

## CHAPTER I

### INTRODUCTION

The selective oxidation of ethylene, especially ethylene epoxidation, is currently the largest hydrocarbon partial oxidation process in industry as desired product, ethylene oxide, is the valuable chemical feedstock or intermediate for many important applications, such as solvents, antifreeze, textiles, detergents, adhesives, polyurethane foam, and pharmaceuticals (<http://www.osha.gov>). Besides, this is in good accordance with the currently global demand for ethylene oxide that exceeds 40 billion pounds per annum (<http://www.dow.com>).

Ordinarily, ethylene can be oxidized to ethylene oxide with high selectivity over unique traditional silver catalyst supported on low surface area alpha-alumina ( $\text{Ag}/(\text{LSA})\alpha\text{-Al}_2\text{O}_3$ ). Commercially, addition of few ppms of chloride to gaseous reactant as moderator in the form of chlorine-containing hydrocarbon species, such as dichloroethane ( $\text{C}_2\text{H}_4\text{Cl}_2$ ) and vinyl chloride ( $\text{C}_2\text{H}_3\text{Cl}$ ), has been reported to significantly increase the selectivity to ethylene oxide by 15-20% (Law *et al.*, 1942; Campbell *et al.*, 1984; Tan *et al.*, 1986; and Yeung *et al.*, 1998). Alkali and alkali earth, such as Cs and Re, also provided the improvement of selectivity to ethylene oxide by 10% (Iwakura, 1985; and Bhasin, 1988). In recent work, silver catalyst supported on high surface area alpha-alumina ( $\text{Ag}/(\text{HSA})\alpha\text{-Al}_2\text{O}_3$ ) and  $\text{Au}/\text{TiO}_2$  were proved to exhibit good selectivity to ethylene oxide (Rojluechai *et al.*, 2006). Moreover, adding small amount of Au to form Au-Ag bimetallic catalyst over high surface area alpha-alumina support favored the epoxidation of ethylene to ethylene oxide (Rojluechai *et al.*, 2006). However, ethylene conversion obtained from these catalysts could not be detected at any temperature below 493 K. Even though the reaction temperature was raised up to 543 K, ethylene conversion was still low at 1-4%. Consequently, this limitation results in high energy consumption for catalyst activation at high temperature, which is a disadvantage for industrial application. The non-traditional catalysis technique is, therefore, expected to overcome this constraint. One of potential techniques is to combine the selective traditional catalysis and non-thermal plasma.

Non-thermal plasma (Eliasson, 1991) is one kind of electric gas discharges. In non-thermal plasmas, the electrons in electrodes gain the energy from applied voltage until they possess energy enough to overcome the potential barrier of metal surface electrodes. Then, they are directly transferred to chemically excited or dissociated gaseous species by colliding with the gaseous components present in the plasma zone. Typically, these excited or dissociated atoms or molecules have a much higher reactivity than neutral species at the ground state where they can easily lead to creation of the new chemical species. Furthermore, the important characteristic of non-thermal plasma is that the electrons in plasma have a higher energy than neutral gas, resulting in relatively low gas temperature. The examples of chemical synthesis using plasma are oxidations of olefins, aromatics, and so on. (Suhr *et al.*, 1988; and Patiño *et al.*, 1996).

In combination of catalysis and non-thermal plasma, this technique tends to offer a number of advantages over the conventional catalytic processes. One of them is low operational temperature close to room temperature at near or slightly higher than atmospheric pressure, as described above. This implies comparatively lower energy consumption used for activating catalysts. Moreover, the catalytic problems at high temperature operation, i.e., catalyst deactivation, catalyst regeneration, and catalyst replacement, could be eliminated. However, they often provide less selectivity to a desired product than the catalysis technique (Pietruszka *et al.*, 2004).

The corona discharge (Eliasson, 1991) was employed for this research due to being capable of operating at low temperature and atmospheric pressure. The characteristic of corona discharge is to use a pair of inhomogeneous metal electrode geometries, which can stabilize the discharge generated. There are many industrial applications involving the utilization of corona discharge such as NO<sub>x</sub> and SO<sub>x</sub> reduction in flue gas, toxic compounds destruction, and ozone production (Chang *et al.*, 1991; Yan *et al.*, 1998; and Bröer *et al.*, 2000). In previous works, it was worked with photocatalyst for degradation of ethylene (Harndumrongsak, 2002 and Saktrakool, 2003) and for VOC removal (Kiatubolpaiboon, 2004).

The objective of this work was to investigate a combined catalytic and corona discharge system for the epoxidation of ethylene using different catalysts: Ag/(LSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Ag/(HSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Au-Ag/(HSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and Au/TiO<sub>2</sub>. In this

study, the effects of various operating parameters, including applied voltage, input frequency, molar ratio of oxygen to ethylene, and feed flow rate, on the activity of ethylene oxidation were examined. Moreover, the optimum condition for maximum ethylene oxide production was determined.