



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Glycerol was obtained from PTT Chemical Public Company Limited ($C_3H_5(OH)_3$, Pharmaceutical grade, 99.99 % purity)
- Gamma aluminum oxide was obtained by Saint-Gobain NorPro Corporation ($\gamma-Al_2O_3$, 99 % purity)
- Aluminum (III) nitrate nonahydrate was obtained from Ajax Finechem Pty Ltd. ($Al(NO_3)_3 \cdot 9H_2O$, ≥ 98 % purity)
- Aluminium isopropoxide (AIP) was obtained from Sigma-Aldrich ($Al(OCH(CH_3)_2)_3$, ≥ 98 % purity)
- Copper (II) nitrate was obtained from Ajax Finechem Pty Ltd. ($Cu(NO_3)_2 \cdot 3H_2O$, Lab grade ≥ 99 % purity)
- Zinc(II) nitrate was obtained from Ajax Finechem Pty Ltd. ($Zn(NO_3)_2 \cdot 6H_2O$, Reagent Grade, 98 % purity)
- Ethylene glycol was obtained from Ajax Finechem Pty Ltd. ($C_2H_4(OH)_2$, Reagent Grade)
- Nitric acid was obtained from Ajax Finechem Pty Ltd. (HNO_3 , 70% v/v)
- Ammonia solution was obtained from BDH Laboratory Supplies (NH_3 , 35% v/v)

3.1.2 Gases

- Hydrogen was obtained from Thai Industrial Gas Public Company Limited (H₂, HP grade, 99.99 % purity)
- Helium was obtained from Thai Industrial Gas Public Company Limited (He, HP grade, 99.99 % purity)
- Nitrogen was obtained from Thai Industrial Gas Public Company Limited (N₂, HP grade, 99.99 % purity)
- Air was obtained from Thai Industrial Gas Public Company Limited (HP grade, 99.99 % purity)

3.2 Equipment

- Continuous flow packed bed reactor
- Rigaku Dmax X-Ray diffractometer, RINT-2200
- X-ray fluorescence spectrometer, Philips model PW 2400
- Micromeritic TPR 2900 equipped with thermal conductivity detector
- Thermo Finnigan TPDRO 1100 equipped with flame ionization detector
- Quantachrome/Autosorb 1 surface area analyzer
- Agilent Technologies model 6890N gas chromatograph equipped with flame ionization detector

3.3 Methodology

3.3.1 Catalyst Preparation

The Cu-ZnO/Al₂O₃ catalysts were prepared by various methods, including incipient wetness impregnation, co-precipitation, and so-gel preparation.

3.3.1.1 *Incipient Wetness Impregnation*

Impregnated Cu-ZnO/Al₂O₃ catalysts were prepared using γ -Al₂O₃ as a support. The γ -Al₂O₃ was first ground and sieved to the size between 20 and

40 mesh (425-850 μm). The copper and zinc were deposited by impregnation of $\gamma\text{-Al}_2\text{O}_3$ support with aqueous solution of copper nitrate and zinc nitrate. The required amounts of copper loading was 7.14 wt% and the Cu:Zn ratio was 1:4. After impregnation, the catalysts were dried at 110 $^\circ\text{C}$ overnight and subsequently calcined at 500 $^\circ\text{C}$ for 6 h.

3.3.1.2 *Co-precipitation*

The aqueous solution which homogeneously contains the desired amounts of copper nitrate, zinc nitrate, and aluminum nitrate was stirred at room temperature. The aqueous solution of NH_3 was added drop wise to the mixed nitrate solution with stirring until the pH 7 was attained. After that, the excess solution was removed by filtration. The precipitate was washed repeatedly by distilled water, followed by drying at 110 $^\circ\text{C}$ overnight and calcining at 500 $^\circ\text{C}$ for 6 h. The obtained catalyst was palletized, ground, and finally sieved to the size between 20 and 40 mesh.

3.3.1.3 *Sol-Gel Method*

The appropriate amounts of aluminum isopropoxide was ground and charged in hot water of 80 $^\circ\text{C}$ by varying AIP to water molar ratio from 1:100, 1:150, to 1:200. The mixture was stirred to disperse aluminum isopropoxide overnight and then copper nitrate, zinc nitrate, and ethylene glycol were added. After that, the mixture was stirred at 80 $^\circ\text{C}$ for 1 h. Then, nitric acid/ammonia solution was added to accelerate hydrolysis, and controlled the solution pH to the expected value. Next, the sol was evaporated at 80 $^\circ\text{C}$, obtaining a gelled solid and then calcined at different calcinations temperature (400-700 $^\circ\text{C}$). The obtained catalyst was grounded and finally sieved to the size between 20 and 40 mesh.

3.3.2 Catalyst Characterization

The prepared catalysts were characterized by various methods described as follows.

3.3.2.1 X-ray Diffraction (XRD)

The crystalline phase of catalyst was analyzed by a Rigaku Dmax X-Ray diffractometer, RINT-2200 with Cu tube for generating CuK α radiation (1.5406 Å). The system consists of a voltage generator of 40 kV. The 2θ is in the range between 20 and 80 with a scanning rate of 5°/min. This 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 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 different samples, the higher intensity indicates the higher content.

3.3.2.2 X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy was used to determine the actual Cu and Zn content of the catalysts. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy is transferred to an innermost electron. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells, and this process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

3.3.2.3 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature. 50 mg of catalyst was placed in a quartz reactor, and heated (10 °C/min) under a N₂ flow up to

150 °C, and held at the temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled down to 30 °C. Then, the sample was exposed to a stream of 5% H₂/Ar with a flow rate of 10 ml/min. After that, the sample was heated to 800 °C with a ramping rate of 10 °C/min. The amount of hydrogen consumed was monitored on-line by an SRI model 110 TCD detector as a function of temperature.

3.3.2.4 *Temperature Programmed Oxidation (TPO)*

This technique was employed to analyze the amount and characteristics of the coke deposited on the catalysts during reaction. TPO of the spent catalysts was performed in a continuous flow of 2% O₂ in He while the temperature was linearly increased with a heating rate of 10 °C/min. The oxidation was conducted in a 1/4" quartz fixed-bed reactor after the spent catalyst was dried at 110 °C overnight, weighed (30 mg), and placed between two layers of quartz wool. The sample was further purged at room temperature by flowing 2% O₂ in He for 30 minute to stabilize the signal before starting a run. The CO₂ produced by the oxidation of the coke species was converted to methane using a methanizer filled with 15% Ni/Al₂O₃ and operated at 400 °C in the presence of H₂. The evolution of methane was analyzed using an FID detector.

3.3.2.5 *Brunauer-Emmett-Tellet Method (BET)*

The surface area of the catalysts was measured by BET surface area analyzer (Quantachrome/Autosorb 1). The sample was first outgassed to remove the humidity and volatile adsorbents adsorbed on surface under vacuum at 150 °C for 6 h prior to the analysis. Then, N₂ was purged to adsorb on surface, measuring the quantity of 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 was used to calculate the BET surface area.

3.3.2.6 *Atomic Absorption Spectroscopy (AAS)*

Atomic absorption spectroscopy (Varian SpectrAA 300) was used to determine the Cu contents in the liquid products. Metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will

be absorbed. The AAS instrument seeks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve is constructed by standard solutions at various concentrations.

3.3.3 Catalytic Activity Measurement

The performance and stability of Cu-ZnO/Al₂O₃ catalysts prepared by impregnation, co-precipitation, and sol-gel method is evaluated by the glycerol dehydroxylation reaction.

3.3.3.1 *Dehydroxylation of Glycerol*

The catalytic activity was examined using a 3/4" O.D. continuous flow stainless steel packed bed reactor. The catalyst was placed at the center of reactor between two layers of glass bead and glass wool. Thermocouple was placed concentrically in the reactor to measure the temperature in the catalyst bed. The reactor was pressurized by hydrogen to a reduction pressure. All catalysts were reduced at 400 °C for 1 h in hydrogen flow prior to the activity evaluation. After that, the reactor was cooled to the working temperature (250 °C), and the hydrogen pressure was adjusted to 500 psig. An aqueous solution of 80 wt% glycerol was continuously supplied to the reactor via a high pressure pump together with a flow of hydrogen controlled by a mass flow controller. The WHSV (WHSV is given as the ratio between the hourly mass flow rate of liquid (g/h) and weight of the catalyst (g)) was fixed at 2.78 h⁻¹. After the reaction, the product was collected in a stainless steel cylinder trap immersed in an ice bath. The flow diagram of the system used for dehydroxylation of glycerol is shown in Figure 3.1.

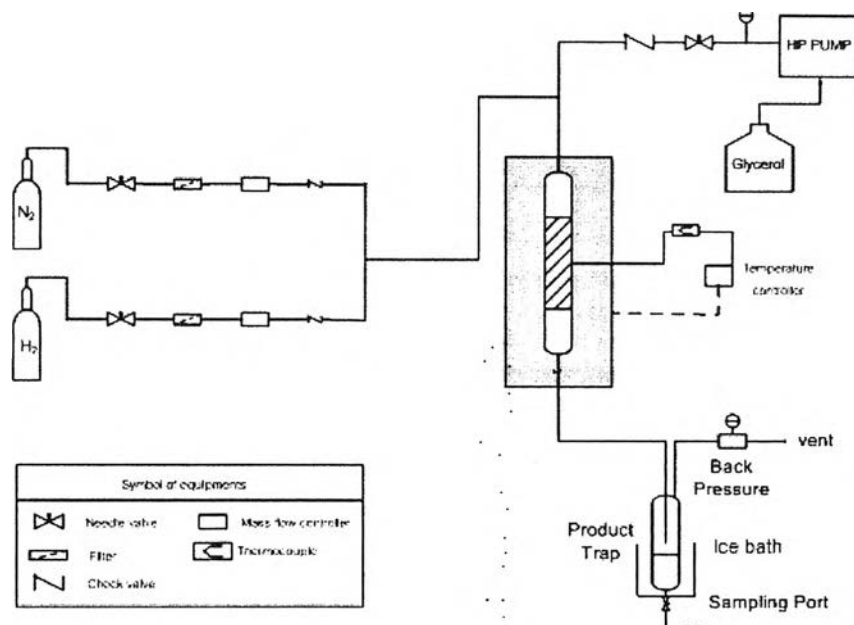


Figure 3.1 Flow diagram of the system used for dehydroxylation of glycerol.

3.3.3.2 Product Analysis

The products obtained from the reaction were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector. A Stibilwax® capillary column (diameter, 0.53 mm; length, 30 m) was used for product separation. The GC operating conditions are summarized as follows:

Injection temperature:	220 °C
Oven temperature:	80 to 200 °C with a heating rate of 10 °C/min, and hold at 200 °C for 10 min.
Carrier gas:	High purity helium
Carrier gas flow rate:	7 mL/min
Carrier gas velocity:	52 cm/sec
Column type:	Capillary column (Stibilwax®)
Detector temperature:	250 °C

For each data point, conversion of glycerol and selectivity of product were calculated. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially present, as shown in Equation 6.

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol used}}{\text{moles of glycerol input}} \times 100 \quad (6)$$

Selectivity is defined as the ratio of the number of moles of the product formed to that of the glycerol consumed in the reaction, taking into account the stoichiometric coefficient, as shown in Equation 7.

$$\text{Selectivity (\%)} = \frac{\text{moles of product obtained}}{\text{moles of glycerol used}} \times 100 \quad (7)$$

3.3.3.3 Comparison of Catalytic Performance

The comparison of catalytic performance of Cu-ZnO/Al₂O₃ catalysts prepared from various methods for the dehydroxylation of glycerol to propylene glycol was also examined in a plug flow reactor at 250 °C, 500 psig under hydrogen atmosphere, 80 wt% glycerol feed, and WHSV = 2.78 h⁻¹. The glycerol conversion, the stability, and the selectivity were used as the parameter to determine the performance.

3.3.4 Catalyst Regeneration

After the reaction, the spent Cu-ZnO/Al₂O₃ catalysts were purged by inert N₂ before regenerating in-situ at 490 °C with a heating rate of 5 °C/min and air flow rate of 10 ml/min with the steps of increasing temperature from reaction temperature to 300 °C, 400 °C, 450 °C, and end up at 490 °C by holding for an hour at each step and 3 h in the last step before cooling down to the room temperature. Then, the regenerated Cu-ZnO/Al₂O₃ catalysts were used for activity testing at the same condition as the fresh catalyst.