



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Preparation Materials

Titanium dioxide (100% purity) was obtained from J.J. Degussa Hüls (T) Co. Ltd. Platinum(II)2,4-pentanedionate, $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ (49.8%Pt) was obtained from Alfa Aesar. Tetraethylorthotitanate (TEOT) (100% purity) was supplied by Fluka. Ethanol with 99.7% purity was supplied by BDH. Nitric acid (65%) was supplied by Lab-Scan. All chemicals were used as received. Distilled water was used throughout this study.

3.1.2 Reactant Gases

Helium (He) with 99.95% purity and Oxygen (O_2) with 99.5% purity were obtained from Thai Industrial Gas (Public) Co., Ltd. Ethylene (C_2H_4) with 99.99% purity was obtained from National Petrochemical (Public) Co., Ltd.

3.2 Catalyst Preparation

Catalysts used in this work were prepared by dipping a glass ring or glass wool as the catalyst support in a slurry of a commercial TiO_2 (Degussa P25) or sol-gel TiO_2 . The glass ring was 7 mm OD, 5 mm ID, and 10 mm long. The internal surface of the glass ring was etched by HF before coated with the catalyst. The glass wool was pretreated to remove all undesirable matters such as wax and binder by calcination at 450°C for 2.5 h. The treated glass wool was then cut to the size of $3 \times 3 \text{ cm}^2$.

To prepare Degussa P25 coated on a glass ring or glass wool. Degussa P25 slurry was prepared by mixing 0.6 g of Degussa P25 with 29.4 ml of distilled water. The glass ring or glass wool was then immersed in this slurry for 5 min and dried in an oven at 100°C for 15 min. The procedure was repeated 8 times for the glass ring

and one time for the glass wool. The coated glass ring or glass wool was annealed in a furnace at 300°C for 3 h, and cooled to room temperature with a cooling rate of 50 °C/min. The catalyst was white after annealing. The amount of TiO₂ loading was about 0.003 g for glass ring and 0.008 g for glass wool.

For a glass ring or glass wool coated with sol-gel TiO₂, TiO₂ slurry was prepared by mixing 1.5 g of Titanium (IV) ethoxide (TEOT) with 20 ml of ethanol and 6 drops of nitric acid. The coating procedure was the same as previously described except using only 400°C and 5 h instead of 300°C and 3 h for annealing.

To prepare 1% Pt/TiO₂, 0.005 g of Pt(C₅H₇O₂)₂ and 2.83 g of TEOT were dissolved in 38.07 ml of ethanol and 14 drops of nitric acid. The same coating and calculation procedures were carried out as described above.

3.3 Catalyst Characterization

Surface areas of the prepared catalysts were determined by a Quantachrom surface area analyzer (Autosorb-1). The samples were degassed at 200 °C overnight before the analysis. Nitrogen was used as a probe gas. A catalyst sample was dried and outgassed in the sample cell at 200 °C for at least 4 h before adsorption. The specific area of each catalyst was calculated from the 5 points adsorption isotherm. The results were analyzed by the Autosorb ANAGAS software version 2.10.

Crystalline phases of the catalysts were determined by a Rigaku X-ray diffractometer (RINT-2200) equipped with a graphite monochromator and a Cu tube for generating CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 30 mA. A nickel filter was used as the K_α filter. The goniometer parameters were divergence slit = 1°(2 θ); scattering slit = 1°(2 θ); and receiving slit = 0.3 mm. The catalyst sample was held on a glass slide holder and was examined between 5 to 90°(2 θ) range at a scanning speed of 5°(2 θ)/minute and a scan step of 0.02°(2 θ). The digital output of proportional X-ray diffractor and the goniometer angle measurements were sent to an online microcomputer to record the data and subsequent analysis. The X-ray patterns of the catalysts were compared with that of Degussa P-25.

3.4 Oxidation Reaction Experiment

Schematic diagrams of the experimental setup and power supply in this work are shown in Figure 3.1 and 3.2, respectively. Reactant gases, ethylene, oxygen, and helium, controlled by mass flow controllers, were introduced into the first reactor at room temperature and atmospheric pressure. Before the reactant gases passed

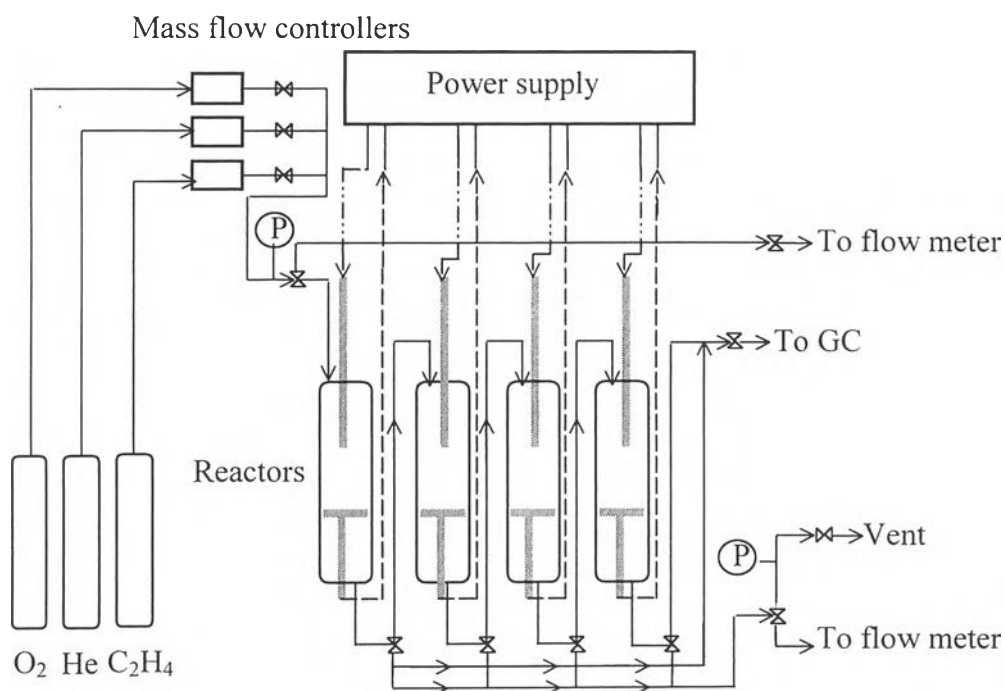


Figure 3.1 Schematic diagram of the experimental setup.

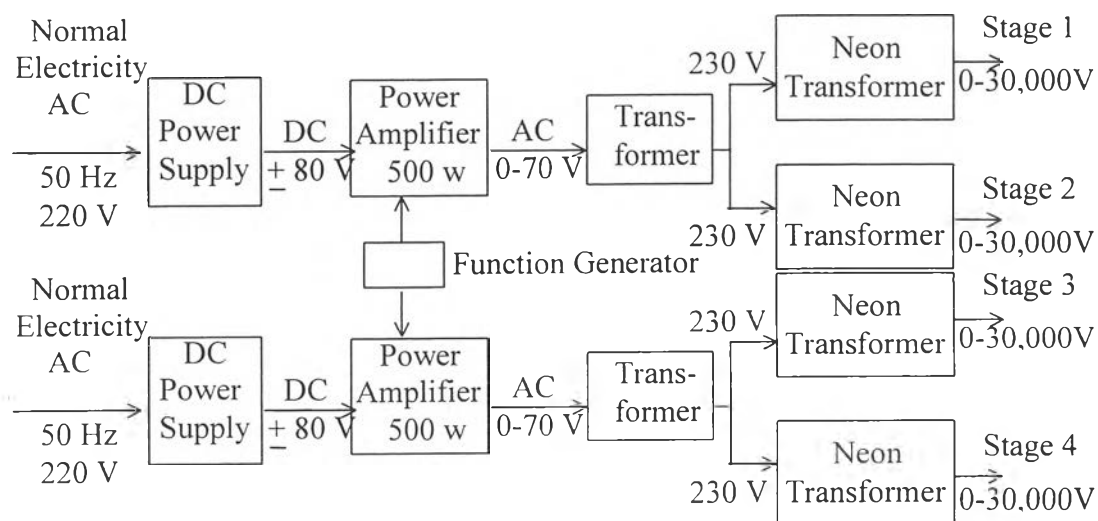


Figure 3.2 Schematic diagram of power supply.

through the mass flow controllers, any foreign particles in the feed gases were trapped by 0.7 μm in-line filters. The feed mixture was controlled to have 3% ethylene and 15% oxygen with helium balance. The four reactors which were made of quartz tubes with 10 mm OD and 8 mm ID were arranged in a series. Plasma was generated in each reactor via a pair of stainless steel pin and plate electrodes. The pin and plate electrodes were located at the center of each reactor. The power used to generate plasma was alternative current power, 220V and 50 Hz, which was transmitted to a high voltage current. The output voltage was increased up to 130 times and the signal of the alternative current was a sine form. The glass ring or glass wool coated with either the sol-gel TiO_2 or Degussa P25 was packed in the space between the two electrodes as shown in Figure 3.3.

The experiment was started with the feed gas composition analysis by a gas chromatograph (Perkin-Elmer, AutoSystem GC) equipped with a thermal conductivity detector. The GC conditions used were summarized as follows:

Injection temperature:	160 °C
Oven temperature:	120 °C for 5 min 170 °C (heating rate 10 °C /min) for 20 min
Carrier gas:	High purity helium
Carrier gas flow rate:	30 mL/min
Column type:	Packed column (Carboxen 1000)
Detector temperature:	200 °C

A ratio of oxygen to ethylene was set constant at 5:1. After the concentration of the feed mixture was constant, the supply power unit was turned on. After 30 min, the composition of the effluent was analyzed every 30 min until the outlet gas composition was constant. Effects of the stage number of the plasma and photocatalytic system on the ethylene removal and product selectivities were investigated by turning off one by one reactor with the fourth one first. The calculation of product selectivities is based on the carbon content of the converted ethylene fraction.

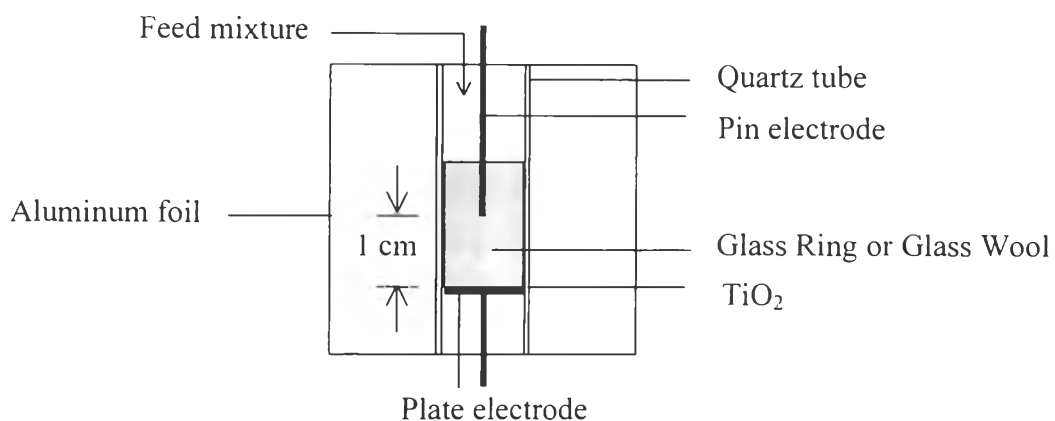


Figure 3.3 Schematic diagram of each reactor.

3.5 Studied Conditions

The experiments were divided into 2 main parts: with and without photocatalyst. All parameters studied were summarized in Table 3.1. All experiments were conducted under ambient conditions.

Table 3.1 Experimental conditions

Effects	Number of plasma generator(s)	Gas flow rate (ml/min)	AC frequency (Hz)	% TiO ₂ Loading(g)
Plasma	1-4	40-240	50-800	-
Plasma and Photocatalyst	1-4	160	50-200	0.008