CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 Chemicals

- Metal Precursors

  – Copper (II) nitrate, ($Cu(NO_3)_2 \cdot 2.5H_2O$, lab grade ≥ 99 % purity) was obtained from Ajax Finechem Pty Ltd.

  – Zinc (II) nitrate, ($Zn(NO_3)_2 \cdot 6H_2O$, reagent grade, 98 % purity) was obtained from Ajax Finechem Pty Ltd.

- Supports

  – Aluminum oxide (γ-Al_2O_3, extrudate with 99% purity) was obtained by Saint-Gobain NorPro Corporation.

  – MgO (Magnesium Oxide, ≥ 98 % purity) was obtained from Panreac Química S.L.U., E.U.

  – Hydrotalcite ($CH_{16}Al_2Mg_6O_{19} \cdot 4H_2O$) was obtained from Sigma-Aldrich Co., USA.

  – ASA (Amorphous Silica Alumina) was obtained from Sigma-Aldrich Co., USA.

- Feedstocks

  – Glycerol ($C_3H_8O_3$, reagent grade) was obtained from Fisher Chemical, UK.

3.1.2 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)

All gases mentioned above were supplied from TIG, Thailand.

3.1.3 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 chromatograph equipped with a Stabilwax® capillary column (0.53 mm × 30 m) and flame ionization detector)
- Surface area analyzer (SAA, Quantachrome/Autosorb1)
- Thermo Finnigan TPDRO 1100 equipped with flame ionization detector
- Temperature programmed reduction (TPR) equipment
- Temperature programmed oxidation (TPO) equipment
- Atomic absorption spectroscopy (AAS, Avanta GBC)
- Stirring hot plate (Cole Parmer)
- Oven (Carbolite CWE 1100)

3.2 Experimental Procedure

3.2.1 Catalyst Preparation

The CuZnO-based catalysts were prepared by incipient wetness impregnation methods. The support was dried at 110 °C overnight and subsequently calcined at 500 °C for 4 h for removing water and impurities from the supports. And then the support was ground and sieved to the size between 20 and 40 mesh (425-850 µm). The copper and zinc oxide were deposited by impregnation of support with aqueous solution of copper nitrate and zinc nitrate. After impregnation, the catalysts was dried at 110 °C overnight and subsequently calcined at 500 °C for 6 h.

3.2.2 Catalyst Characterization

The prepared catalysts will be 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. 50 mg of catalyst will be 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 will be then cooled down to 30°C. Then, the sample will be exposed to a stream of 5% H_2/Ar with a flow rate of 20 ml/min. After that, the sample will be heated to 600°C with a ramping rate of 10 °C/min. The amount of hydrogen consumed will be 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 Carbon Dioxide (CO_2-TPD)

Basicity measurements were performed by temperature programmed desorption of carbon dioxide. 0.3 g of catalyst was placed in a quartz reactor, and heated (10 °C/min) under a N_2 flow up to 120 °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 40 °C. Then, the sample was desorbed by CO_2 for 150 min. After that, the sample was flushed by N_2 for 1 h. Then, the sample was exposed to a stream of He with a flow rate of 20 ml/min. After that, the sample was heated to 800 °C with a ramping rate of 10 °C/min. The amount of CO_2 desorbed was monitored on-line by an SRI model 110 TCD detector as a function of temperature. Pulse of carbon dioxide was used for calibrating desorbed carbon dioxide to calculate basicity.

3.2.2.4 Brunauer-Emmett-Tellet 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 BET surface area.

3.2.2.5 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 seeked 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 measureed 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.

3.2.2.6 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. The 2θ is in the range between 20 and 80 with a scanning rate of 5 °C /min. This analysis was generally performed based on the fact that an x-ray diffraction pattern was unique for each crystalline substance. Thus, if an exact match could be found between the pattern of an unknown and sample, chemical identity can be assumed. It was 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.

3.2.3 Catalytic Activity Measurement

The performance and stability of Cu-ZnO/Al_2O_3 catalysts were evaluated by the glycerol dehydroxylation reaction.

3.2.3.1 Dehydroxylation of Glycerol

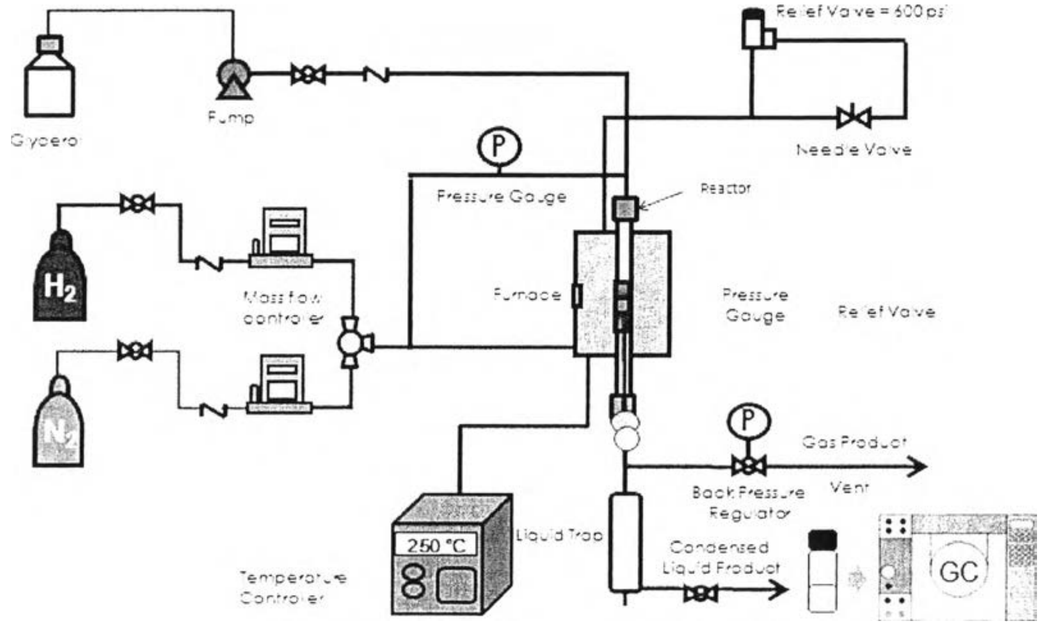

Figure 3.1 Flow diagram of the system used for dehydroxylation of glycerol

The catalytic activity was examined using a 16 mm O.D. continuous flow stainless steel packed bed reactor. In each test, 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 will be 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) will be 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.

3.2.3.2 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) will be used for product separation. The GC operating conditions are summarized as follows:

Injection temperature:	200 °C
Oven temperature:	40 °C held 5 min, 40 °C 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:	48 cm/s
Column type:	Capillary column (Stabilwax®)
Detector temperature:	300 °C

For each data point, selectivity of product and conversion of glycerol were calculated. Conversion of glycerol is defined as the ratio of number of mass of glycerol consumed in the reaction to the total mass of glycerol initially present, as shown in Equation 3.1.

$$\text{Glycerol conversion (\%)} = \frac{\text{mass of glycerol input} - \text{mass of glycerol output}}{\text{mass of glycerol input}} \times 100 \qquad (3.1)$$

Selectivity is defined as the ratio of the number of mass of the product formed to that of the glycerol converted in the reaction, taking into account the stoichiometric coefficient, as shown in Equation 3.2.

$$\text{Selectivity (\%)} = \frac{\text{mass of product obtained}}{\text{mass of glcerol converted}} \times 100 \qquad (3.2)$$

3.2.4 Catalyst Regeneration

After the reaction, the spent Cu-ZnO/MgO catalysts were purged by inert N_2 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/MgO catalysts were used for activity testing at the same condition as the fresh catalyst.