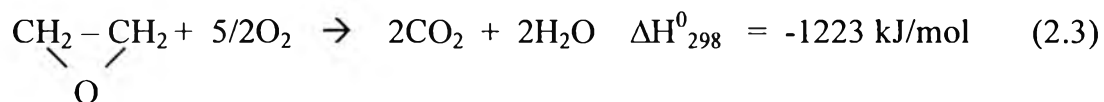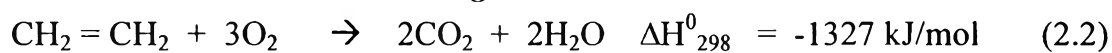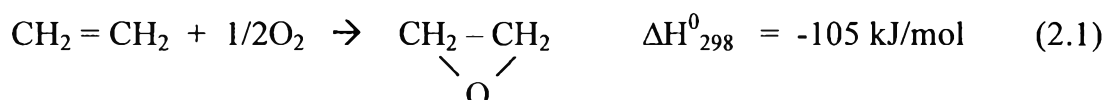# CHAPTER II

LITERATURE SURVEY

2.1 Silver Catalyst and Ethylene Oxidation Reaction

The experimental catalytic activity of silver for a number of partial oxidation reactions, particularly ethylene oxidation reaction has been known for nearly a century. The following reactions are involved in the ethylene oxidation.

$$CH_2 = CH_2 + 1/2O_2 \rightarrow CH_2 - CH_2 \quad \Delta H^0_{298} = -105 \text{ kJ/mol} \quad (2.1)$$
$$\diagdown O \diagup$$

$$CH_2 = CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^0_{298} = -1327 \text{ kJ/mol} \quad (2.2)$$

$$CH_2 - CH_2 + 5/2O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^0_{298} = -1223 \text{ kJ/mol} \quad (2.3)$$
$$\diagdown O \diagup$$

All these reactions and especially the latter two, which are complete combustion of ethylene and of its oxide, are highly exothermic and complete in operating conditions of EO synthesis. Much of the effort in catalyst and process development has been directed toward minimizing the side-reactions (Chauvel and Lefebvre, 1989).

Silver catalysts employed in the manufacture of ethylene oxide have undergone significant changes since their initial period of development. As reported by many researchers, silver powder exhibited a low epoxidation rate where as silver (Ag) deposited on support materials were more effective for this reaction. This fact suggested that the Ag-support interaction or the manner in which distribution of Ag over the support played an important role in this catalytic reaction (Minahan and Hoflund, 1997).

Moreover, the effect of silver particle size on the reaction rate is a well-known property of supported silver catalysts. Large Ag particles are more

effective in catalyzing the ethylene epoxidation reaction than small Ag crystallites (Goncharova *et al.*, 1995). Numerous researchers observed a catalytic size effect of Ag within the $100\text{-}1,000^0A$ range and explained it by the changes in the surface structure, particle morphology, support effect and others. This crystallite size effect can cause changes in catalytic activity. The small particles ($<100^0A$) are known to exhibit no catalytic activity due to the over-oxidation of small Ag particles to inactive Ag_2O (Goncharova *et al.*, 1995).

In addition, the influence of metal crystallite size is also dependent on the support employed. To ascertain this fact, they investigated the effect of support and they found that the low or zero apparent selectivity of silver supported on various supports was primarily due to isomerization and oxidation of ethylene oxide on sites supplied by the support material. All conventional and non-conventional supports examined exhibited activity towards ethylene oxide isomerization and combustion with exception of α-alumina.

One of the most important roles of silver catalyst towards ethylene oxidation reaction is its mechanism of oxygen adsorption. The adsorption of oxygen on Ag has been investigated employing a large variety of experimental techniques such as calorimetric studies, infrared spectroscopy, isotopic exchange, electron diffraction, and kinetic studies of adsorption rates on single crystal, on silver film and foils, and on crystallites dispersed on metal oxide carriers (Kondarides and Verykios, 1993).
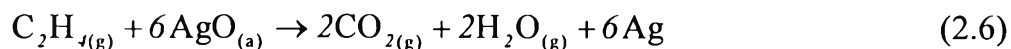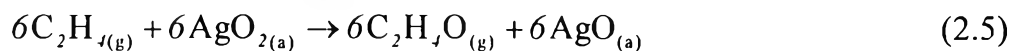
A number of theories abound about the mechanism of the reaction of ethylene with oxygen. It is sufficient to say that none is universally accepted. What appears to be accepted is that oxygen in some fashion combines with solid silver and through that combination, oxygen is caused to react with ethylene to form ethylene oxide. Accompanying that reaction is the combustion of ethylene and/or ethylene oxide to carbon dioxide and water.

Some have theorized that at least a portion of carbon dioxide is generated by the isomerization of ethylene oxide to acetaldehyde, which immediately goes to combustion products (Bhasin, 1990).
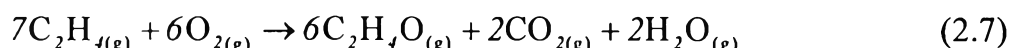
In particular, ethylene oxide formation was shown to require adsorbed oxygen in two states: 'ionic' (nucleophilic) oxygen similar to that in Ag_2O and 'covalent' (electrophilic) oxygen localized at the surface defects. The former (or Ag^+ cations involved) serves for the ethylene adsorption, while the 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).

However, there is a no general agreement either about the reaction mechanism on the surface of the silver catalyst, or about the reaction kinetics. Three different oxygen species (molecular, atomic and subsurface) can be found on the catalyst surface, and although molecular oxygen is usually considered to be responsible for epoxidation and atomic oxygen for combustion (Kondarides and Verykios, 1994). The Ag (100) and Ag (111) planes have been the subject of the majority of the role of various oxygen species on the overall mechanism, particularly whether atomic or molecular oxygen reacts to form ethylene oxide.

Nakutsuji et al. (1997) studied the mechanism of ethylene epoxidation over silver catalyst by using dipped adcluster model (DAM). They found that the active species for epoxidation is the superoxide O_2^- that is molecularly adsorbed in a bent end-on geometry on the silver surface and that atomically adsorbed oxygen contributes less selectivity to both partial and complete oxidation. If only molecularly adsorbed oxygen is involved in the partial oxidation and the atomically adsorbed oxygen species gives carbon dioxide and water by complete oxidation, the overall reaction on the silver surface can be written as,

$$6Ag + 6O_{2(g)} \rightarrow 6AgO_{2(a)} \qquad (2.4)$$

$$6C_2H_{4(g)} + 6AgO_{2(a)} \rightarrow 6C_2H_4O_{(g)} + 6AgO_{(a)} \qquad (2.5)$$

$$C_2H_{4(g)} + 6AgO_{(a)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)} + 6Ag \qquad (2.6)$$

the overall reaction is:

$$7C_2H_{4(g)} + 6O_{2(g)} \rightarrow 6C_2H_4O_{(g)} + 2CO_{2(g)} + 2H_2O_{(g)} \qquad (2.7)$$

This overall reaction shows that ethylene oxide is formed from ethylene at a maximum selectivity of 6/7 (85%). However, some recent experiments have exceeded this limit, and have achieved selectivity as high as 85-87%. Nakatsuji et $al.$ (1997) proved that the selectivity of superoxide is very high (99%) and the atomically adsorbed oxygen also contributes to this selectivity, even though its contribution is low.

The most significant contribution to improving selectivity or efficiency and activity is the addition of gas phase organic chloride compound such as ethylene chloride, and vinyl chloride. Another class of additives is these incorporated into the silver catalyst and is not part of the gas phase feed. There are many metals that beneficially effect the performance of the catalyst when it added into the catalyst. They act as promoters and others attribute the benefit to an inhibiting or suppressing action.

The influence of alkali species, and in particular the interaction between alkali and other promoter species added to individual catalysts to enhance performance has been extensively studied. Goncharova et $al.$ (1995) studied effect of promoters to selectivity of EO with respect to the silver crystallite size. They found that silver particles deposited on α-Al_2O_3 are not stable at elevated temperature due to the absence of metal-support interaction and Ag particles are highly mobile. As regards the interaction of alkali metals with support can change significantly the acid-base properties of supports due to exchange of protons by the ions of the alkali elements, the α-Al_2O_3 surface was modified by adding alkali metal to decrease the particle mobility.

Recent studies (Hoflund and Minahan, 1996, 1997) contrasted the interaction of cesium and silver with alumina. The cesium promoter was observed between the silver film and the alumina support and acted as a binder between two and probably affects the electronic structure of the silver and alumina interface.

Moreover, Jun *et al.* (1992) proposed that the increase in selectivity and activity by using a suitable quantity of rhenium be due to decrease of electron density of adsorbed oxygen. In this case, rhenium competed with adsorbed oxygen for the silver lattic electrons.

Apart from the above promoting effect, it is well known that a higher oxygen concentration also promotes the selectivity of the reaction towards EO, but the risk of explosion also grows with the oxygen concentration. Pena *et al.* (1998) studied the performance of the both packed-bed membrane reactor and fixed-bed reactor at different reaction temperatures and different feed reactant concentrations. They also found that the ethylene oxide production was favored by high oxygen/ethylene molar ratio.

Likewise, the silver catalyst is quite a good catalyst for the oxidation of both carbon monoxide and hydrogen. However, the steam cracking of ethane as the source of ethylene for the petrochemical industry, there are two related factors create. One is that currently known catalysts work effectively only under methane rich conditions and second is the fraction of ethylene in the product stream is small. It would be preferable to use couple partial oxidation of methane. But this process also has difficulty that is the partial oxidation of methane gives rise to significant amounts of by-products particularly carbon monoxide, carbon dioxide, hydrogen and water.

As regards from the enormous literature about ethylene oxidation, this process can be operated advantageously with some methane, ethane or carbon dioxide in the feed (Bhasin, 1990, and Yeung *et al.*, 1998). These gases are

generally considered as an inhibitor, and the effect of these inhibitors on the process efficiency may be variable with its concentration.

Yong and Cant (1990) studied the effect of carbon monoxide and hydrogen on the ethylene oxidation reaction under synthesis conditions by using silver catalyst. They concluded that the ethylene oxidation was only slightly affected if added carbon monoxide or hydrogen was rapidly consumed. If conditions were such that this process is spread throughout the bed then the rate of ethylene oxidation was reduced.

2.2 Support Material

Furthermore, as known previously that the ethylene epoxidation reaction is also very sensitive to the support, a little attention being paid to support properties, such as surface area, pore volume and chemical inertness. It is also known widely that the supports of the silver catalyst to be used for the production of ethylene oxide are porous particulate refractories and with large variations.

The selection of a support has a specific set of properties. Among other properties, the specific surface area deserves particular attention because it also relates to pore diameter and affects the performance of a produced catalyst. From the standpoint of activity and durability, the catalyst is preferable to have a large specific surface area, for this reason, the support is preferable to have a large specific surface area. For the support to have a large specific surface area, the alumina particles to be selected, as the material for the support, are required to have a small diameter.

Besides, the degree of dispersion can be very low with low surface area (LSA) support. In a different way a higher degree of dispersion could be achieved, with same active area by using significantly smaller amount of silver. As a consequence of this, the precious metal could be utilized more

efficiently and the process would become more economical. A high degree of metal dispersion can usually be achieved by employing high surface area (HSA) supports.

Even though there are advantages of using (HSA) support; these advantages can diversely effect to selectivity in the ethylene epoxidation reaction due the isomerization of ethylene oxide to acetaldehyde on alumina and subsequent oxidation on silver. To prove this fact, Yong *et al.* (1991) investigated the product distribution of the reactions of ethylene oxide over non-selective supports in the presence and absence of oxygen.

However, most (HSA) supports gave very low selecivities, the significant selectivity was achieved only when the area was reduced below 20 m^2/g by sintering. Mao and Vannice (1995) examined whether the (HSA) α-alumina can contribute high selectivity for ethylene oxide production. From their result, all silver supported on (HSA) α-alumina catalysts showed no selectivity to ethylene oxide due to the high activity of catalyst for ethylene oxide isomerization to acetaldehyde, which is then quickly oxidized to carbon dioxide. As the light of all these facts, most supports employed on a commercial scale have specific surface areas not exceeding 1 m^2/g.

2.3 Sol-Gel Technology

Sol-gel processing received extensive attention in the last two decades. The sol-gel method enables the researchers to explore the use of supports other than silica and alumina and to prepare mixed oxide supports by well-defined synthesis routes.

In recent years, a great deal of emphasis has been placed on the synthesis of ceramic monolithic materials and catalytic membranes used as support materials for automotive catalytic converters and other catalytic applications. Whereas two steps are needed to prepare ceramic monolithic
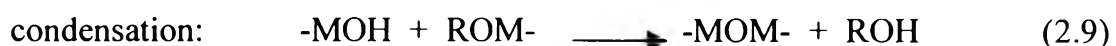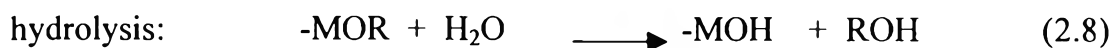
materials, using sol-gel-processing technology can be accomplished in a single step. The properties of the supported metal catalysts are comparable and in some cases superior to catalysts prepared using conventional methods of preparation (Gonzalez *et al.*, 1997).

Results to date in reactions such as hydrogenation, isomerization, oxidation, and catalytic reforming have been encouraging regarding the sol-gel processing in the synthesis of catalytic materials. Catalytic reactions take place on the surface of metal particles in a supported metal catalyst. Not only the activities but also the product selectivity may be improved on size of metal particles. The sol-gel method is one of the promising techniques to control metal particle sizes in the supported metal catalysts (Gonzalez *et al.*, 1997).

In order to stabilize supported metal catalyst in the high temperature range, the size of the metal particle is matched to the size of the pore. The sol-gel method can produce supported metal catalyst with high thermal stability. Furthermore, other advantages of sol-gel method are higher BET surface area, well-defined pore sizes distributions, and the ease with the addition of additional elements.

2.3.1 The Preparation of Supported Metal Sol-Gel Catalyst

Sol-gel chemistry can be described in terms of two classes of reaction (Ward and Ko, 1995):

hydrolysis: $\quad$ -MOR + H$_2$O $\longrightarrow$ -MOH + ROH $\qquad$ (2.8)

condensation: $\quad$ -MOH + ROM- $\longrightarrow$ -MOM- + ROH $\qquad$ (2.9)

$\qquad$ or $\qquad$ -MOH + HOM- $\longrightarrow$ -MOM- + H$_2$O

where

$\qquad$ M = metal corresponding to the alkoxide

$\qquad$ R = alkyl group (CH$_3$, C$_2$H$_5$, C$_3$H$_7$, etc.)

In which, the initial stage is pregelation, where metalorganic precursors are mixed with metal precursors to form a homogeneous solution. The metalorganic precursor is hydrolyzed through the addition of water while carefully controlling the pH and the reaction temperature. After that, the condensation or polymerization can be achieved when alkoxide groups (MOR) react with hydroxyl groups (MOH) formed during the hydrolysis to form metaloxanes (M-O-M).

The second stage is the postgelation step, where changes are occurred during the drying and calcination of the gel. These changes are desorption of water, the evaporation of the solvent, the desorption of organic residues, dehydroxylation reactions and structural changes.

In fact, there are many variables, which influence the sol-gel product such as the type of precursor, type of solvent, water content, acid or base content, precursor concentration, and temperature. These parameters affect the structure of the initial gel and, in turn, the properties of the material at all subsequent processing steps.

2.4 Incipient Wetness Impregnation Technique

Impregnation of the support is the preferred technique for silver deposition because it utilizes silver more efficiently than coating procedures, the latter being generally unable to effect substantial silver deposition onto the interior surfaces of the support. In addition, coated catalysts are more susceptible to silver loss by mechanical abrasion. Silver deposition is generally accomplished by heating the support at elevated temperatures to evaporate the liquid within the support and effect deposition of the silver onto the interior and exterior carrier surfaces. If the drying step is performed slowly, the salt will migrate towards the external surface of the support

particle. If it is desired to have a uniform distribution of metal throughout the support, it is better to dry quickly.

When the volume of the solution used does not exceed the pore volume of the support, the method is called incipient wetness impregnation. The average size of the metal particles depends on the concentration of solution used, so that high metal loading tend to give larger particles than low metal loading, and the variation in the volumes of individual pores leads to a somewhat broad size distribution.