CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

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

3.1.1.1 Silver nitrate (AgNO₃), assay 99.9%, obtained from Carlo Brea, was used as silver catalyst precursor.

3.1.1.2 Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), ACS, 49.5%, supplied from Alfa Aesar A Johnson Matthey Company, was employed as gold catalyst precursor.

3.1.1.3 Low surface area alpha-alumina, $(LSA)\alpha-Al_2O_3$, supplied from Institute for Reference Materials and Measurements, was used as catalyst support.

3.1.1.4 High surface area alpha-alumina, $(HSA)\alpha-Al_2O_3$, or AEROXIDE® Alu C trademark obtained from Aerosil® was used as catalyst support.

3.1.1.5 Hydrophilic fumed titanium dioxide (TiO_2) or AEROXIDE® TiO_2 P-25 obtained from Aerosil® was also used as another catalyst support.

3.1.2 Reagent Gases for Reaction

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

3.1.2.1 99.995% Helium (HP grade)

3.1.2.2 40% Ethylene balanced with helium

3.1.2.3 97% Oxygen 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-Al$_2$O$_3$)

Alumina catalyst support ((LSA)α-Al$_2$O$_3$, Institute for Reference Materials and Measurements, 0.104 $\pm$ 0.012 m^2/g) was impregnated with aqueous solutions of silver nitrate (AgNO$_3$, Carlo Erba, 99.9%) to achieve various nominal loadings ranging from 0 – 15 wt% and then dried in air at 110°C overnight. These catalysts were calcined in air at 400°C for 12 h. After that, each catalyst was sieved in order to obtain the desired grain size range of 221-425 μm for the activity studies.

3.2.2   Silver supported on high surface area alpha-alumina (Ag/(HSA)α-Al$_2$O$_3$)

Fumed alumina catalyst support ((HSA)α-Al$_2$O$_3$, AEROXIDE$^®$ Alu C, 100 $\pm$ 15 m^2/g) was impregnated with an aqueous solution of silver nitrate (AgNO$_3$, Carlo Erba, 99.9%) to achieve nominal silver loading of 13.18 wt% exhibiting the superior activity from previous work and then dried in air at 110°C overnight. This catalyst was calcined in air at 500°C for 5 h. After that, the catalyst was sieved in order to obtain the desired grain size range of 221-425 μm for the activity studies.

3.2.3   Bimetallic gold-silver supported on high surface area alpha-alumina (Au-Ag/(HSA)α-Al$_2$O$_3$)

For the preparation of gold-silver on alumina catalyst, a silver catalyst on (HSA)α-Al$_2$O$_3$ support with a constant nominal 13.18 wt% Ag loading exhibiting the superior activity from previous work was prepared and dried at 110°C for 2 h. This catalyst was then impregnated with appropriate amount of an aqueous solution of tetrachloroaurate (III) trihydrate ((HAuCl$_4$·3H$_2$O), ACS, 49.5%, Alfa Aesar) to achieve nominal gold loading of 0.63 wt%. This loaded catalyst was again dried in

air at 110°C overnight and calcined in air at 500°C for 5 h. After that, the catalyst was sieved in the same manner as above explained.

3.2.4 Gold Supported on Titania (Au/TiO$_2$)

For the preparation of gold on titania catalyst, gold on titania support (TiO$_2$, AEROXIDE® TiO$_2$ P-25, 60 $\pm$ 15 m^2/g) with nominal 1 wt% Au loading using an aqueous solution of tetrachloroaurate (III) trihydrate ((HAuCl$_4$·3H$_2$O), ACS, 49.5%, Alfa Aesar) was prepared. Then, this loaded catalyst was dried in air at 110°C overnight and calcined in air at 500°C for 5 h. After that, the catalyst was finally sieved as in above explained manner.

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 are surface area measurement, Atomic Absorption Spectroscopy (AAS), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), and Temperature Programmed Oxidation (TPO).The details are described as follows:

3.3.1 Surface Area Measurement

The surface areas of all prepared catalysts were determined by measuring the quantity of N$_2$ 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 of 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 carried out 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 used to analyze the results.

3.3.2 Atomic Absorption Spectroscopy (AAS)

The actual contents of gold and silver loadings in the prepared catalysts were determined by an atomic absorption spectroscopy. The standard solutions of 1,000 ppm of gold and silver used in this work are manufactured by Merck. Firstly, a known weight around 0.02 g of a catalyst was completely dissolved in a aqueous solution of nitric acid (water and nitric acid with a ratio of 18:82). The solution was then diluted to the measuring range. The concentrations of gold and silver were obtained by comparing its absorbance with the calibration curve of the standard solution. A Varian Spectr AA-300 was employed to determine the compositions of gold and silver in the catalysts prepared.

3.3.3 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.

X-ray diffraction patterns of all catalyst samples were obtained by using a Rigaku RINT 2000 diffractometer equipped with a Ni filtered CuKα radiation source ($\lambda = 1.542$ Å) 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° /min. The XRD results showed peak parameters, including the centroid 2θ, the full line width at half the maximum of intensity (β), d-value, and intensity.

3.3.4 Transmission Electron Microscopy (TEM)

A transmission electron micrograph was employed for investigating the average particle size of Ag particles and identifying the microstructure of catalyst. The catalyst sample was 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 in a JEOL 2000 CX 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 is inserted in the area of the objective lens. The image from selected area was viewed through projection onto a view of screen. Additionally, the electromagnetic lenses were used for focusing the electron beam.

3.3.5 Temperature Programmed Oxidation (TPO)

The TPO technique can be used to quantitatively investigate the coke formation on used catalysts. The TPO analysis was performed at a continuous flow of O_2/He (ratio 2:1) with a total flow rate of 40 mL/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/Al_2O_3 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 Reaction Activity Experiments

The experimental study of ethylene oxidation was conducted in one-to-four corona discharge reactors, which were operated at ambient temperature and atmospheric pressure. The schematic of corona discharge system is shown in Figure 3.1. Each reactor comprises 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 each reactor via pin-

and-plate electrodes, which were located at the center of each reactor. The desired distance between pin and plate could be adjusted. The power used to generate plasma was alternating current power, 200 V and 50 Hz, which was transmitted to a high voltage current via power supply unit. The output voltage was adjusted by function generator, whereas sinusoidal wave signal was controlled and monitored by oscilloscope. The catalyst bed of four 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 3.2. The reactor tubes were connected to the gas handling system.

Reactant gases, ethylene, oxygen, and helium, flowing through the reactor were controlled by electronic mass flow controllers. Impurities in all reactant gases were be trapped by 0.7 μm in-line filter before the reactant gases passed through electronic mass flow controllers. Reactor pressure was controlled by a needle valve; the outlet of reactor was vented to atmosphere via exhausted rubber tube before entering an on-line gas chromatograph. After reaction occurred, the product gases were trapped by water trap filter before they were fed through heated stainless steel lines to an on-line gas chromatograph. The composition of product gases was analyzed by an automatic gas chromatograph (Perkin-Elmer, AutoSystem GC). The gas chromatography 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 nitrogen (N_2), oxygen (O_2), and C_1-C_2 hydrocarbons. For the FID channel, the capillary column (OV-Plot U) was used for ethylene oxide and by-product analysis. The GC was operated under the following conditions:

TCD injection temperature	120°C
FID injection temperature	150°C
Oven temperature	40°C for 5 min
	165°C (heating rate 10°C/min)
Carrier gas	High purity helium
Carrier gas flow rate	30 mL/min (TCD channel)
	25 mL/min (FID channel)
Detector temperature	190°C in TCD and 280°C for FID

The catalyst was initially pretreated with oxygen at 150°C for 2 h in order to diminish some impurities and remove residual moisture from the catalyst. Mixtures of 40% ethylene in helium, high purity oxygen (HP grade), and high purity helium (HP grade) were used as feed gases. Catalysts were tested over a wide range of feed gas compositions with molar ratio of oxygen to ethylene ranging from 1/1 to 5/1.

Calculations for the ethylene conversion, ethylene oxide selectivity, and yield were done based on the following equations:

Ethylene conversion (X) (%) $\quad = \quad [F\ C_2H_4\ in - F\ C_2H_4\ out][100]/[F\ C_2H_4\ in]$

Ethylene oxide selectivity (S) (%) $= \quad [F\ C_2H_4O\ out]\ /\ [F\ C_2H_4\ in - F\ C_2H_4\ out]$

Ethylene oxide yield (Y) $\quad = \quad X \cdot S = [F\ C_2H_4O\ out]\ /\ [F\ C_2H_4\ in]$

where 　$F\ C_2H_4$ in 　　$=$ 　　the inlet molar flow rate of ethylene (mol/min)

　　　　$F\ C_2H_4$ out 　$=$ 　　the outlet molar flow rate of ethylene (mol/min)

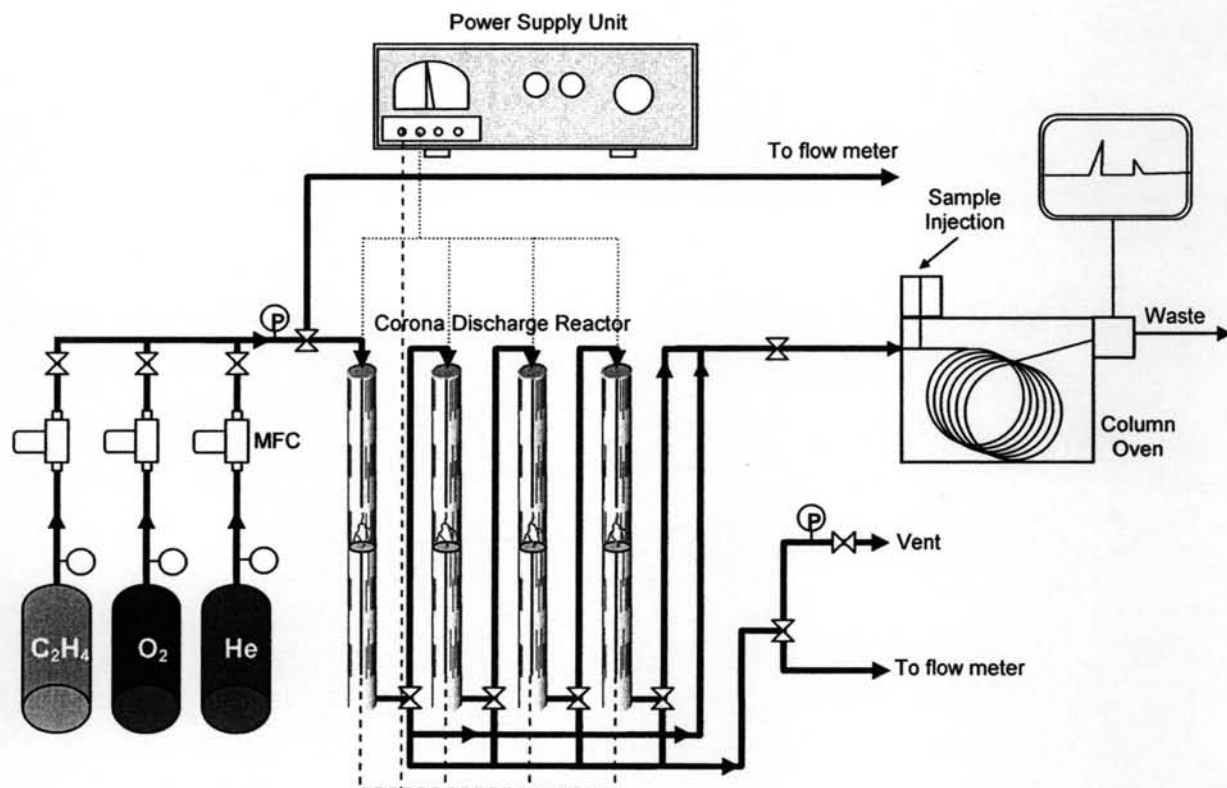　　　　$F\ C_2H_4O$ out 　$=$ 　　the outlet molar flow rate of ethylene oxide (mol/min)

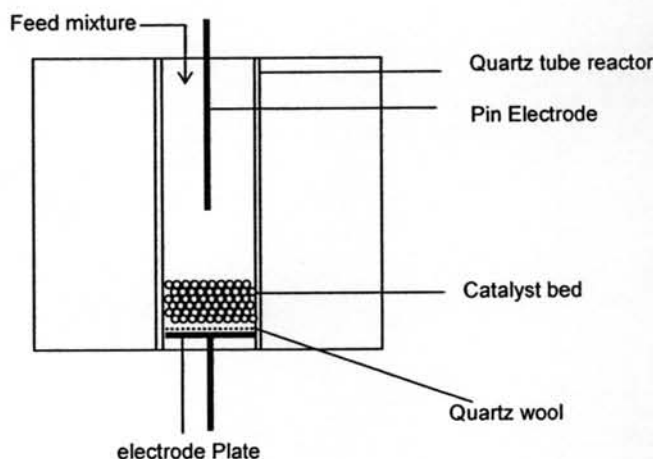**Figure 3.1** Schematic of experimental setup for ethylene oxidation reaction.

Figure 3.2 The configuration of each corona discharge reactor.

3.5 Studied Conditions

After the composition of the feed had remained constant, the power supply unit was turned on. After 60 min, the composition of the effluent gas was analyzed for every time interval of 60 min until it was constant. The plasma reactors were turned off one by one starting with the fourth one first for studying the effect of the stage number of the plasma reactors on the ethylene conversion and product selectivity. The experiments were classified into 2 main parts: (1) effects of catalysts and metal loading contents, and (2) effects of operating parameters of plasma system. The conditions for all studied parameters (applied voltage, input frequency, molar ratio of oxygen to ethylene ratio, and feed flow rate) are shown in Table 3.3.

Table 3.3 Experimental conditions for this research

Effect	Applied voltage (kV)	Input frequency (Hz)	$O_2:C_2H_4$ ratio	Feed flow rate (mL/min)
Plasma with catalyst	7-15	300-800	1/1-5/1	50-150