

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

Silver nitrate (AgNO_3), with 99.9% purity, supplied by Merck was used as a precursor for Ag catalysts. Alumina particles (Al_2O_3), supplied by PTT Co., Ltd., and silica particles (SiO_2), supplied by Merck, were used as catalyst supports. The Al_2O_3 and SiO_2 particles have average diameters of 3–4 μm and 2 μm , respectively. All chemicals were used as received without further purification.

3.1.2 Reagent Gases for Reaction Experiment

Helium (high purity grade, 99.995%), 40% ethylene balanced with helium, 97% oxygen balanced with helium, and 30% Ethylene oxide balanced with helium used in this study were ordered from Thai Industrial Gas Co., Ltd.

3.2 Catalyst Preparation Procedures

The incipient wetness impregnation was used to prepare all supported Ag catalysts. The Al_2O_3 or SiO_2 particles were impregnated with an aqueous AgNO_3 solution to achieve various Ag loadings of 5, 10, 15, and 20 wt.%. The mixtures were then dried in air at 110 °C overnight. Finally, the prepared catalyst samples were calcined at 500 °C for 5 h (Rojluechai *et al.*, 2006). For preparing the Ag loading over 20 wt.%, after the 20 wt.% Ag/ SiO_2 was dried in air at 110 °C for 2 h, this catalyst was impregnated again with an aqueous AgNO_3 solution to achieve 25 and 30 wt.% Ag loadings.

3.3 Catalyst Characterization Techniques

The characteristics of all prepared catalysts were determined with regard to their physical and chemical properties. The catalyst characterization techniques applied in this research were surface area analysis (BET), X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) with energy dispersive x-ray fluorescence spectrometer (EDX) and temperature programmed oxidation (TPO).

3.3.1 BET Surface Area Measurement

The specific 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 the 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 a surface area analyzer (Quantachrome, Autosorb I). A catalyst sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on the sample surface under vacuum at 150°C for 10 h before starting the analysis. Autosorb ANYGAS Version 2.10 was used to analyze the results. The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1) P}{V_m c P_0} \quad (3.1)$$

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:

$$c = \exp\left(\frac{H_i - H_L}{RT}\right) \quad (3.2)$$

where

H_i = 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:

$$S_g = \frac{V_m}{0.0224} + (6.02 \times 10^{23})(A) \quad (3.3)$$

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 is generally performed based on the fact that an X-ray diffraction pattern is 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 is 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 indicates the higher content.

The X-ray diffraction patterns of all catalyst samples were obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered $\text{CuK}\alpha$ radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mV. A catalyst sample was first pressed into a hollow of glass holder and held in place by a glass window. After that, 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 (Matar *et al.*, 1989).

$$T = K\lambda / \beta \cos\theta \quad (3.4)$$

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

$$\beta^2 = \beta_M^2 - \beta_S^2 \quad (3.5)$$

where

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

3.3.3 Field Emission Scanning Electron Microscope (FE-SEM)

Field Emission Scanning Electron Microscope (FE-SEM) operated at 1 to 20 kV equipped with Energy Dispersive X-Ray Fluorescence Spectrometer (EDX) was employed to observe the surface structure of a catalyst sample to identify the elements proportion over that area and to evaluate approximately the particle size distribution. The catalyst samples placed on the stubs were coated by platinum (Pt) prior to load them into the microscope. 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, the FE-

SEM columns had to 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 the spent 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 a 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 then 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. The produced 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 Experiment Setup and Reaction Activity Experiments

This work consisted of four parts with four different plasma reactors. Only the first part used the combined catalytic and plasma system for the ethylene epoxidation. The experimental study of ethylene epoxidation over Al₂O₃ and SiO₂ supported Ag catalysts was firstly investigated in a parallel dielectric barrier discharge (DBD) at ambient temperature and atmospheric pressure (Chapter IV). The cylindrical DBD and corona discharge without catalysts were investigated by mainly focusing on the effect of separate C₂H₄/O₂ feed for the second part (Chapter V) and third part (Chapter VI), respectively. Finally, the DBD jet, modified from the corona discharge and cylindrical DBD for combination of their advantages was employed for the ethylene epoxidation (Chapter VII). The schematics and all details of each experimental setup were illustrated in the following chapters.

For experimental in Chapter IV-VI, the power used to generate plasma was alternating current power, 220 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 the sinusoidal wave signal was controlled and monitored by an oscilloscope.

The block diagram of the power supply unit was shown in Figure 3.1. For the first step, the AC input of 220 V and 50 Hz was converted to DC of about 70-80 V by a DC power supply converter. Next, 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 the sinusoidal waveform. For the final step, the amplified AC passed through the input transformer to convert to 230 V AC. Thereafter, the variable output was transmitted to a high voltage current by a nominal factor of 130 times of low side (input). A power analyzer (Extech[®] series 380801) was used to measure power, power factor, current, frequency, and voltage at the low side of the power supply unit.

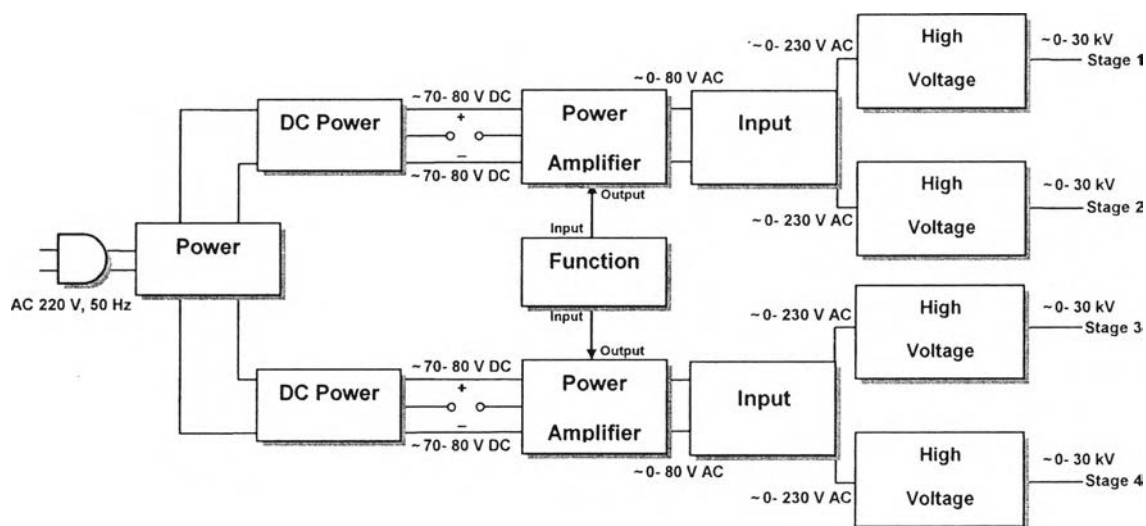


Figure 3.1 Block diagram of the power supply unit used in this study.

The flow rates of ethylene, oxygen, and helium flowing through the reactor were controlled by electronic mass flow controllers. The impurities in each reactant gas were trapped by a 7 μm in-line filter before the reactant gas passed through the

electronic mass flow controller. The reactor pressure was controlled by a needle valve, and the outlet of reactor was vented to the atmosphere via an exhausted rubber tube before entering an on-line gas chromatograph. The composition of reactants was measured to be constant then the power supply unit was turned on. After the studied plasma systems reached steady state, the composition of the effluent gas was analyzed for every time interval of 20 min until the exhaust gas composition was invariant. 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 compositions of product gases were analyzed by an online 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), and carbon dioxide (CO_2). For the FID channel, the capillary column (OV-Plot U) was used for analysis of ethylene (C_2H_4), ethylene oxide (C_2H_4O , EO), and other product gases, i.e. methane (CH_4), acetylene (C_2H_2), ethane (C_2H_6), and propane (C_3H_8). The GC was operated under the following conditions:

TCD injector temperature	120°C
FID injector temperature	150°C
TCD detector temperature	190°C
FID detector temperature	280°C
TCD carrier gas flow rate	30 ml/min
FID carrier gas flow rate	25 ml/min
Carrier gas	High purity helium
Oven temperature	40°C for 5 min 165°C (heating rate 10°C/min)

3.5 Calculations for Process Evaluation

To evaluate the process performance, the experimental data (with a standard deviation of less than 5%) were averaged and then used to calculate the CH_4 and O_2

conversions, the selectivities for products, including EO, H₂, CO, CO₂, CH₄, C₂H₆, C₂H₂, and traces of C₃, and the EO yield. The conversion of either ethylene or oxygen was defined as:

$$\% \text{ Reactant conversion} = \frac{(\text{moles of reactant in} - \text{moles of reactant out}) \times 100}{(\text{moles of reactant in})} \quad (3.1)$$

The product selectivity was calculated from the following equation:

$$\% \text{ Product selectivity} = \frac{[(\text{number of carbon or hydrogen atom in product})(\text{moles of product produced})] \times 100}{[(\text{number of carbon or hydrogen atom in C}_2\text{H}_4)(\text{moles of C}_2\text{H}_4 \text{ converted})]} \quad (3.2)$$

The EO yield was calculated from the following equation:

$$\% \text{ EO yield} = \frac{(\% \text{ C}_2\text{H}_4 \text{ conversion}) \times (\% \text{ EO selectivity})}{100} \quad (3.3)$$

To determine the energy efficiency of the plasma system, the power consumption was calculated in a unit of Ws per molecule of converted C₂H₄ or per molecule of produced EO using the following equation:

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

where P = Power (W)

N = Avogadro's number = 6.02 X 10²³ molecules/mol

M = Rate of converted C₂H₄ molecules in feed or rate of produced EO molecules (mol/min).