

## CHAPTER I

### INTRODUCTION

In the modern petrochemical industry, products derived from crude oil are converted into useful products, chief amongst which are plastics, elastomers, and synthetic fibers. Almost all of the organic products of the petrochemical industry are made from aromatics and alkenes, especially ethylene, propylene, and butylene.

Of all the reactions used to convert alkenes into more useful and valuable products, none is more widely exploited than selective oxidation. Among the oxidation of other alkenes, the selective oxidation of ethylene to ethylene oxide (EO) is an important reaction in the chemical industry and has attracted academic and industrial interest. The main use of EO is hydration to ethylene glycol, which is used as antifreeze in automobile cooling system and as one of the two monomers in polyethylene terephthalate (polyester) fibers and polymers. Some is also converted to alcohol ethoxylates, which are used as detergents and surfactants.

In the last two decades, two processes were employed to manufacture ethylene oxide (EO):

- (a) Indirect oxidation of ethylene, with chlorohydrin as an intermediate.
- (b) Direct oxidation by air or oxygen.

Although the indirect oxidation process gave a high molar yield in relation to ethylene (80%), this method is now rarely used due to its disadvantages from the economical point of view.

Production today is almost entirely by direct oxidation of ethylene with air or oxygen over silver catalyst. Early plants used air as the oxidant, but

later, despite the added cost, pure oxygen was often used, as it simplifies recycle, allows higher reactor productivity and lowers overall cost.

Despite a vast amount of published information, silver is unique in its ability to selectively catalyze ethylene epoxidation and silver supported on low surface area (LSA)  $\alpha$ -alumina is the only catalyst used commercially to selective oxidation of ethylene to EO. Industrial operating selectivities are normally close to 80% compared to about 68% during 1960s. Much of this improvement is due to the addition of a chlorine-containing hydrocarbon species to the gaseous reactants as a moderator and addition of alkali promoters. In addition, others varieties of modifications such as the support employed, the physical form of the silver on the support, the method of production, and reactant molar ratio have been proposed to improve the activity and selectivity of the silver supported on alumina ( $\text{Ag}/\text{Al}_2\text{O}_3$ ) catalyst.

The deposition of silver onto the support can be achieved by a number of techniques but the impregnation and precipitation techniques are most frequently used. Impregnation of the support is the preferred technique for silver deposition because it utilizes silver more efficiently than coating procedures. The impregnated technique can be accomplished by two ways. More precise control is achieved by a technique termed incipient wetness impregnation, which is commonly used industrially. The sol-gel method is also one of the techniques to prepare the both thermally stable and highly active supported metal catalysts for most oxidation reactions due to its well known potential advantages.

The influences of the support, on the selectivity to EO have been known for many years. However, there are some reports about most high surface area (HSA) supports gave very low selectivities to EO, the activity of (HSA)  $\text{Ag}/\text{Al}_2\text{O}_3$  catalyst prepared by sol-gel method has not yet been explored for ethylene epoxidation reaction.

Although a number of studies have been published on the partial oxidation of ethylene with oxygen or air over silver supported catalyst in the presence of different kinds of promoters and inhibitors like carbon monoxide, carbon dioxide, ethane and organic chloride, there is a very little research on the effect of hydrogen on the ethylene epoxidation reaction under synthesis conditions.

The goals of the present study were separated into two parts. The first part was to investigate whether high surface area (HSA) Ag/Al<sub>2</sub>O<sub>3</sub> catalyst, which prepared by sol-gel technique, has activity for selective oxidation of ethylene. The second part was to study catalytic activity of the low surface area (LSA) Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst, which prepared by incipient wetness impregnation method.

The activity and selectivity of both catalysts were determined by a number of catalysts subjected to different metal loadings and different calcination and oxidation-reduction methods. Moreover, the effects of reactant molar ratio and promoting effect of hydrogen on the catalytic activity were also studied.