.* (1991) showed that SiO_2 and α-Al_2O_3 were almost inactive in the conversion of EO to acetaldehyde in contrast to TiO_2 and γ-Al_2O_3, which were both very active in the above reaction due to the presence of weak Brönsted acid sites (surface hydroxyl groups). Dioxane and C_4 oxygenates were also formed with the latter two supports. Bulushev *et al.* (1995) proposed that in addition to Brönsted acid sites, the Lewis acid sites on supports, such as alumina, also catalyze the isomerization of EO to acetaldehyde. Besides the formation of acetaldehyde via the isomerization of EO, glycol-like intermediate species ($-OCH_2CH_2OH$) were

also formed on surface basic hydroxyl groups of alumina and titania supports. These glycol species can further be oxidized on the silver sites.

2.2 Support Materials

2.2.1 Alumina

Ayame *et al.* (2003) investigated the performance of Ag/α-alumina catalyst using 2-18 μm α-alumina crystal particles. The studied support had high purity, homogeneous pore structure, specific mean pore diameter in the range of 0.3-2.3 μm, and almost no acidic or basic properties because of calcination above 1400 °C in atmosphere. The pores comprised cavities surrounded by crystal planes of the primary α-alumina particles. The Cs and Re-copromoted Ag catalysts supported on the α-alumina crystal carriers, in the epoxidation of ethylene without organic halides, showed good performances, i.e. high and very stable ethylene conversion and ethylene oxide selectivity. The best mean pore diameter of the α-alumina crystal carriers required for the epoxidation existed in the range of 0.5–1.2 μm

Rojluechai *et al.* (2007) revealed that the support played an important role in ethylene epoxidation reaction. Au, Ag, and Au–Ag catalysts on different supports of alumina, titania, and ceria were studied for their catalytic activity of ethylene oxidation reaction. The epoxidation of ethylene was found to occur over the Ag catalysts on Al_2O_3, while Ag catalysts on both TiO_2 and CeO_2 gave only total oxidation reaction. For the Au catalysts on Al_2O_3, no activity was found toward the ethylene epoxidation reaction. The addition of an appropriate quantity of Au on 13.18 wt.% Ag/Al_2O_3 catalyst was found to enhance both the ethylene conversion and the selectivity for ethylene oxide. Among the three supports, the bimetallic Au-Ag/Al_2O_3 catalyst was the best candidate for the ethylene epoxidation. On the other hand, the Au/TiO_2 catalysts provided the highest selectivity of ethylene oxide with relatively low ethylene conversion, whereas the Au/CeO_2 catalysts were shown to favor the total oxidation reaction at very low temperatures. The results also showed that the catalytic activity of Au catalysts depended on not only the size of the Au particle and support material, but also the catalyst preparation method which governed the Au particle size and the interaction between the Au particles and the support.

2.2.2 <u>Silica</u>

In contrast to alumina, silver catalysts supported on relatively high surface area silica (specific surface area up to ca. 350 m^2/g) were shown to be active in EO production, reaching in some cases EO selectivity similar to those obtained with low surface area alumina (Harriott, 1971). The results indicated that the surface area of the support is not as crucial as other parameters, such as the acidic properties, in determining the activity and selectivity in ethylene epoxidation.

Previously, microporous zeolitic aluminosilicates were used. However, their catalytic activity was strongly affected by mass diffusion limitations as well as by their acidic properties. As result of that, the mesoporous silicates (such as HMS, SBA-15, and MCF) were developed (Beck *et al.*, 1992). These supports exhibited very high surface area (~700–1300 m^2/g) with tunable pore size in the range of 2–20 nm (pore diameter) and different pore structures, i.e. hexagonal (MCM-41, SBA-15), wormhole-like (HMS), and foam-like (MCF). The very high surface area and the narrow pore size distributions of the mesoporous silicates allow homogeneous dispersion of metal active sites even at high metal loadings. They possess surface hydroxyls (terminal), which are not acidic (compared to relatively strong zeolitic acidity or the acidity found in γ-Al_2O_3), and they do not induce negative effects on catalytic reaction rates due to diffusion limitations.

Recently, Fotopoulos and Triantafyllidis (2007) compared the activity of Ag catalysts supported on non-porous SiO_2, microporous silicalite zeolite, and mesoporous MCM-41 and HMS silicates to conventional low surface area α-Al_2O_3. Ag catalysts supported on MCM-41 and HMS mesoporous silicates were active in ethylene epoxidation reaction, exhibiting ethylene oxide (EO) selectivity similar or slightly lower to that of the non-porous SiO_2 and the conventional low surface area α-Al_2O_3 based catalysts at relatively low temperature (up to ~230 °C). While above 300 °C, their activity and selectivity decreased significantly. Although the catalysts based on microporous silicalite zeolite were very active in ethylene conversion, they exhibited relatively low EO selectivity. Among the two types of mesoporous silicates, the HMS with wormhole-like structure was a more appropriate support for preparing catalysts with moderate Ag loadings (up to ca. 20 wt.%). The main benefit of using HMS and MCM-41 mesoporous materials was their ability to support very

high loadings of Ag (ca. 40 wt.%) without increasing the size of Ag crystallites more than ca. 20 nm, resulting in very active epoxidation catalysts. As a consequence, the highly loaded mesoporous-based catalysts showed very high ethylene conversion activity (up to 65 %) at relatively low temperatures (~220 °C), with acceptable ethylene oxide selectivity (~30–35 %).

2.2.3 Titania

When support is a reducible oxide, the strong metal-support interaction (SMSI) is of a great interest. SMSI indicates the ability of the oxygen migration of reduced support particles onto the surface of metallic particles. Moreover, the formation of a suboxide of the support can be initiated by the reduction being facilitated by the metallic particles. For instance, group VIII noble metals supported on TiO_2 exhibits a strong metal-support interaction effect. Furthermore, TiO_2 plays a special role compared to other typical catalyst supports. It can stabilize high dispersion of Au up to 700 °C. Shastri *et al.* (1984) found that no phase transformation of anatase to rutile occurred at 700 °C on TiO_2 impregnated with Au compared with the complete phase transformation in the blank TiO_2.

A lot of works employed various catalyst loading methods, i.e. impregnation, precipitation-deposition, photochemical deposition, sol-gel, etc., on TiO_2, which provided different advantages for certain reactions. Bollinger and Vannice (1996) found that titania-supported gold catalysts were extremely active for room temperature CO oxidation. Impregnated Au/TiO_2 was the most active after a sequential pretreatment consisting of high temperature reduction at 500 °C, calcination at 400 °C, and low temperature reduction at 200 °C. It should be noted that a catalyst prepared by coprecipitation had much smaller Au particles than impregnated Au/TiO_2 and was active at 0 °C.

On the other hand, Ag/TiO_2 is not an effective catalyst for ethylene epoxidation. Seyedmonir (1990) found that ethylene oxide selectivity over Ag/TiO_2 was low about 10 % as compared to 60 % over the $Ag/\alpha-Al_2O_3$ 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. Yong *et al.* (1991) studied the relationship between selectivity and acidic prop-

erties of TiO$_2$. They explained that TiO$_2$ was very active in the conversion of EO to acetaldehyde due to the presence of weak Brönsted acid sites (surface hydroxyl groups). Dioxane and C$_4$ oxygenates were also formed with TiO$_2$ support. Besides the formation of acetaldehyde via isomerization of EO, glycol-like intermediate species ($-OCH_2CH_2OH$) were also formed on the surface basic hydroxyl groups of titania support. These glycol species can be further oxidized on silver sites.

2.3 Mesoporous Catalysts

In the past decade, mesoporous materials have been of great interest as catalysts because of their unique textural and structural characteristics.

2.3.1 Mesoporous TiO$_2$

Several key techniques have been adopted to synthesize mesoporous TiO$_2$, such as sol–gel process, hydrothermal process, and ultrasonic irradiation process. Furthermore, the use of templating materials as pore-forming agents has been demonstrated for synthesis of highly active mesoporous TiO$_2$ photocatalysts (Stone and Davis, 1998; Dai et. al., 2002).

In 2005, Sreethawong et al. synthesized nanocrystalline mesoporous TiO$_2$ via a combined sol–gel process with surfactant-assisted templating method. In this synthetic method, surfactant molecules were applied to function as both mesopore-forming and gelation-assisting agents. Beyond a calcination temperature of 600 °C, the partial phase transformation from anatase to rutile of the TiO$_2$ was observed. The calcination conditions and crystalline phases existing in the products had a significant effect on the photocatalytic hydrogen evolution activity. Indeed, the activity of the synthesized titania treated under appropriate calcination conditions was dramatically higher than that of commercial titania powders, i.e. Ishihara ST-01 and Degussa P-25. Thus, the introduction of mesopore into titania photocatalyst substantially improved the photocatalytic performance.

In the same year, Sreethawong and Yoshikawa (2005) investigated the photocatalytic hydrogen evolution over Cu-, Pd-, and Au-loaded mesoporous TiO$_2$ photocatalysts. The photocatalytic activity tests revealed that the optimum contents

for Cu, Pd, and Au loadings were 1.5, 1, and 2 wt.%, respectively. At the optimum values, the H_2 evolution results showed that the photocatalytic capability of the cocatalysts was in the order of Au > Pd > Cu. Therefore, the 2 wt.% Au-loaded mesoporous TiO_2 could be stated to be very active as H_2 evolution photocatalyst.

Sreethawong and Yoshikawa (2006) compared single-step sol–gel (SSSG) method with the conventional loading methods, namely incipient wetness impregnation (IWI) and photochemical deposition (PCD). In the single-step sol–gel (SSSG) method, Pt precursor was introduced into the completely hydrolyzed TiO_2 sol prepared with a mesopore-directing surfactant template. The mesoporous Pt/TiO_2 photocatalyst prepared by the SSSG method showed higher photocatalytic activity for H_2 evolution over entire range of Pt loading content (optimum loading of 0.6 wt.%), as well as broader photocatalytic activity window with respect to the amount of loaded Pt than those prepared by the other two methods and Pt/Degussa P-25 TiO_2. As a consequence, the SSSG method has been postulated as a beneficial alternative for synthesis of effective metal-loaded mesoporous photocatalyst.

2.3.2 Mesoporous SrTiO$_3$

The mesoporous-assembled $SrTiO_3$ nanocrystal photocatalyst was successfully synthesized via sol-gel method with the aid of structure-directing surfactant. The synthesizing step used strontium nitrate ($Sr(NO_3)_2$) and tetraisopropyl orthotitanate (TIPT) as precursors. Anhydrous ethanol (EtOH), ethylene glycol (EG), or EtOH/EG was selected as a solvent, while laurylamine hydrochloride (LAHC), cetyltrimethylammonium bromide (CTAB), or cetyltrimethylammonium chloride (CTAC) was used as a structure-directing surfactant. The mesoporous-assembled structure with a high pore uniformity of $SrTiO_3$ played the most important role affecting the photocatalytic activity of the $SrTiO_3$ photocatalyst. The optimal conditions for photocatalytic methyl orange degradation activity for $SrTiO_3$ with the mesoporous-assembled structure and narrow pore size distribution were a calcination temperature of 700 °C, a heating rate of 1 °C min^{-1}, a LAHC-to-TIPT molar ratio of 0.25:1, and using an EtOH solvent, which had much higher activity than that of the non-mesoporous-structured commercial $SrTiO_3$. It was concluded that the important

parameters for photodegradation of methyl orange by $SrTiO_3$ were the crystallinity, specific surface area, and pore characteristic (Puangpetch *et al.*, 2008).

From the previous work on the $SrTiO_3$ photocatalyst, Puangpetch *et al.* (2009) further studied the effect of hole scavengers: methanol, ethanol, 2-propanol, D-glucose, and Na_2SO_3 on the photocatalytic H_2 production activity of mesoporous $SrTiO_3$. It was found that MeOH exhibited the highest photocatalytic H_2 production enhancement ability, as compared to the other studied hole scavengers. MeOH behaved as both a hole scavenger to enhance H_2 production and a reactant for providing the H^+ species to form H_2. Indeed, Pt co-catalyst loading was found to enhance the photocatalytic H_2 production activity of the pristine mesoporous-assembled $SrTiO_3$. Pt co-catalyst loading decreased the band gap energy of the $SrTiO_3$ photocatalysts, resulting in an increase in the visible light harvesting ability and leading to photocatalytic activity enhancement.

2.4 Bimetallic Catalysts

Silver is known to exhibit unique catalytic properties for ethylene epoxidation. However, the main drawback to use silver catalysts is that the selectivity drops significantly after use, and there are no generally applicable methods of regeneration, although its initial selectivity is as high as 79-83 %. Silver catalysts may age due to abrasion, deposition of carbon-containing compounds, and recrystallization of the silver. The life span of the catalyst is 2-5 years, and due to this limitation, new catalysts are being investigated.

Jankowiak and Barteau (2005) investigated the performance of monolith-supported Ag and Cu–Ag bimetallic catalysts. Cu–Ag bimetallic catalysts prepared by sequential impregnation offered improved selectivities compared with silver alone in the direct epoxidation of ethylene over a wide range of feed compositions at similar ethylene conversions. Activation energy measurements showed a 1–2 kcal/mol decrease in ethylene consumption for the Cu–Ag bimetallic catalysts relative to pure silver catalysts.

Rojluechai *et al.* (2007) studied the effect of gold addition to silver catalyst supported on high surface area alumina on the ethylene epoxidation activity. They

found that an addition of Au with small amount created Au-Ag bimetallic, which favored the ethylene epoxidation reaction. Gold acts as a diluting agent on the silver surface, resulting in destroying multiple Ag sites which favored atomic oxygen adsorption, and creates new single silver sites which favored molecular oxygen to atomic oxygen adsorption, leading to an enhancement of the epoxidation reaction. Indeed, this bimetallic catalyst has a lower electron density at the surface, resulting in increasing its capacity for the chemisorption of electron acceptor species. On the contrary, an addition of Au at very high loadings was found to form Au-Ag alloy, resulting in the reduction of the ethylene epoxidation activity since Au-Ag alloy favored a complete oxidation reaction. They also found that the optimum Ag to Au ratio was 13.18 wt.% to 0.63 wt.% in the optimum temperature range of 237-247 °C for the ethylene epoxidation reaction.

2.5 Effect of Promoters

Epoxidation catalysts are usually operated with alkali metal promoters, which are electron-donating species, usually cesium and chlorine-containing inhibitors. Electron donors, such as cesium, are thought to increase oxygen electron density, thereby favoring combustion. But, it was found that cesium promoters did not affect the electronic properties of the oxygen, but they instead affected the electronic properties of the ethylene (Tan, 1986). Cesium prevents both ethylene and ethylene oxide from isomerizing to an isomer that is more active to combustion. Thus, their presence increases the selectivity of the epoxidation. Alkali metal promoters are dissolved in the catalyst by adding an alkali metal salt to the catalyst mixture during preparation. Chlorine inhibitors can also be adsorbed onto the catalyst in the reactor by adding a small amount of a chlorine-containing gas, such as dichloroethane, to the reactor. The amount of chlorine added must be tightly controlled, since high coverage of chlorine can deactivate the catalyst.

The positive effect of Cs increases with decreasing Ag particle size (increase in defects). At the same time, the deep oxidation rate decreases monotonously and independently of the Ag particle size. Pinaeva *et al.* (1990) explained such action of Cs in the following way. On one hand, 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 (Bukhtiyarov, 1994). Since the epoxidation rate does not decrease and even increases, it can be supposed that the number of interface regular/defect surface regions required for ethylene epoxidation remains the same or increases slightly. Thus, Cs can provide a significant change in the surface structure, especially when decreasing Ag_2O islands and at the expense of increasing (stabilization) defect regions. The excess Cs can block the active surface and thus decreases reaction rates in both directions.

Podgornov *et al.* (2000) compared various Cs oxides formed on the $Ag(111)$ and $Ag(110)$ single crystals at various cesium coverages and oxygen pressures. The TPD spectra of O_2 showed the existence of few Cs oxides with various stoichiometries: from suboxide, Cs_{2+x}, to superoxide, Cs_2O_4. Their roles in silver-catalyzed ethylene epoxidation are different: peroxide seems to suppress the total oxidation, while the suboxide promotes ethylene epoxidation. The mechanisms described above are summarized in Figure 2.4.
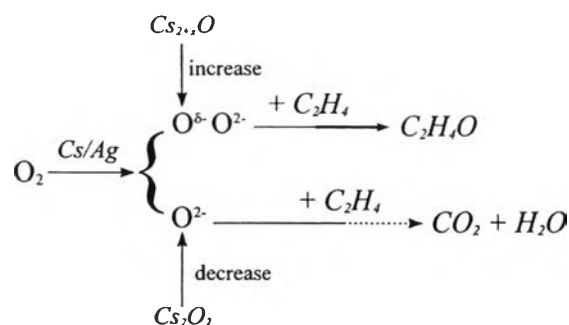

Figure 2.4 The scheme illustrating the proposed mechanisms of influence of Cs suboxide and Cs peroxide upon silver-catalyzed ethylene epoxidation (Podgornov *et al.*, 2000).

Yeung *et al.* (1998) identified the effect of 1,2-dichloroethane (DCE) addition on ethylene epoxidation activity of a Ag/α-Al_2O_3 catalyst. DCE adsorbs on the surface of silver and decomposes to adsorbed chlorine and ethylene (Stepanov *et al.*, 1960). Through either electronic or ensemble effects, chlorine affects the oxidation

of ethylene over silver catalyst. Ethylene oxide selectivity for the uniform catalyst increases with DCE addition at low concentrations, reaching a maximum between 1 and 1.5 ppm. Along with the monotonic decrease in conversion, this indicates that addition of DCE promotes catalyst selectivity, but inhibits the overall reaction. With increasing DCE at high concentrations, the catalyst activity rapidly decreases with negligible selectivity enhancement because the primary effect of DCE addition on the surface Dirac-type catalyst is indiscriminate poisoning of both combustion and epoxidation sites.

Rhenium remains the least understood promoter of silver catalysts for the epoxidation of ethylene. Recently, Dellamorte *et al.* (2007) studied rhenium-promoted Ag and Cu–Ag bimetallic catalysts prepared by a sequential impregnation method instead of co-impregnation technique under chlorine-free operating conditions. They observed that rhenium addition improved the selectivity of both the monometallic and bimetallic catalysts, while decreasing activity in each case. Furthermore, Re only promoted EO selectivity at very small loadings, where a large decrease in catalyst activity was observed as loading increased above 50 ppm. Optimization of preparation procedures showed that maximum ethylene oxide selectivities were obtained with a rhenium loading of 25 ppm for the monometallic catalysts and between 50 and 100 ppm for Cu–Ag bimetallic catalysts. The reaction kinetics for rhenium-promoted Ag and unpromoted Ag catalysts suggested that the catalysts containing rhenium presented a more uniform distribution of sites for oxygen adsorption than unpromoted catalysts, thus enhancing the ethylene oxide selectivity. Moreover, the selectivity trends were attributed to step and defect site blocking, shifting oxygen adsorption and reaction to more uniform Ag terraces, which was suggested to be more selective toward EO. In addition, the addition of Cs and Cu to the Re–Ag system showed that the catalyst activity and selectivity could be modified by the action of co-promoters with Re.

On the other hand, Torres *et al.* (2008) claimed that chlorine was the best halogen used as promoters. Due to the presence of the additional subsurface Cl that favors EO formation with respect to acetaldehyde (AC), facilitates EO desorption, and also hampers further transformations (unfavorable secondary chemistry), the unwanted further conversion of EO was minimized. Ultimately, they concluded that

the presence of co-adsorbed halogens significantly decreased the energy barrier from the oxametallacycle intermediate (OMME) to EO relative to that from the same OMME intermediate to the undesired AC product. However, co-adsorbed halogens were also found to increase the desorption energy of the reaction products.