



CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst Supports

- Gamma aluminum oxide was obtained by Saint-Gobain NorPro Corporation ($\gamma\text{-Al}_2\text{O}_3$, 99 % purity)
- Zinc oxide was obtained from Sigma-Aldrich (ZnO, Reagent grade, 99.9 % purity)

3.1.2 Chemicals

- Aluminum (III) nitrate nonahydrate was obtained from Sigma-Aldrich ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ≥ 98 % purity)
- Ammonia solution was obtained from BDH Laboratory Supplies (NH_3 , 35% v/v)
- Cerium (III) nitrate hexahydrate was obtained from Fluka Corporation ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ≥ 99 % purity)
- Chromium (III) nitrate nonahydrate was obtained from Fluka Corporation ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ≥ 97 % purity)
- Copper (II) nitrate hemipentahydrate was obtained from Ajax Finechem Pty Ltd. ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, ≥ 99 % purity)
- Iron (III) nitrate nonahydrate was obtained from Fluka Corporation ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ≥ 98 % purity)
- Glycerol was obtained from PTT Chemical Public Company Limited ($\text{C}_3\text{H}_5(\text{OH})_3$, 99.99 % purity)
- Zirconium oxychloride octahydrate was obtained from Fluka Corporation ($\text{ZrCl}_2\text{O} \cdot 8\text{H}_2\text{O}$, ≥ 99 % purity)
- Zinc (II) nitrate hexahydrate was obtained from Ajax Finechem Pty Ltd. ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Reagent Grade, 98 % purity)

3.1.3 Gases

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

3.2 **Equipment**

- Continuous flow packed bed reactor
- Bruker SRS3400 X-ray fluorescence spectrometer
- Bruker D8 Advance X-ray diffractometer
- Micromeritic TPR 2900 equipped with thermal conductivity detector
- Thermo Finnigan TPDRO 1100 equipped with flame ionization detector
- Thermo Finnigan Sorptomatic 1990 surface area analyzer
- Agilent Technologies model 6890N gas chromatograph equipped with a flame ionization detector
- Fisons GC8000-MS800 gas chromatograph equipped with mass spectroscopy

3.3 **Methodology**

3.3.1 Catalyst Preparation

The catalysts prepared in this work are listed in Table 3.1

Table 3.1 Preparation of the catalysts used in this work

Catalyst	Preparation method	Calcination temperature (°C)
Cu/ZnO	IWI ¹	600
Cu/Al ₂ O ₃	IWI	600
CuCr ₂ O ₃ /Al ₂ O ₃	IWI	600
CuCeO ₂ /Al ₂ O ₃	IWI	600
CuFe ₂ O ₃ /Al ₂ O ₃	IWI	600
CuZnO/Al ₂ O ₃	IWI	400
	IWI	500
	COP ²	500
	IWI	600
	IWI	700

¹ IWI = Incipient wetness impregnation, ² COP = Co-precipitation

For Cu/ZnO catalyst, the zinc oxide supports were first pelletized, grounded, and sieved to the size between 20 and 40 mesh (425–850 μm). The catalysts were prepared by incipient wetness impregnation of supports with aqueous solutions of copper nitrate containing copper loading of 10 wt%. After impregnation, the catalyst was dried at 110°C overnight, and then calcined at 600°C for 6 h.

For Cu/Al₂O₃ catalyst, the catalyst was prepared by incipient wetness impregnation of aluminum oxide support with aqueous solution of copper nitrate containing the required amount of copper content (10 wt%). The aluminum oxide used as support was obtained by grinding and sieving to the size in the range of 425–850 μm. After impregnation, the catalyst was dried at 110°C overnight and subsequently calcined at 600°C for 6 h.

For the promoted Cu/Al₂O₃ catalysts, the catalysts were prepared by incipient wetness impregnation of aluminum oxide support with aqueous solution, which homogeneously dissolved both of the copper nitrate and the corresponding nitrate as precursor compound for ZnO, Cr₂O₃, CeO₂, and Fe₂O₃. In this study, the ratio of Cu to metal oxide was 1:4 followed the previous study (Swangkotchakorn., 2008). After impregnation, the samples were dried at 110°C overnight and subsequently calcined at 600°C for 6 h. In case of the CuZnO/Al₂O₃ catalyst, the samples were prepared by incipient wetness impregnation of aluminum oxide support with aqueous solution, which homogeneously dissolved both of the copper nitrate and zinc nitrate. The support was ground, and then sieved through 20–40 mesh. Impregnated supports were dried at 110°C overnight and subsequently calcined at different calcinations temperature (400–700°C) for 6 h.

For the co-precipitated CuZnO/Al₂O₃ catalyst, the aqueous solution which homogeneously dissolved the prescribed amounts of both copper nitrate, zinc nitrate, and aluminum nitrate was stirred. The aqueous solution of NH₃ was added dropwise to the mixed nitrate solution with stirring until the pH 7 was attained. After that, the excess solution was removed by filtration. Precipitate was washed repeatedly by distilled water followed by drying at 110 °C overnight, calcined at 500 °C for 6 h. Finally, the catalyst was palletized, crushed and 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 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 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.

3.3.2.2 *X-ray Diffraction (XRD)*

The crystalline phase of catalyst was analyzed by a JEOL JDX 3530 X-ray diffractometer 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 10 and 70 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 standard, 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.

3.3.2.3 *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. Fifty mg of catalyst was placed in a quartz tube reactor (1/4" O.D.), and heated (10°C/min) under a He flow up to 550°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 20 ml/min. After that, the sample was heated to 600°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 *Brunauer-Emmett-Tellet Method (BET)*

The surface area of the fresh and spent 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 4 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 is established. This volume-pressure data was used to calculate the BET surface area.

3.3.2.5 *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 12°C/min. The oxidation was conducted in a 1/4" quartz fixed-bed reactor after the spent catalyst is 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 min 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.

3.3.2.6 *X-ray Absorption Spectroscopy (XAS)*

X-ray absorption spectroscopic measurements were performed with a synchrotron radiation at beamline BL8 station of the photon laboratory, at the National Synchrotron Research Center (Nakhon Ratchasima), operated at 1.2 GeV. The data were recorded in transmission mode at room temperature using Ge(220) double crystal monochrometer. Energy was calibrated with Cu K-edge absorption (8979.0 eV), and the energy step of measurement in the XANES region was 0.2 eV.

3.3.2.7 *Transmission Electron Microscopy (TEM)*

This technique was employed to characterize size of the and morphology of the catalyst, and particle size distribution of the CuZnO/Al₂O₃ catalysts. The TEM images of the catalysts were acquired in a JEOL JEM-2100 transmission electron microscope. The pre-reduced catalyst samples were ultrasonicated for 5 min in isopropanol until a homogeneous suspension was formed.

In each determination, one drop of this mixture was placed over a TEM nickel grid and subsequently dried before the analysis.

3.3.2.8 *Scanning Electron Microscopy (SEM)*

This technique was employed to observe the morphology of the CuZnO/Al₂O₃ catalysts. The samples were first placed on the stub and coated with a thin layer of gold. The SEM images of the catalysts were acquired in a JEOL JSM-6400 scanning electron microscope attached with an energy dispersive X-ray spectrometer.

3.3.2.9 *Thermogravimetric-differential thermal analyzer (TG-DTA)*

Simultaneous thermogravimetry and differential thermal analysis (TG-DTA) was used to study the thermal decomposition behavior of the impregnated catalyst and obtain suitable calcination temperature for removing metal precursors. The dried sample of 5-20 mg was heated from 30 to 700°C with a heating rate of 10°C/min in nitrogen gas.

3.3.3 Catalytic Activity Measurement

The performance and stability of catalysts were evaluated by the glycerol dehydroxylation reaction.

3.3.3.1 *Dehydroxylation of Glycerol*

The catalysts prepared were tested for their catalytic performance and stability in converting glycerol to propylene glycol. The dehydroxylation reaction was performed in a continuous flow stainless steel packed bed reactor (3/4" O.D.). The catalyst was placed at the center of reactor between two layers of glass bead and glass wool. A thermocouple was placed concentrically in the reactor to measure the temperature in the catalyst bed. The catalyst was first activated in a stream of hydrogen from room temperature to 300°C with a heating rate of 5°C/min and held at this temperature for 1 h. The catalyst was brought up to the reaction temperature (250°C) and pressure (500 psi). An aqueous solution of 80 wt% glycerol is continuously supplied to the reactor via a high pressure pump together with a flow of hydrogen controlled by a mass flow controller. The LHSV (LHSV is given as the ratio between the volumetric flow rate and the volume of

catalyst) is 6 h^{-1} . After the reaction, the product is 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.

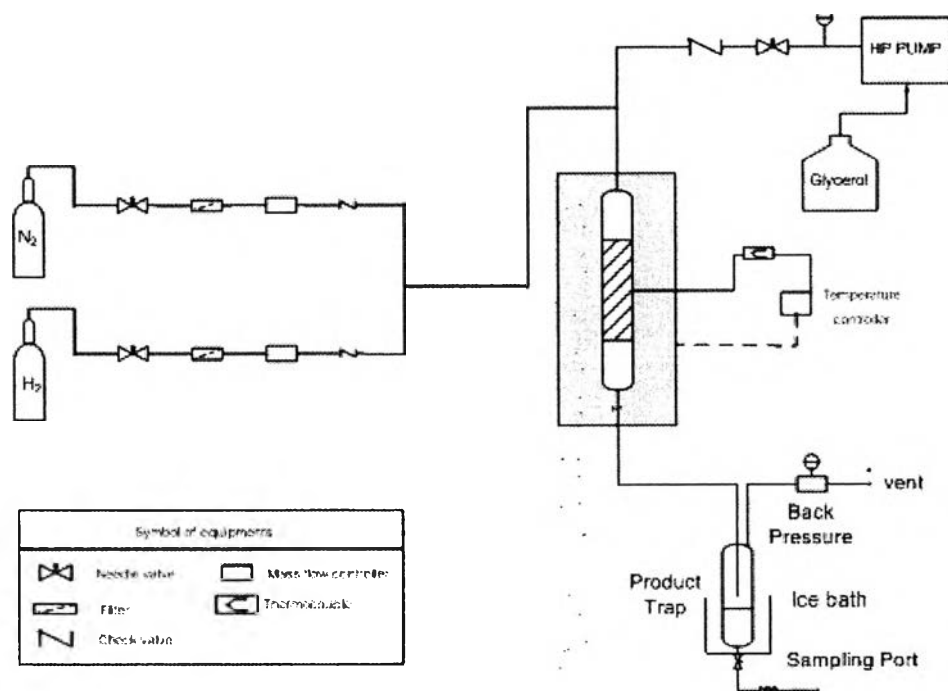


Figure 3.1 Flow diagram of the system used for dehydroxylation of glycerol.

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 Stabilwax® 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 held 10 min (heating rate 10°C/min)
Carrier gas:	High purity helium
Carrier gas flow rate:	7 mL/min
Carrier gas velocity:	52 cm/sec

Column type:	Capillary column (Stabilwax [®])
Detector temperature:	250°C

For each data point, selectivity of product, conversion of glycerol, and yield 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 1.

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol used}}{\text{moles of glycerol input}} \times 100 \quad (1)$$

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 2.

$$\text{Selectivity (\%)} = \frac{\text{moles of product obtained}}{\text{moles of glycerol used}} \times 100 \quad (2)$$

Yield of product is defined as the ratio of the number of moles of product produced to the theoretical number of moles of the product, as shown in Equation 3.

$$\text{Yield (\%)} = \frac{\text{moles of product obtained}}{\text{moles of glycerol input}} \times 100 \quad (3)$$

3.3.3.3 Comparison of Catalytic Performance

The comparison of catalytic performance between Cu-based binary and Cu-based ternary catalysts in the dehydroxylation of glycerol to propylene glycol was also determined.