



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

All chemicals used for catalyst preparation and analytical procedures are described as follows:

1) Silver nitrate (AgNO_3), assay 99.9%, obtained from Carlo Erba, was used as silver catalyst precursor.

2) Cesium nitrate (CsNO_3), supplied from Merck, was used as a precursor of cesium promoter.

3) Copper nitrate ($\text{Cu}(\text{NO}_3)_2$), supplied from Merck, was used as a precursor of copper promoter.

4) Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), supplied from Alfa Aesar, was used as a precursor of gold promoter.

5) Low-surface-area alpha-alumina, (LSA) $\alpha\text{-Al}_2\text{O}_3$, supplied from A.C.S. Xenon Limited Partnership, was used as catalyst support.

6) Distilled water

3.1.2 Reagent Gases for Reaction

All gases used for reaction were obtained from Thai Industrial Gas Co., Ltd. as follows:

1) Helium (HP grade).

2) 40% Ethylene balanced with helium.

3) 97% Oxygen balanced with helium.

4) 30% Ethylene oxide balanced with helium.

3.2 Catalyst Preparation Procedures

The procedures used for catalyst preparation have been described previously (Rojluechai, 2006). All catalysts were prepared by incipient wetness impregnation method.

3.2.1 Silver supported on low-surface-area alpha-alumina (Ag/(LSA) α -Al₂O₃)

Alumina support ((LSA) α -Al₂O₃, A.C.S. Xenon Limited Partnership, 0.104 \pm 0.012 m²/g) was impregnated with an aqueous solution of silver nitrate (AgNO₃, Carlo Erba, 99.9%) to achieve optimum nominal loading of 12.5 wt.% (Tansuwan, 2007) and then dried in air at 110°C overnight. These catalysts are calcined in air at 400°C for 12 h. After that, the catalyst was sieved in order to obtain the desired grain size range of 221-425 μ m for the activity studies.

3.2.2 Cesium-silver, copper-silver, and gold-silver supported on low-surface-area alpha-alumina (Cs-Ag/(LSA) α -Al₂O₃, Cu-Ag/(LSA) α -Al₂O₃, and Au-Ag/(LSA) α -Al₂O₃)

For the preparation of cesium-silver, copper-silver, and gold-silver on alumina catalyst, a silver catalyst with a constant optimum nominal 12.5 wt.% Ag exhibiting the superior activity from the previous work was initially prepared and dried at 110°C for 2 h. This catalyst was impregnated with appropriate amounts of an aqueous solution of cesium nitrate, copper nitrate, or hydrogen tetrachloroaurate (III) trihydrate to achieve various nominal cesium, copper, or gold loadings of 0.2 and 1 wt.%. Then, these loaded catalysts were again dried in air at 110°C overnight and calcined in air at 400°C for 12 h. After that, each catalyst was sieved in the same manner as above explained.

3.3 Catalyst Characterizations

The characteristics of all catalysts were determined with regard to their physical and chemical properties. The characterization techniques and equipments applied in this research were BET surface area analysis, X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Temperature Programmed Oxidation (TPO). The details are described as follows:

3.3.1 BET Surface Area Measurement

The surface areas of all prepared catalysts were determined by measuring the quantity of gas adsorbed onto or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample was maintained at a constant temperature in the sample cell until the equilibrium was established. This volume-pressure data were used to calculate the BET surface area.

The BET surface area measurement was done by using Quantachrome Corporation Autosorb I. The catalyst sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150°C for 10 h before starting the analysis. Autosorb ANYGAS Version 2.10 was also used to analyze the results.

The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c - 1) P}{V_m c P_0}$$

where

V = The volume of gas adsorbed;

P = The pressure of gas;

P₀ = The saturated vapor pressure of the liquid at the operating temperature;

V_m = The volume equivalent to an adsorbed monolayer; and

c = The constant related to the energy of adsorption in the first adsorbed layer, the magnitude of adsorption in the first adsorbed layer, and

the magnitude of adsorbate/adsorbent interaction, which is given by:

$$c = \exp\left(\frac{H_1 - H_L}{RT}\right)$$

where

H_1 = The fixed heat of adsorption;

H_L = The latent heat of evaporation;

R = The gas constant; and

T = The temperature

The surface area can be determined by using the following equation:

$$S_g = \frac{V_m}{0.0224} + (6.02 \times 10^{23})(A)$$

where

S_g = The specific surface area (m^2/g); and

A = The area occupied by each adsorbate molecule (m^2)

3.3.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) analysis was generally performed based on the fact that an X-ray diffraction pattern was unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed. It was also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity indicated the higher content.

X-ray diffraction patterns of all catalyst samples were obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered $CuK\alpha$ radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mV. A catalyst sample was pressed into a hollow of glass holder and held in place by glass window. Then, it was scanned in the 2θ range from 5 to 90° in the continuous mode with the rate of $5^\circ/\text{min}$.

The XRD results consisted of peak parameters, including the centroid 2θ , the full line width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size was calculated from the XRD data from X-ray line broadening, using the full line width at half maximum of intensity and the 2θ value and plugging them into the Debye-Scherrer equation. (Cullity, 1956 and Matar *et al.*, 1989)

$$T = K\lambda / \beta \cos\theta$$

where

- λ = The X-ray wavelength (0.1542 nm for Cu anode source);
- K = The Debye-Scherrer constant which to some degree depends on the shape of the peak (assume equal to 0.9);
- β = The full width at half maximum (FWHM) of the broadened peak;
- θ = The Bragg angle of the reflection (radian); and
- T = The mean crystallite size (nm)

This equation works well for particle sizes of less than 1,000 Å. The broadening of diffraction lines measured at half the maximum intensity (β) was corrected by using Warren's method, which is

$$\beta^2 = \beta_M^2 - \beta_S^2$$

where

- β_M = The breadth of the diffraction line; and
- β_S = The breadth of the line from a standard.

3.3.3 Transmission Electron Microscopy (TEM)

The transmission electron micrographs were employed for investigating the average particle size and identifying the microstructure of prepared catalysts. The catalyst samples were grounded into fine powder and ultrasonically dispersed in ethanol. A small droplet of the suspension was deposited on a copper grid, and the solvent was evaporated prior to loading the sample into the microscope. TEM was carried out using a JEOL 2000CX operated at an accelerating voltage of

200 kV in bright field modes. A beam was passed through a series of lenses to form a magnified image of a sample that was inserted in the area of the objective lens. The image from selected area was viewed through projection onto a view of screen. Because electron beams can be easily scattered by air molecules, TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focusing the electron beam.

3.3.4 Temperature-Programmed Oxidation (TPO)

The TPO technique was used to quantitatively investigate the coke formation on used catalysts. The TPO analysis was performed at a continuous flow of O₂/He (ratio 2:1) with a total flow rate of 40 cm³/min. A spent catalyst about 10-12 mg was placed in the quartz tube, and it was secured with packing quartz wool. The sample temperature was linearly increased with a constant rate of 10°C/min to reach a maximum temperature of 850°C. The carbon fraction of the sample was reacted with oxygen to produce products, such as water and carbon dioxide. After this reaction, these products in the effluent gas were passed to a methanator containing Ni/Al₂O₃ catalyst to convert carbon dioxide to methane. Consequently, methane was detected with a flame ionization detector (FID SRI model 110). The area under the curve obtained was used to calculate carbon content in the sample.

3.4 Catalytic Activity Measurement

The experimental study of ethylene epoxidation was conducted in two discharge systems, i.e. dielectric barrier discharge (DBD) and corona discharge, which were operated at ambient temperature and atmospheric pressure. For dielectric barrier discharge system, the experimental setup of the reactor is shown in Figure 3.1. The reactor sizes were 2 cm height x 3 cm width x 15 cm length for inner dimension, and 3 cm height x 7 cm width x 19 cm length for outer dimension. As shown in Figure 3.2, it consisted of a dielectric glass plate placed between parallel stainless steel electrodes. The gap distance between the electrodes could be varied from 10 to 14 mm, corresponding to residence time in the range of 0.9-1.3 min. The reactor was connected to the gas handling system. The microdischarge plasma was generated

between the electrode gap. The output power used to generate plasma was alternating current power, 200 V and 50 Hz, which was transmitted to a high voltage current via a power supply unit. The output voltage was adjusted by a function generator, whereas sinusoidal wave signal was controlled and monitored by an oscilloscope. For corona discharge system, the experimental setup of the corona discharge reactor is shown in Figure 3.3. The reactor comprised an 11 $\frac{1}{4}$ -inch-long quartz tube with an outer diameter of 10 mm and an inner diameter of 8 mm. Plasma was generated in the reactor between pin and plate electrodes, which were located at the center of the reactor. The gap distance between pin and plate electrodes was fixed at 10 mm. The catalyst bed of different catalysts was placed on quartz wool in space between the two inhomogeneous electrodes at the center of the quartz tube, as shown in Figure 3.4. The power supply unit and its operation for the corona discharge system were the same as those for the dielectric barrier discharge system.

The flow rates of ethylene, oxygen, and helium flowing through the reactor were controlled by electronic mass flow controllers. Impurities in all reactant gases were trapped by 7- μ m in-line filter before the reactant gases passed through electronic mass flow controllers. The reactor pressure was controlled by a needle valve, and the outlet of reactor was vented to atmosphere via exhausted rubber tube before entering an on-line gas chromatograph. The moisture in the product gas stream was trapped by a water trap filter before entering a heated stainless steel line to an on-line gas chromatograph. The composition of product gas stream was analyzed by a gas chromatograph (Perkin-Elmer, AutoSystem GC). The gas chromatograph was equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). For the TCD channel, the packed column (Carboxen 1000) was used for separating the product gases, which were hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), and ethylene (C_2H_4). For the FID channel, the capillary column (OV-Plot U) was used for analysis of ethylene oxide and other by-product gases, i.e. CH_4 , C_2H_2 , C_2H_6 , and C_3H_8 . However, it must be noted that there were still some unknown products, which were not detectable.

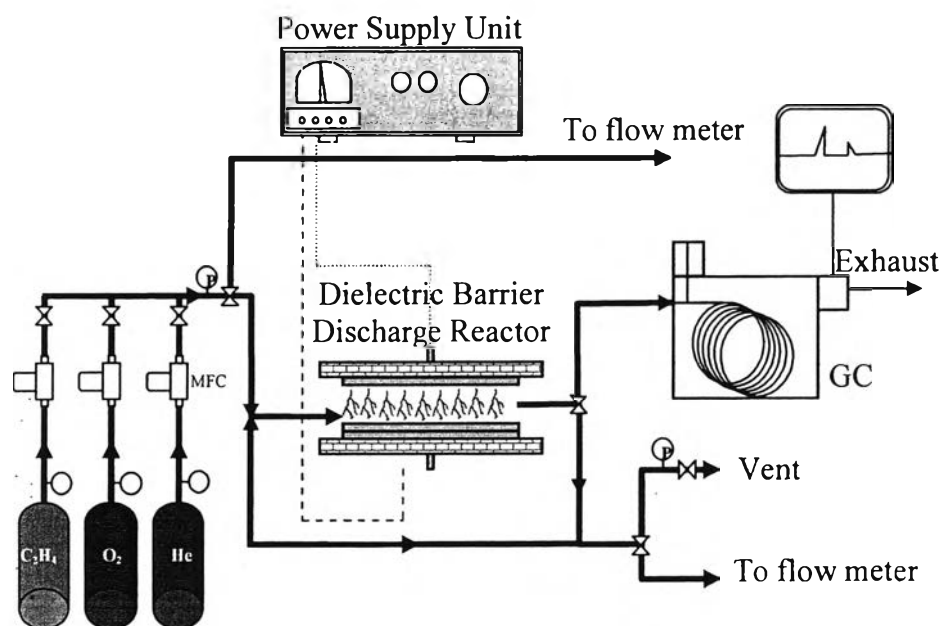


Figure 3.1 Schematic of experimental setup for ethylene epoxidation reaction in dielectric barrier discharge plasma system.

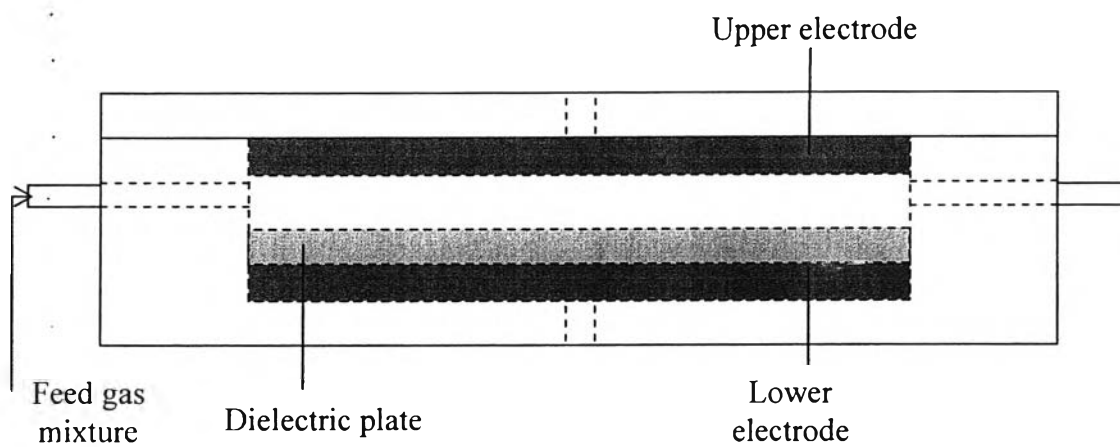


Figure 3.2 The configuration of the dielectric barrier discharge reactor.

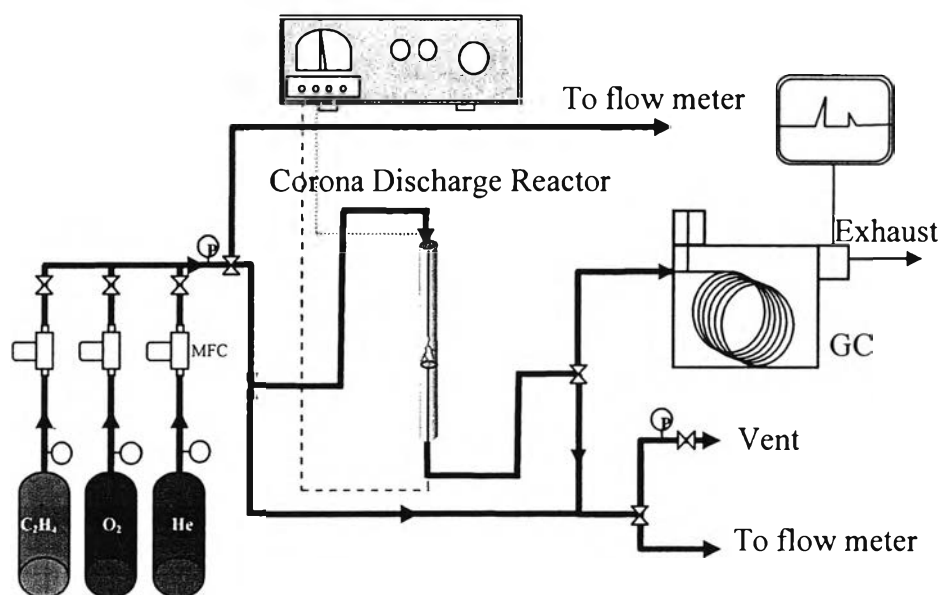


Figure 3.3 Schematic of experimental setup for ethylene epoxidation reaction in corona discharge plasma system.

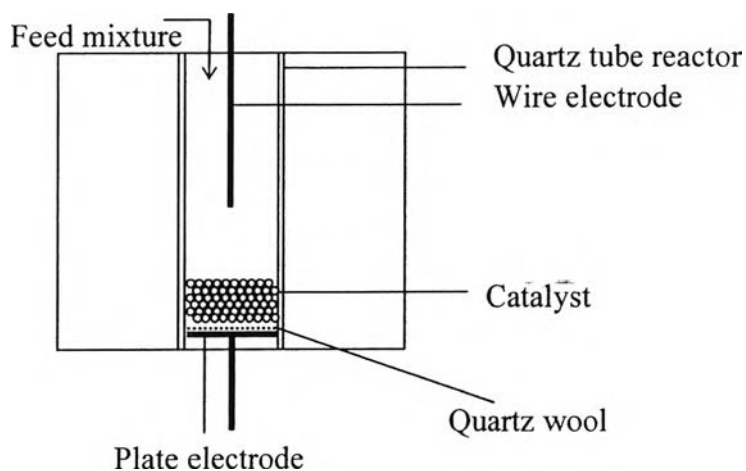


Figure 3.4 The configuration of the corona discharge reactor.

To evaluate the process performance, the conversions of ethylene and oxygen, the selectivities for products, including CO , CO_2 , C_2H_4O , CH_4 , C_2H_6 , C_2H_2 , and traces of C_3 , and the ethylene oxide yield were considered. The conversion of either ethylene or oxygen is defined as:

$$\% \text{ Reactant conversion} = \frac{(\text{moles of reactant } in - \text{moles of reactant } out) \times 100}{(\text{moles of reactant } in)}$$

The product selectivity is calculated from the following equation:

$$\% \text{ Product selectivity} = \frac{[(\text{number of carbon or hydrogen atom in product}) (\text{moles of product produced})] \times 100}{[(\text{number of carbon or hydrogen atom in ethylene}) (\text{moles of ethylene converted})]}$$

The ethylene oxide yield is calculated from the following equation:

$$\% \text{ Ethylene oxide yield} = (\% \text{ ethylene conversion}) \times (\% \text{ ethylene oxide selectivity}) \times 100$$

To determine the energy efficiency of the plasma system, the specific power consumption is calculated in a unit of Ws per molecule of converted ethylene or per molecule of produced ethylene oxide using the following equation:

$$\text{Specific power consumption} = \frac{P \times 60}{N \times M}$$

where P = Power (W)

N = Avogadro's number = 6.02×10^{23} molecules/mol

M = Rate of converted ethylene molecules in feed or rate of produced ethylene oxide molecules (mol/min).

3.5 Power Supply Unit

The block diagram of the power supply unit is shown in Figure 3.5. For the first step, the AC input of 220 V and 50 Hz was converted to DC current of about 70-80 V by DC power supply converter. For the second step, the DC was supplied through a 500-W power amplifier, which was connected to the Instek function generator to generate waveform and to amplify voltage and frequency. The signal of alternating current was a sinusoidal waveform. For the final step, the amplified AC

was passed through the input transformer to convert to 230 V AC. Thereafter, the variable output was transmitted to a high voltage current by nominal factor of 130 times of low side voltage (input). An Extech® series 380801 power analyzer was used to measure power, power factor, current, frequency, and voltage at the low side of the power supply unit.

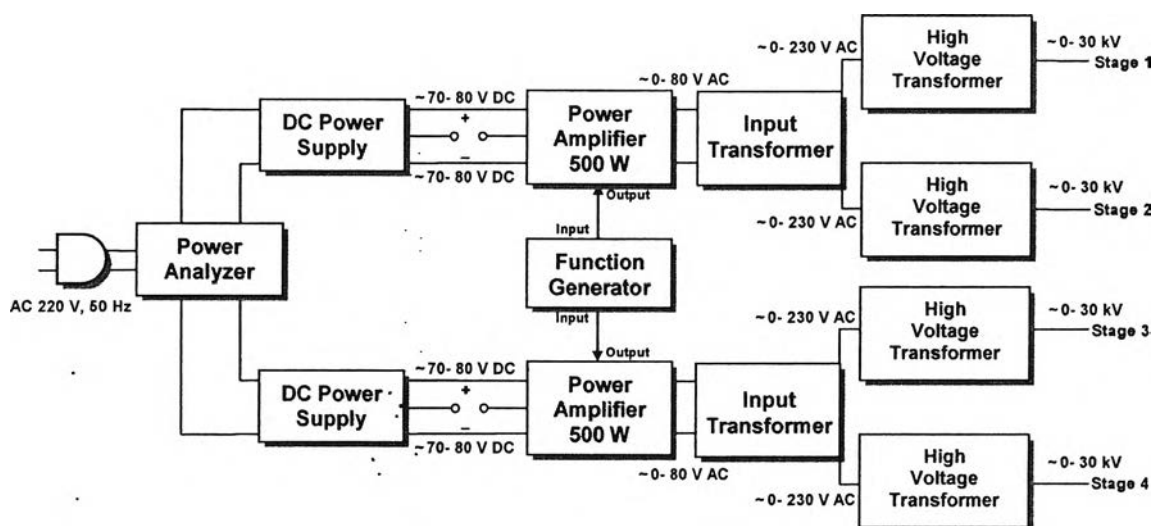


Figure 3.5 Block diagram of the power supply unit.

3.6 Studied Conditions

After the composition of the feed remained constant, the power supply unit was turned on. After 40 min, the composition of the effluent gas was analyzed for every time interval of 18 min until the exhaust gas composition was constant. Several process performances were investigated, including the ethylene and oxygen conversion, product selectivity, and ethylene oxide yield. The experiments were classified into 2 main parts; first part: to find the optimum conditions for DBD reactor under various effects, including O_2/C_2H_4 molar ratio, feed flow rate, input frequency, applied voltage, and electrode gap distance, and second part: to compare the epoxidation activity with corona discharge reactor operated different catalysts, including $Ag/(LSA)\alpha-Al_2O_3$, $Cs-Ag/(LSA)\alpha-Al_2O_3$, $Cu-Ag/(LSA)\alpha-Al_2O_3$, and $Au-Ag/(LSA)\alpha-Al_2O_3$.

The experimental conditions for this research were as follows:

3.6.1 Condition for GC

Gas chromatography	Perkin-Elmer, AutoSystem GC
Detector	TCD and FID
TCD channel	Packed column (Carboxen 1000)
TCD injector temperature	150°C
FID channel	Capillary column (OV-Plot U)
FID injector temperature	150°C
Oven temperature	65°C for 18 min
Carrier gas	High purity helium
Carrier gas flow rate	30 cm ³ /min (TCD channel) 15 cm ³ /min (FID channel)
TCD detector temperature	190°C
FCD detector temperature	300°C

3.6.2 Dielectric barrier discharge reactor

Gap distance:	10 - 14 mm
Feed flow rate:	50 - 150 cm ³ /min
Applied voltage:	13 - 21 kV
Input frequency:	500 - 800 Hz
Number of plasma reactor:	1 reactor
Oxygen to oxygen ratio:	1:1 - 4:1

3.6.3 Corona discharge reactor

Gap distance:	10 mm
Feed flow rate:	50 cm ³ /min
Applied voltage:	19 kV
Input frequency:	500 Hz
Number of plasma reactor:	1 reactor
Oxygen to oxygen ratio:	1:1