CHAPTER I
INTRODUCTION

Ethylene oxide (C_2H_4O, EO) is an important industrial chemical used as an intermediate in the production of various useful chemicals. The major use of ethylene oxide is in the production of ethylene glycol. Ethylene oxide is also important in the manufacture of surfactants and detergents by a process called ethoxylation, sterilants for foodstuffs, solvents, antifreezes, and adhesives (http://www.prlog.org). Because ethylene oxide is a valuable chemical feedstock in many applications, the partial oxidation of ethylene to ethylene oxide, so-called ethylene epoxidation, has been of great interest in many global research works.

The most widely used technique for ethylene epoxidation is catalytic process using silver catalysts. Practically, silver catalysts supported on low-surface-area alpha-alumina (Ag/(LSA)α-Al_2O_3) provide high selectivity for ethylene oxide (Matar *et al.*, 1989). Some previous research found that the alkali and transition metals, especially Cs and Cu, also provided the improvement of selectivity for ethylene oxide (Iwakura, 1985; and Bhasin, 1988). Recently, it was confirmed that copper-silver bimetallic catalysts could offer selectivity improvement compared with bare silver catalysts in the ethylene epoxidation (Jankowiak and Barteau, 2005). The role of cesium was proposed that the presence of cesium could reduce the acidic sites on the support, resulting in suppressing the isomerization of ethylene oxide to acetaldehyde (Mao and Vannice, 1995; and Epling *et al.*, 1997). Moreover, cesium addition could decrease the concentration of nucleophilic oxygen, which is responsible for carbon dioxide formation (Goncharova *et al.*, 1995). Therefore, in the presence of cesium added, the selectivity for ethylene oxide is enhanced by the suppression of the rate of ethylene oxide oxidation, resulting in the decrease in the rate of direct combustion. With the role of gold in ethylene epoxidation, there are relatively confused points of view for existing literatures as follows. The effects of alloying silver with gold on the oxygen adsorption properties of Ag over a set of 15 wt.% bimetallic Ag-Au/α-Al_2O_3 were studied (Kondaries and Verykios, 1996). The results showed that the presence of Au influenced the population and the activation energy of adsorbed oxygen species. Especially, when Au content increased, the

molecular oxygen was more favorable in adsorption on Ag than atomic oxygen, which was indicated by its lower activation energy of adsorption. Based on molecular oxygen theory, this adsorbed species exhibited the vital role for ethylene oxide formation, whereas atomic oxygen was considered to be an unselective oxidant for partial oxidation (Kilty *et al.*, 1973). While other research group reported in the different way that the selectivity for ethylene oxide was observed at constant value up to approximately 10 wt.% Au content on the surface and decreased continuously at higher Au contents (Tories and Verikios, 1987). On the other hand, Geenen et al. (1982) reported that at the high Au loading, the selectivity for ethylene oxide decreased and rapidly dropped to zero, which was more rapidly dropped than Tories and Verikios' experiments. The discrepancies might originate from the various alloying catalyst preparation techniques (Tories and Verikios, 1987).

Non-thermal plasma is one kind of electric gas discharges, of which electrons gain enough energy resulting from the applied voltage to overcome the potential barrier of metal surface electrodes while the bulk gas temperature is relatively low. These energetic electrons can collide with gaseous molecules in the plasma zone to generate active species and radicals for subsequent reactions. The great advantage of non-thermal plasma is that the electrons generated have much higher energy than neutral gas with relatively low temperatures, leading to a lower energy consumption (Suhr *et al.*, 1988 ; and Patiño *et al.*, 1996; Tansuwan, 2007).

The combination of catalysis and non-thermal plasma techniques tends to offer a number of advantages over the conventional catalytic process. One of them is low operational temperature close to room temperature at near or slightly higher than atmospheric pressure. 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 (Pietruszka *et al.*, 2004). As reported by Heintze *et al.*, (2004), they investigated the combined DBD and Ni/α-Al_2O_3 in the partial oxidation of methane. The results were reported that at lower temperatures, this combined catalyst-plasma had no influence on the conversion and product selectivity. At these temperatures, the plasma showed the dominant role. At the higher temperatures, however, the catalyst promoted the oxidation of CO to CO_2. Tansuwan (2007)

studied the epoxidation of ethylene in a low-temperature corona discharge system in the presence of different catalysts, including Ag/(low-surface-area, LSA)α-Al_2O_3, Ag/(high-surface-area, HSA)γ-Al_2O_3, Au-Ag/(HSA)γ-Al_2O_3, and Au/TiO_2. The results showed that Ag/(LSA)α-Al_2O_3 offered the highest selectivity for ethylene oxide, as well as the lowest selectivities for carbon monoxide and carbon dioxide. The selectivity for ethylene oxide increased with increasing applied voltage, but remained unchanged when frequency was varied within 300 to 500 Hz, and eventually decreased with the frequency over 500 Hz. The optimum Ag loading on (LSA)α-Al_2O_3 was found to be 12.5 wt.% with ethylene oxide selectivity of 12.98% at input voltage and frequency of 15 kV and 500 Hz, respectively.

In this work, ethylene epoxidation under low-temperature dielectric barrier discharge (DBD) was studied and compared with that under low-temperature corona discharge with cesium-, copper-, and gold-promoted silver catalysts supported on low-surface-area alpha-alumina (Cs-Ag/(LSA)α-Al_2O_3, Cu-Ag/(LSA)α-Al_2O_3, and Au-Ag/(LSA)α-Al_2O_3). The effects of various operating parameters, including oxygen-to-ethylene molar ratio, feed flow rate, input frequency, applied voltage, and electrode gap distance, on the activity of ethylene epoxidation were extensively examined.