

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Reactant Gases

All gases that were used in this experiment are as follows:

- a)  $40.13 \pm 0.40$  % propylene ( $C_3H_6$ ) in helium (Thai Industrial Gas Public Co., Ltd.)
- b) High purity propylene (polymer grade, 99.99%) (National Petrochemical Public Company Limited)
- c) Oxygen ( $O_2$ )  $20.2 \pm 0.2$  % in helium (Thai Industrial Gas Public Co., Ltd.)
- d) Ultra high purity (UHP) hydrogen (99.999%) (Thai Industrial Gas Public Co., Ltd.)
- e) High purity (HP) helium (99.99%) (Thai Industrial Gas Public Co., Ltd.)

#### 3.1.2 Chemicals

All chemicals used in catalyst preparation were analytical grade as described below.

- a) Aluminum isopropoxide ( $Al(OC_3H_7)_3$ ) of 98% purity (Fluka Co., Ltd.)
- b) Silver nitrate ( $AgNO_3$ ) of 99.9% purity (BDH Laboratory Supplies)
- c) 1,3-Butanediol anhydrous ( $C_2H_4(OH)C_2H_4OH$ ) of 99% purity (Fluka Co., Ltd.)
- d) Nitric acid of 65% purity (Labscan Co., Ltd.)

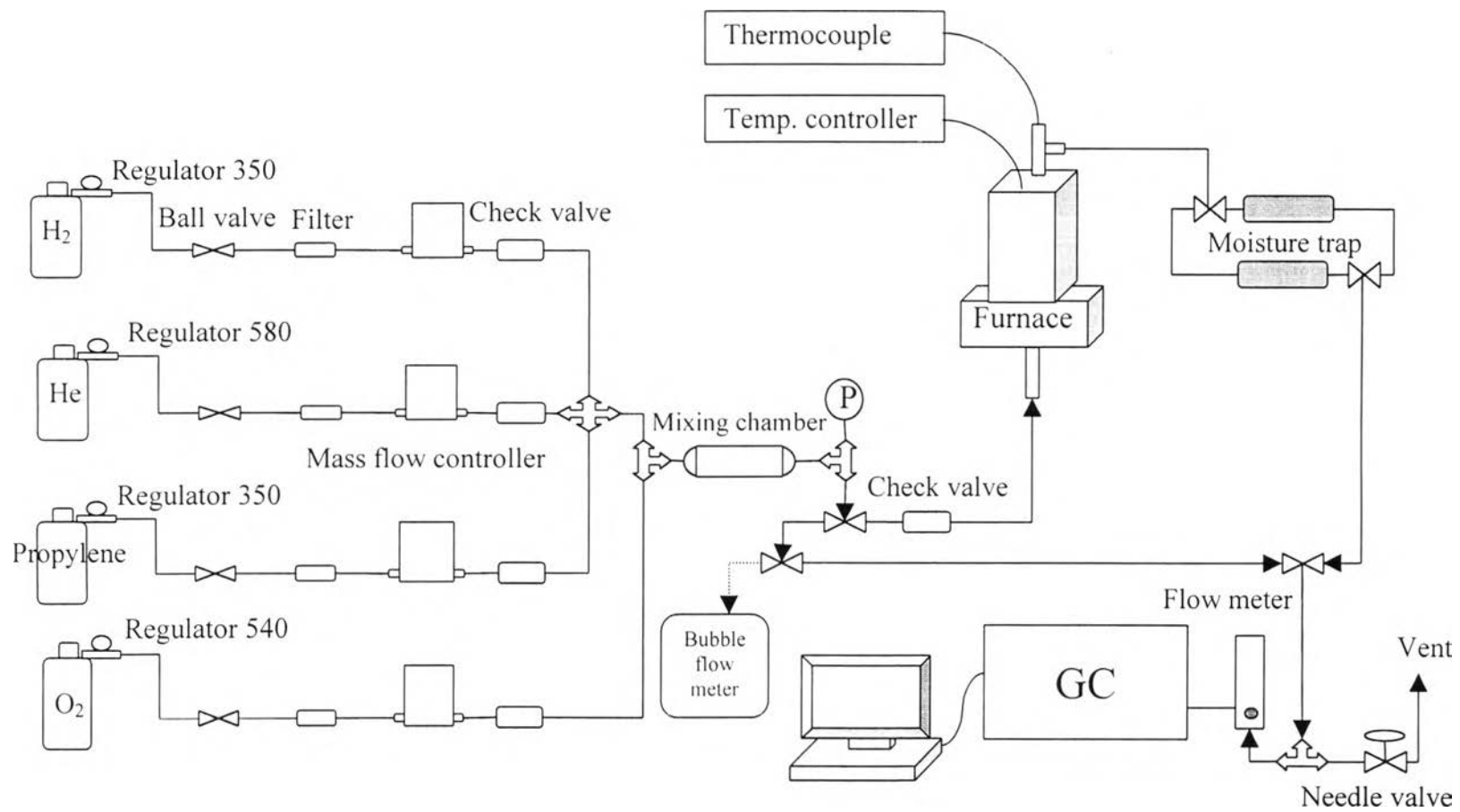
- e) Fuming titanium dioxide ( $\text{TiO}_2 >99\%$ ) (Fluka Co., Ltd.)
- f) Gold chloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ )
- g) Ammonia solution (30%  $\text{NH}_4\text{OH}$ ) for analysis (RPE CARLO ERBA Reagent)
- h) Anhydrous calcium sulfate (97%  $\text{CaSO}_4$ , 3%  $\text{CoCl}_2$ ) 8 mesh with indicator (Aldrich Chemical Co., Ltd.)
- i) Propylene oxide or 1,2-epoxypropane ( $\text{C}_3\text{H}_6\text{O}$ ) of 99% purity (Aldrich Chemical Co., Ltd.)

## 3.2 Apparatus

The experimental apparatus shown schematically in Figure 3.1 was divided into 3 parts: (i) gas blending system, (ii) catalytic reactor, and (iii) analytical instrumentation.

### 3.2.1 Gas Blending System

The reactant gas mixture consisted of propylene, oxygen, and hydrogen balanced in helium. Each gas was passed through a micron line filter to remove small particles and a check valve to prevent the reverse flow. The gas flow rate was controlled by a mass flow controller (Sierra Instruments, Inc. model 840) having the gas flow rate of 50 to 100 ml/min. The mixed gas was adjusted to the desirable direction by a three-way valve, and sent to a reactor. All fittings and tubings were made of stainless steel having outside diameters of 1/4" and 1/8" obtained from SWAGelok Co., Ltd.



**Figure 3.1** Schematic flow diagram.

### 3.2.2 Catalytic Reactor

The partial propylene oxidation was carried out in an 8 mm inside diameter quartz tube reactor at atmospheric pressure. The temperature was varied from 100 to 250 °C. The 0.2 g catalyst was packed between quartz wool in the middle of the reactor which was heated using an electrical heater. The temperature of the catalyst bed was monitored and controlled by PID controller (Yamatake. Honeywell, model SDC10) equipped with a thermocouple which was inserted at the middle of catalyst bed. The product gas leaving from the top of the reactor was passed through a moisture trap and sent to a gas chromatograph.

### 3.2.3 Analytical Instrumentation

The effluent gas from the reactor was analyzed by Hewlett Packard 5890 series II gas chromatograph equipped with both thermal conductivity detector (TCD) and flame ionization detector (FID). A Porapak N packed column (80/100, 12' x 1/8"SS) connected to TCD was used to separate H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>6</sub>O. In addition, a GS-GasPro capillary column (0.32 mm inner diameter) connected to FID was also used to separate C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>6</sub>O at 70°C. The sampling loop was applied to inject the analyzed gas with a 10-port valve (Valco Instrument Co, Inc.) every 30 minutes into the GC for analysis. The chromatograms were attained using a PC installed with a Hewlett Packard 3365 series II Chemstation.

## 3.3 Catalyst Preparation

The catalysts were prepared by single-step sol-gel and deposition-precipitation methods. In order to clarify the effects of catalyst type and silver loading, the silver amount was varied in the range of 0 to 10.0 wt% based on the following equation.

$$\text{Metal loading} = \frac{\text{Metal}(\text{weight}) \times 100\%}{\text{Metal}(\text{weight}) + \text{Support}(\text{weight})} \quad (3.1)$$

In addition, to study the calcination temperature effect, the prepared catalysts were calcined at different temperatures.

### 3.3.1 Sol-gel Method

The supported silver catalysts were prepared by sol-gel method. Fibrillar aluminum hydroxide sols were obtained by addition of aluminum isopropoxide (AIP) to hot water (85°C) under vigorous stirring in ratio of 1 g to 10 ml. Then a small amount of nitric acid (the mole ratio of nitric acid/AIP was 0.195) was introduced into the hot slurry for the peptization of aluminum hydroxide to a clear solution. After that the solution of silver nitrate dissolved in 1,3-butanediol with AIP/1,3-butanediol molar ratio of 1 to 4 was slowly added to the fibrillar sol solution. The temperature of this mixed solution was controlled at 85°C for an hour. The solution was kept stirring at room temperature for 24 hours. After vigorous stirring, the gel was dried at 110°C for one day and calcined at different temperatures i.e., 500, 550, 570 and 600°C for 5 hours. The prepared catalysts were sieved between 70 and 120 mesh and stored in a dessicator.

### 3.3.2 Deposition-precipitation Method

The supported gold catalysts were prepared by deposition-precipitation of Au(OH)<sub>3</sub> onto TiO<sub>2</sub> in an aqueous solution of HAuCl<sub>4</sub> at pH of 8. The amount of HAuCl<sub>4</sub>.3H<sub>2</sub>O was washed with distilled water under stirring and heating conditions at 70°C. This solution was maintained at pH of 8 by continuous dropping 1 M ammonium solution into the aqueous solution. Then the amount of TiO<sub>2</sub> supporter was added into the mixed solution. The

precursor was continuously maintained at 70°C and pH of 8 for 1 hour. The precursor was washed several times, dried, and calcined at 400 and 500°C for 3 hours.

### **3.4 Catalyst Characterization**

#### **3.4.1 Surface Area Measurement**

The surface area, total pore volume, and average pore diameter of all prepared catalysts were determined using Autosorb-1 Gas Sorption system (Quantachrome Corporation) in which the Brunauer-Emmett-Teller (BET) method was employed. It was operated by measuring the quantity of gases adsorbed onto or desorbed from a solid surface at equilibrium vapor pressures. Nitrogen gas with a cross sectional area of  $1.62 \times 10^{-2} \text{ nm}^2/\text{molecule}$  was employed as an adsorbate at a liquefied nitrogen temperature (77 K). Before adsorption, the sample amount of 800 mg was dried and outgassed in a sample cell at 300°C for at least 2 hours to eliminate volatile adsorbents on the surface. Autosorb ANYGAS Software version 2.10 was used to analyze the results.

#### **3.4.2 X-ray Diffraction Method**

The X-ray Diffraction method (XRD) was utilized to identify the internal structure, bulk phase, and composition of crystalline catalyst. A Rigaku X-ray diffractometer system RINT 2000 SERIES was used to obtain the XRD patterns. The sample was ground to the fine homogeneous powder and was held in the beam in thin-walled glass. Constructive interference may be achieved with monochromatic irradiation by varying the angle of incidence (5 to 90 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements were sent to an online computer for the storage and subsequent data analysis.

### 3.5 Catalyst Activity Measurement

Selective oxidation of propylene with oxygen and hydrogen over silver/gold supported catalysts was carried out to study the effect of the following factors:

- (a) type of catalyst (silver and gold) with different preparation methods.
- (b) metal loading of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst (1-10 % Ag)
- (c) metal loading of Au/TiO<sub>2</sub> catalyst (1 and 1.5 % Au)
- (d) total flow rate of feed gas mixture (50-100 ml/min)
- (e) calcination temperature of Ag/Al<sub>2</sub>O<sub>3</sub> catalyst (500-600°C)
- (f) calcination temperature of Au/TiO<sub>2</sub> catalyst (400-500°C)
- (g) presence of hydrogen in feed gas (0-20 % mol of hydrogen)
- (h) composition of feed gas (C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub>, H<sub>2</sub>)

#### 3.5.1 Experimental Procedure

The amount of 0.2 g of 70/120 mesh size catalyst was packed into the reactor. The reactant gas mixture of C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub>, H<sub>2</sub>, and He at desired concentration and total flow rate, was passed continuously through the catalyst bed at room temperature and switched to the gas chromatograph to check the feed stream compositions. After that the catalyst sample was pretreated at 300°C in a 20 mol % O<sub>2</sub> flow for 2 hours. The temperature was then decreased to the desired reaction temperature. The product gas composition from the reactor was measured every 30 minutes until it reached equilibrium. Data were collected at six different temperatures between 80 and 225°C with a 25°C interval.

The activities of the catalyst were defined in terms of percentage conversion of propylene, selectivity to PO, yield to PO, and PO production rate (Hayashi *et al.*, 1998).

The overall conversion of  $C_3H_6$ , X, was defined as:

$$X = \frac{[(C_{C_3H_6})_{out} - (C_{C_3H_6})_{in}]}{(C_{C_3H_6})_{in}} * 100 \quad (3.2)$$

The selectivity to PO, S, was defined as:

$$S = \frac{(C_{C_3H_6O})_{out}}{[(C_{C_3H_6})_{out} - (C_{C_3H_6})_{in}]} \times 100 \quad (3.3)$$

The yield to PO, Y, was defined as:

$$Y = XS = \frac{(C_{C_3H_6O})_{out}}{(C_{C_3H_6})_{in}} \times 100 \quad (3.4)$$

The PO production rate was defined as

$$\text{PO production rate} = \frac{(C_{C_3H_6O})_{out} \times \text{total molar flow rate}}{\text{catalyst weight}} \quad (3.5)$$

where

C is the concentration of chemical compound.