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/Autosorb-1MP)

- Temperature programmed reduction equipment (TPR)

- Temperature programmed oxidation equipment (TPO)

- Temperature programmed desorption equipment (TPD)

- X-ray diffraction (XRD)

- X-ray Fluorescence Spectroscopy (XRF)

- X-ray Photoelectron Spectroscopy (XPS)

- Fourier Transform Infrared Spectroscopy (FTIR)

- Stirring hot plate (Cole Parmer)

- Oven (Carbolite CWE 1100)

3.1.2 Chemicals

Metal Precursors

- Copper (II) nitrate, ($Cu(NO_3)_2 \cdot 2.5H_2O$, Lab grade ≥ 99 % purity)
- Zinc (II) nitrate, ($Zn(NO_3)_2 \cdot 6H_2O$, Reagent Grade, 98 % purity)

Supports

- Magnesium (II) nitrate, (Mg(NO$_3$)$_2$·6H$_2$O, Reagent Grade, 99 % purity)
- Aluminium nitrate, (Al(NO$_3$)$_3$·9H$_2$O, Reagent Grade, 98 % purity)

Feedstocks

- Glycerol (C$_3$H$_5$(OH)$_3$, Refined grade, 99.99 % purity)
- Glycerol (C$_3$H$_5$(OH)$_3$, Yellow grade, 80 % purity)

Gases

- Hydrogen (H$_2$, HP grade, 99.99 % purity)
- Helium (He, HP grade, 99.99 % purity)
- Nitrogen (N$_2$, 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-Al$_2$O$_3$ mixed oxide support prepared by incipient wetness impregnation (IWI) and co-precipitation (COP) methods respectively.

The MgO(x)–Al$_2$O$_3$(y) mixed oxide supports were prepared by co-precipitation method by varying ratios of x:y from 5:95, 10:90, 15:85, 20:80, and 30:70. These oxides were precipitated by adding aqueous ammonia to mixed solutions of aluminum nitrate and magnesium nitrate (final pH = 9.5). Then the gels were dried at 110 °C for 24 h and calcined at 500 °C for 8 h. The CuZnO/ MgO-Al$_2$O$_3$ catalysts were prepared by depositing solution of copper nitrate and zinc nitrate on the mixed oxide supports by the impregnation method. The atomic ratio of Cu:Zn is maintained as 1: 4. The catalysts were dried at 110 °C for 24 h and calcined at 500 °C for 24 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% H_2/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% O_2 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 CO_2 produced by the oxidation of the coke species were converted to methane using a methanizer filled with 15% Ni/Al_2O_3 and operated at 400 °C in the presence of H_2. The evolution of methane was analyzed using an FID detector.

3.2.2.3 Temperature-Programmed Desorption of Ammonia (NH₃-TPD)

Acidity properties of the catalysts were determined by ammonia temperature-programmed desorption, NH_3-TPD. The NH_3-TPD was performed in a homemade flow apparatus using a quarter inch quartz tube reactor. Sample was first reduced at 400 °C in H_2 flow of 30 mL/min for 1 h. And then the reactor was cooled to 50 °C in He, exposed to 10% NH_3/He for 30 min, purged by He for 1 h at 50 °C in order to eliminate the physical adsorbed NH_3. Temperature

programmed desorption was conducted by ramping to 550 °C at 10 °C/min and NH_3 ($m/e = 17$) in effluent was detected and recorded as a function of temperature by an online MS detector (MKS Cirrus).

3.2.2.4 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, N_2 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 surface area.

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 CuKα 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°/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.

3.3.2.6 X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy was used to determine the actual Cu, Zn, Mg, and Al contents 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.

3.2.2.7 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) spectra were carried out using a Kratos UltraX-ray photoelectron spectrometer. The monochromatic $AlK\alpha$ was used as an X-ray source (anode HT = 15 kV). The spectrometer was operated with the pass energy of 160 and 40 eV for wide and narrow scan, respectively. The XPS peaks were referenced to the binding energy of C (1s) peak at 285 eV.

3.2.2.8 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) analysis was performed to identify the species that absorbed to the surface of the fresh and spent catalysts. The IR spectra were collected using a Nicolet, Nexus 670 FTIR spectrometer. The spent catalyst samples were grounded into fine powder and mixed with KBr. The mixture was used for the preparation of KBr pellets. The IR spectrum was obtained over a frequency between 400 and 4000 cm^{-1}.

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 catalysts were evaluated for the glycerol dehydroxylation reaction

3.4.1 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.
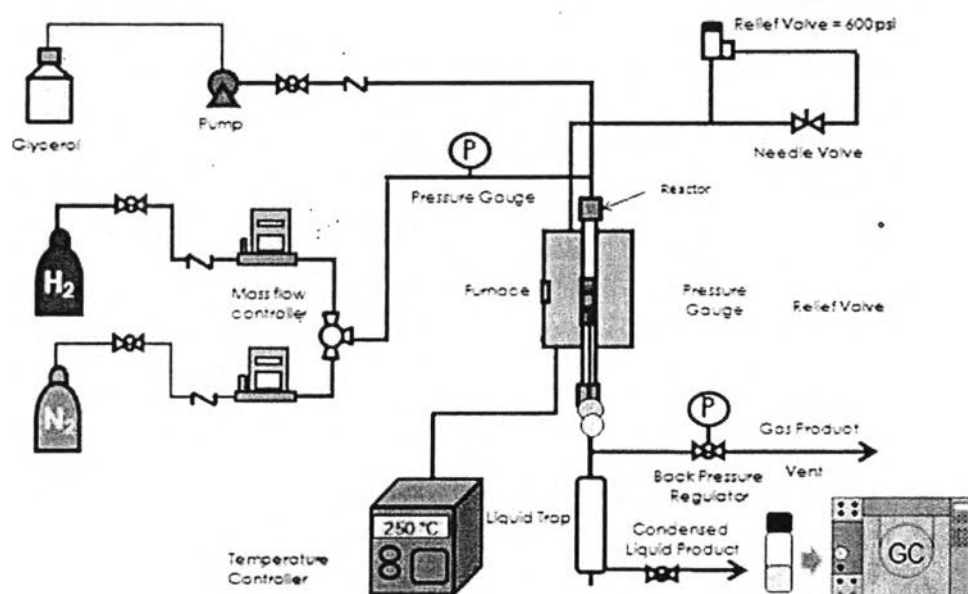
Figure 3.1 Flow diagram of the system used for dehydroxylation of glycerol.

3.4.2 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:	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.

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

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.

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

3.4.3 Comparison of Catalytic Performances

The comparison of catalytic performance of CuZnO/MgO–Al$_2$O$_3$catalysts prepared by varying the proportions of MgO and Al$_2$O$_3$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.