

CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Equipment

• High pressure packed-bed continuous flow reactor system consisting of;

- Mass flow controller (Brooks Instrument 5850E)
- High pressure liquid pump (TELEDYNE ISCO D-Series)
- Back pressure regulator (Swagelok)
- 16 mm I.D. × 40 mm long stainless steel reactor (Swagelok)

• Gas chromatograph (Agilent Technology model 6890N network gas equipped with a Stabilwax[®] capillary column (0.53 mm × 30 m) and flame ionization detector)

- Surface area analyzer (SAA, Quantachrome/Autosorb1)
- Temperature programmed reduction equipment (TPR)
- Temperature programmed oxidation equipment (TPO)
- Atomic absorption spectroscopy (AAS, Varian)
- X-ray fluorescence spectrometer, Philips model PW 2400
- X-ray absorption spectroscopy (XAS)
- Stirring hot plate (Cole Parmer)
- Oven (Carbolite CWE 1100)

3.1.2 Chemicals

Metal Precursors

- Copper (II) nitrate, (Cu(NO₃)₂·2.5H₂O, Lab grade ≥ 99 % purity)
- Zinc (II) nitrate, (Zn(NO₃)₂·6H₂O, Reagent Grade, 98 % purity)

Supports

- Magnesium oxide (MgO, Lab grade ≥ 99 % purity)
- Magnesium (II) nitrate, (Mg(NO₃)₂·6H₂O, Reagent Grade, 99 % purity)

Feedstocks

- Glycerol (C₃H₅(OH)₃, Refined grade, 99.99 % purity)

Gases

- Hydrogen (H₂, HP grade, 99.99 % purity)
- Helium (He, HP grade, 99.99 % purity)
- Nitrogen (N₂, HP grade, 99.99 % purity)
- Air (HP grade, 99.99 % purity)

3.2 Experimental Procedure

3.2.1 Catalyst Preparation

In this study, the catalytic dehydroxylation of glycerol to propylene glycol was conducted over the CuZnO catalyst supported on MgO prepared by two different methods—incipient wetness impregnation (IWI) and co-precipitation (COP).

The CuZnO/MgO (COP) catalyst was prepared using an aqueous solution containing desired amounts of copper nitrate, zinc nitrate, and magnesium oxide. First the mixture was stirred with a magnetic stirrer at room temperature. Then, ammonia solution was added to the mixture at a rate of one drip of dropper per second under vigorously stirring until the pH of the mixed solution reached 10.5. After that, the catalyst was aged at room temperature for 12 h followed by filtration and thoroughly washed with distilled water until free of ions. This precipitate was dried at 110 °C overnight and calcined at 550 °C for 4 h. The obtained catalyst was palletized, ground, and finally sieved to the size between 450 and 850 μm (20-40 mesh).

The CuZnO/MgO (IWI) catalyst was prepared using magnesium oxide as the catalyst support. The magnesium oxide was pretreated at 550°C for 4 h. Copper and zinc were impregnated into the magnesium support with a mixed aqueous solution of copper nitrate and zinc nitrate. After the impregnation the catalyst was dried in ambient air at 110 °C overnight and calcined at 550 °C for 4 h. The obtained catalyst was palletized, ground, and finally sieved to the size between 450 and 850 μm (20-40 mesh).

3.2.2 Catalyst Characterization

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

3.2.2.1 *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. In each test, 50 mg of catalyst was placed in a quartz reactor, 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.

3.2.2.2 *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 were performed in a continuous flow of 2% O₂ in He while the temperature will be linearly increased with a heating rate of 10 °C/min. The oxidation was conducted in a 1/4" quartz fixed-bed reactor. The spent catalyst was placed between two layers of quartz wool. The CO₂ produced by the oxidation of the coke species were 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.

3.2.2.3 *Brunauer-Emmett-Teller Method (BET)*

The surface area of the fresh and spent catalysts were 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 intained 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.

3.2.2.4 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy (Varian SpectrAA 300) was used to determine the Cu contents in the liquid products. Metals absorbed ultraviolet light when they were excited by heat. Each metal had a characteristic wavelength that was absorbed. The AAS instrument sought 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 was aspirated into the flame. If that metal was present in the sample, it absorbed some of the light, thus reducing its intensity. The instrument measured the change in intensity. A computer data system converted the change in intensity into an absorbance. As a concentration increases, an absorbance increases. A standard calibration curve was constructed by standard solutions at various concentrations.

3.2.2.5 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 $\text{CuK}\alpha$ radiation (1.5406 Å). The system consists of a voltage generator of 40 kV and 30 mA. The 2θ is in the range between 20° and 80° with a scanning rate of $5^\circ/\text{min}$. 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.

3.2.2.6 *X-ray Absorption Spectroscopy (XAS)*

The electronic structure of the catalysts was studied by using X-ray absorption spectroscopic measurements performed with synchrotron radiation at beam line BL8 station of the photon factory, operated at 2.5 GeV with about 10^6 - 10^8 mA of ring current. The data were recorded in transmission mode at room temperature using Ge (220) double crystal monochromator. Energy was calibrated with Cu K-edge absorption (8981.0 eV) and energy step of measurement in the XANES region was 0.3 eV. For the extended X-ray absorption fine structure (EXAFS) analysis, the oscillation was normalized by edge height around 50 eV higher than the absorption edge. The data analysis was performed using the Athena version 0.9.18.2.

3.3 Feedstock Characterization

3.3.1 Gas Chromatography with Flame Ionization Detector (GC/FID)

All feedstock obtained from the reaction were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector to find amount of glycerol. A Stibilwax® capillary column (diameter, 0.53 mm; length, 30 m) was used for product separation and identification.

3.4. Catalytic Activity Measurement

The performance and stability of CuZnO/MgO catalysts were evaluated for the glycerol dehydroxylation reaction.

3.4.1 Dehydroxylation of Glycerol

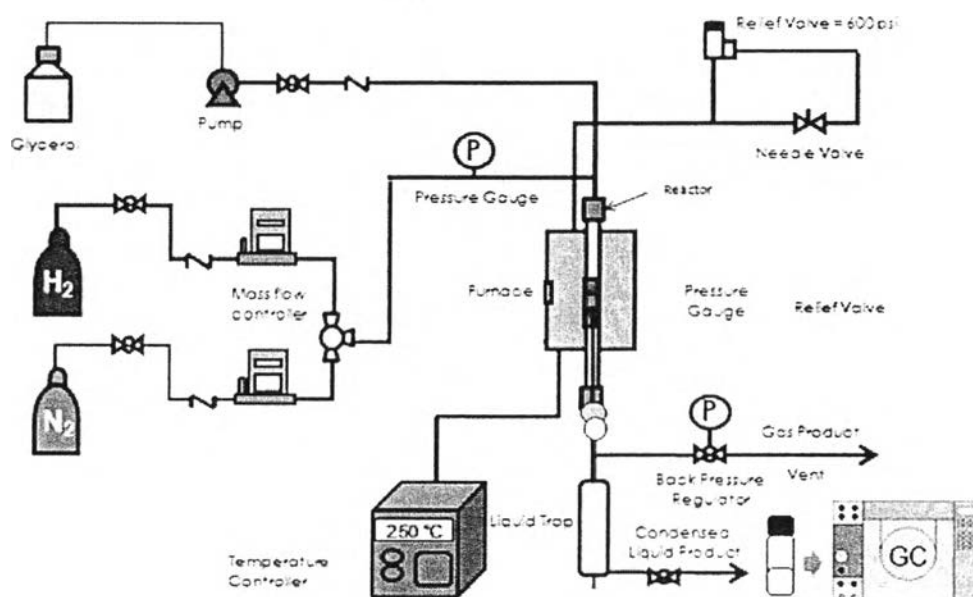


Figure 3.1 Flow diagram of the system used for dehydroxylation of glycerol.

The catalytic activity was examined using a 16 mm O.D. continuous flow packed bed stainless steel reactor. In each test, about 2 gram of catalyst was placed at the center of reactor between two layers of glass bead and glass wool. Thermocouples were 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 flow of liquid and the weight of the catalyst) was 3.77 h^{-1} . After the reaction, the products were 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.

3.4.2 Product Analyses

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: | 493 K |
| Oven temperature: | 353 to 473 K held 10 min (heating rate 10 K/min) |
| Carrier gas: | High purity helium |
| Carrier gas flow rate: | 7 mL/min |
| Carrier gas velocity: | 52 cm/s |
| Column type: | Capillary column (Stabilwax®) |
| Detector temperature: | 523 K |

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 4.1.

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol used}}{\text{moles of glycerol input}} \times 100 \quad (4.1)$$

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 4.2.

$$\text{Selectivity (\%)} = \frac{\text{moles of product obtained}}{\text{moles of glycerol used}} \times 100 \quad (4.2)$$

3.4.3 Comparison of Catalytic Performances

The comparison of catalytic performance of CuZnO/MgO 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 = 3.77 h⁻¹. The glycerol conversion, the stability, and the selectivity were used as the parameters to determine the performance.

3.5 Catalyst Regeneration

After the reaction, the spent CuZnO/MgO 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 room temperature. Then, the regenerated CuZnO/MgO catalysts were reused for activity testing at the same condition as the fresh catalyst.