

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Reactant Gases

All gases used in this experiment were as follows:

- a) 38.58 ± 0.39 % propylene (C_3H_6) in helium (Thai Industrial Gas Public Co., Ltd.)
- b) High purity propylene (C_3H_6 polymer grade, 99.99%) (National Petrochemical Public Co., Ltd.)
- c) 39.2 ± 0.2 % Oxygen (O_2) in helium (Thai Industrial Gas Public Co., Ltd.)
- d) High purity (HP) hydrogen (99.99% H_2) (Thai Industrial Gas Public Co., Ltd.)
- e) High purity (HP) helium (99.99% He) (Thai Industrial Gas Public Co., Ltd.)

3.1.2 Chemicals

All chemicals used in catalyst preparation and analytical procedure were analytical grade as described below:

- a) Alumina tri-isopropoxide ($Al(OC_3H_7)_3$) of 98% purity (Fluka Co., Ltd.)
- b) Nitric Acid of 65% purity (Labscan Co., Ltd.)
- c) Ammonia Solution (30% NH_4OH) (RPE CARLO ERBA Reagent)
- d) Hydrogen Tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$) (Fluka Co., Ltd.)

- e) Gold Atomic Spectroscopy Standard Solution
(Au 1000 g/l) (Fluka Co., Ltd.)
- f) Tetrabutyl Orthotitanate ($C_{16}H_{36}O_4Ti$) (Fluka Co., Ltd.)
- g) Tri-Magnesium Dicitrate Nanohydrate
($C_{12}H_{10}Mg_3O_{14} \cdot 9H_2O$) (Fluka Co., Ltd.)
- h) Anhydrous calcium sulfate (97% $CaSO_4$, 3% $CoCl_2$)
8 mesh with indicator (Aldrich Chemical Co., Ltd.)
- i) Titanium diisopropoxide 75%wt solution in 2-propanol
[$CH_3COCH=C(O-CH_3)_2Ti[OCH(CH_3)_2]_2$] (Aldrich Chemical Co., Ltd.)
- j) Zinc nitrate ($Zn(NO_3)_2$) (MERK CO., Ltd.)
- k) Sodium carbonate (Na_2CO_3) (APS Finechem)
- l) Propylene oxide or 1,2-epoxypropane (C_3H_6O) of 99%
purity (Aldrich Chemical Co., Ltd.)
- m) Hydrochloric acid (HCl) (Labsan Co., Ltd.)
- n) Ethanol (C_2H_5OH) (Labsan Co., Ltd.)
- o) Butanol (C_4H_9OH) (Labsan Co., Ltd.)
- p) 1,3-Butanediol ($CH_2OHCH_2CHOHCH_3$) (Fluka Co., Ltd.)
- q) Titanium dioxide P-25 (TiO_2) (Degussa Co., Ltd.)

3.2 Experimental Setup

The experimental apparatus as shown schematically in Figure 3.1 was divided into 3 parts:

1. Gas blending system
2. Catalytic reactor
3. Analytical instrument

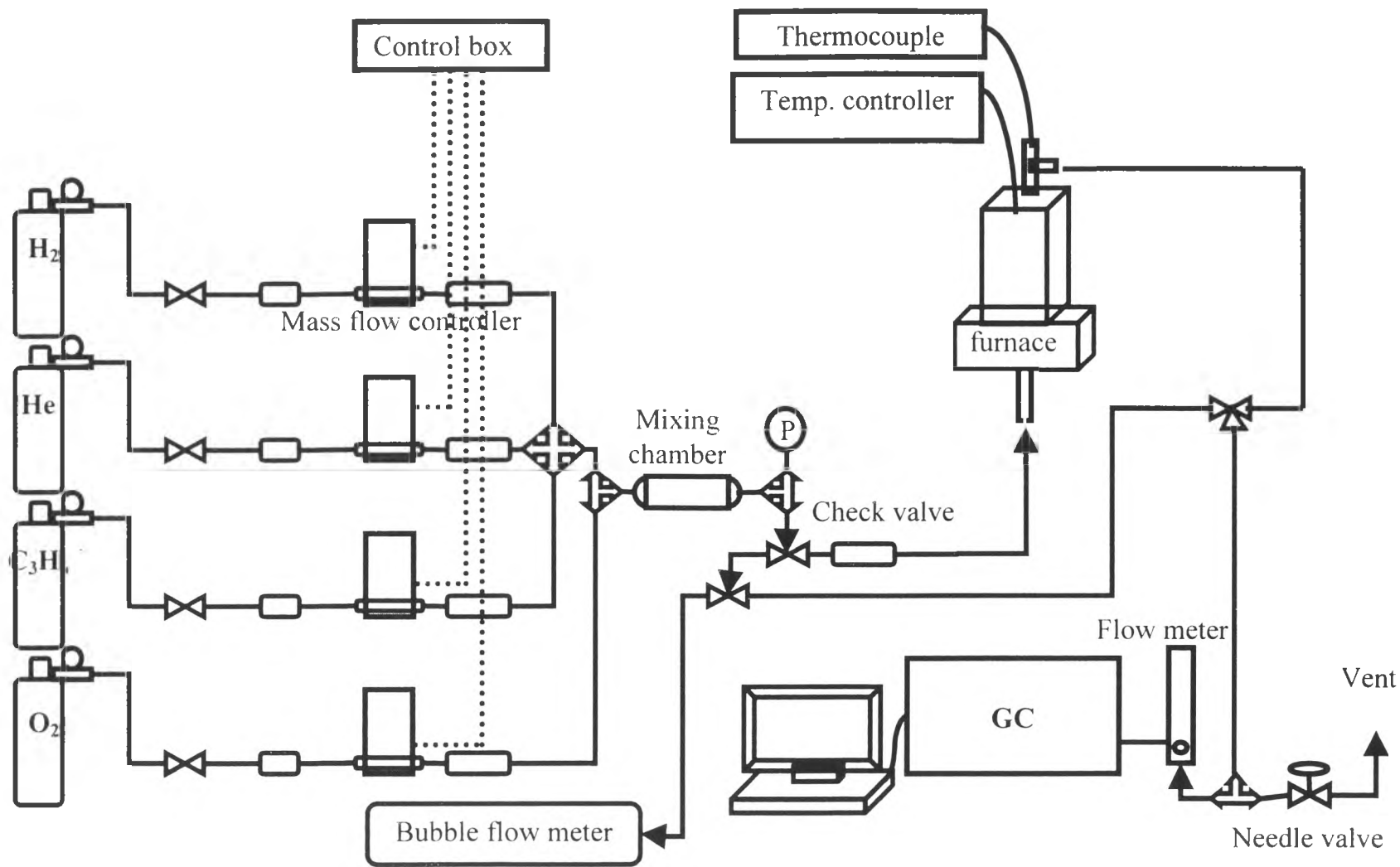


Figure 3.1 Schematic flow diagram of the experimental apparatus

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 7-micron line filter to remove small particles. After that, each gas flow rate was controlled by a mass flow controller (Sierra Instruments, Inc. model 840) to having a total gas flow rate of 70 ml/min and then passes a check valve to prevent the reversed flow. The mixed gas was adjusted to the desirable direction to check the gas flow rate, by-passed the reactor, or sent to the reactor by switching valves. All fittings and tubing were made of stainless steel having outside diameters of $\frac{1}{4}$ and $\frac{1}{8}$ inch obtained from SWAGELOK Co., Ltd.

3.2.2 Catalytic Reactor

The partial propylene oxidation was carried out in an 8 mm inside diameter glass tube reactor at atmospheric pressure. The temperature was varied from 40 to 200° C. The 0.4 g of catalyst was packed between glass wool in the middle of the reactor, which was heated by using an electrical heater. The temperature of the catalyst bed was determined and controlled by PID controller (Yamatake. Honeywell, Model SDC10). The product gas leaving from the top of the reactor was passed to the gas chromatograph.

3.2.3 Analytical Instrument

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' \times $\frac{1}{8}$ " SS) connected to TCD was used to separate hydrogen, oxygen, carbon dioxide, propylene, and propylene oxide. In addition, a GS-Gaspro capillary Column (0.32 mm inner diameter) connected to FID was used to separate propylene, and propane. After injection for 6 minutes, the oven temperature was raised up from 70 to 150°C to

decrease the retention time. The 10-port sample valve (Valco Instrument Co, Inc.) equipped with a 200 μ l sampling loop was applied to inject the analyzed gas every 30 minutes into the GC for analysis. The chromatograms were obtained 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, deposition-precipitation, and co-precipitation methods. In order to clarify the effects of catalyst types and gold loading, the amount of gold was varied in the range of 0 to 2.0 wt% based on the following equation.

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

3.3.1 Sol-gel Method

The supported gold catalysts were prepared by sol-gel method. Fibrillar aluminum hydroxide sols were obtained by addition of aluminum triisopropoxide (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 gold chloride dissolved in 1,3-butanediol with AIP/1,3-butanediol molar ratio of 1 to 4 was continuously stirred for 24 hours, dried at 110°C for one day and calcined at 400°C for 5 hours. The prepared catalysts were stored in a dessicator (Ishiguro *et al.*, 1990, and Takagi *et al.*, 1998).

For synthesis of sol-gel Au/TiO₂, it was prepared by refluxing at 70°C and continuously stirring 1.2 mol of butanol, 3.2 mol of distilled water,

1.2 mol of HCl (to obtain pH 3), and 0.2 mol of titanium diisopropoxide, which gave a water/alkoxide molar ratio of 16. In order to have 1.0 wt% of gold, added the corresponding amount of hydrogen tetrachloroaurate solution to this mixture. Refluxing and stirring were maintained until the gel was formed. In this system sample was dried at 70°C for 24 hours and then calcined at 400°C for 5 hours (Sánchez *et al.*, 1996).

3.3.2 Co-precipitation Method

The gold supported on zinc oxide catalysts were prepared by co-precipitation of Au(OH)₃ and zinc nitrate in the phase of aqueous solution at pH of 8. The amount of HAuCl₄·3H₂O and zinc nitrate were dissolved with distilled water under stirring at room temperature. This solution was maintained at pH of 8 by continuous dropping 1 M of ammonium solution (or sodium carbonate) into the aqueous solution. The precursor was continuously maintained at pH of 8 for 1 hour. The precursor was washed several times until the conductivity was constant, then dried, and calcined at 400°C for 5 hours (Fujita *et al.*, 1998, and Fujitani and Nakamura, 2000).

3.3.3 Deposition-precipitation Method

The gold supported on titanium dioxide catalysts were prepared by deposition-precipitation of Au(OH)₃ on titanium dioxide (Degussa P-25, primarily mainly anatase with surface area of approximately 60 m²/g) in the phase of aqueous solution at pH of 8. The amount of HAuCl₄ was washed with distilled water under continuous stirring and heating at 70°C. This solution was maintained at pH of 8 by continuous dropping the 1M of ammonium solution into the aqueous solution. Then the amount of TiO₂ supporter was added into the mixed solution. The precursor was continuously maintained at pH of 8 for 1 hour and then was washed several times until the

conductivity was constant, then dried, and calcined at 400°C for 5 hours (Tsubota *et al.*, 1995, and Uphade *et al.*, 2000).

3.4 Catalyst Characterization

In this thesis, the catalysts were characterized by these following methods.

3.4.1 Surface Area Measurement (BET)

The surface area, total pore volume, and average pore diameter of all prepared catalyst samples have been determined by Brunauer-Emmett-Teller (BET) method using Autosorb-1 Gas Sorption System (Quantachrome Corporation). This method was used to measure the quantity of gases adsorbed onto or desorbed from 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 3 hours. The objective of these procedures was to eliminate volatile adsorbents on the surface. Autosorb ANYGAS software version 2.10 was used to analyze the adsorption and desorption results.

3.4.2 X-ray Diffraction (XRD)

The X-ray diffractometer has been used to identify the internal structure, bulk phase, and composition of crystalline catalysts. A Rikagu X-ray diffractometer system RINT 2000 Series was used to obtain the X-ray patterns. The sample was ground to the fine homogeneous powder and was held in the beam in thin wall glass. Constructive interference may be achieved with the monochromatic irradiation by varying the angle of incidence (5 to 90 degrees). An approximated crystallite size can be found from the broadening

of an X-ray diffraction peak, measured at one-half the height. An estimated dimension of the crystallites was calculated by the Scherrer formular.

$$d = \frac{k\lambda}{b \cdot \cos\theta}$$

where

d = crystallite size

k = constant

λ = wave length

θ = corresponding Bragg angle

b = peak width at the middle height

3.4.3 Atomic Absorption Spectroscopy (AAS)

The AAS has been used to determine the exact gold loading on the supporter. The amount of catalyst was digested with aqua regia solution. This solution contains the mixture of concentrated hydrochloric and nitric acids, 82 percent by volume of the former to 18 percent of the latter. The concentration of gold in the digested catalyst solutions was compared to the standard solution to calculate the amount of gold in catalysts using Varian Specter AA300.

3.5 Catalytic Activity Measurement

Selective oxidation of propylene with oxygen and hydrogen over gold supported catalysts were carried out at atmospheric pressure. The 0.4 g of catalysts placed in a glass reactor tube with glass wool plugs were heated up to 200°C in a stream of 20% oxygen balanced with helium at the flowrate of 70 ml/min. The catalysts were left at this temperature for 2 hours and were then decreased to the desired reaction temperature. The catalysts were kept at

the reaction temperature while the gaseous reactant was bypassed to analyze the feed stream composition. After feed stream checking, the activity studies were started and the amount of products and reactants gas were measured continuously every 30 minutes until it reached equilibrium. The data were collected at different temperatures between 40 and 200°C with 20°C interval. The activities are defined in the terms of percentage conversion of propylene, selectivity to PO, yield to PO, and PO production rate (Fogler, 1999 and Rase, 1977), which are described as followed:

$$\% \text{ conversion of propylene, } X = \frac{C_{C_3H_6,m} - C_{C_3H_6,out}}{C_{C_3H_6,m}} \times 100 \quad (3.1)$$

$$\% \text{ yield to PO, } Y = \frac{C_{C_3H_6O}}{C_{C_3H_6,m}} \times 100 \quad (3.2)$$

$$\% \text{ selectivity to PO, } S = \frac{C_{C_3H_6O}}{C_{C_3H_6,m} - C_{C_3H_6,out}} \times 100 \quad (3.3)$$

$$PO \text{ production rate} = \frac{C_{C_3H_6O} \times \text{total molar flowrate}}{\text{catalyst weight}} \quad (3.4)$$

where C is concentration of chemical compound.