

CHAPTER III

EXPERIMENTAL

3.1 Materials

The bio-ethanol used for the catalytic dehydration of ethanol was obtained from Saphthip Company Limited at the concentrations of 99.5% ethanol.

3.2 Equipment

1. Bench-scale U-tube reactor
2. Ice-water cooling system
3. Oven
4. Syringe pump
5. Sieves, Mesh 20-40
6. Agilent Technologies 6890, Gas chromatography (GC)
7. Grinder machine
8. Hydraulic pellet machine
9. Condensing flask
10. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
11. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption/Reduction/Oxidation)
12. X-Ray diffractometer system (X-Ray Diffraction. XRD)
13. X-Ray photoelectron spectroscopy (XPS)
14. X-Ray Fluorescence (XRF)
15. A Gas Chromatography-equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent© 7890 with 2D dimension mode

3.3 Chemicals and Solvents

1. Deionized water
2. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
3. Cobalt (III) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
4. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)
5. Chromium (III) nitrate hydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$)
6. Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)
7. Palladium (II) nitrate hydrate ($\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$)
8. Helium gas
9. γ -Alumina ($\gamma\text{-Al}_2\text{O}_3$)
10. Carbon disulfide (CS_2)

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

To prepare the metal-promoted catalyst, alumina was purchased from Sigma-Aldrich and was calcined in the furnace at 500°C for 2 h. A solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pd}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, was used as a precursor of Ni, Co, Fe, Cr, Cu, and Pd, respectively. The solution of these compounds was individually loaded on the calcined $\gamma\text{-Al}_2\text{O}_3$ support by using incipient wetness impregnation technique. After impregnation, the wet catalyst was dried in an oven at 120°C overnight, followed by calcination at 600°C for 3 hours. The calcined catalysts were reduced in hydrogen atmosphere at 500°C for 2 h with a heating rate of $10^\circ\text{C}/\text{min}$. The last step was to pelletize, and after that sample was hydraulically pressed to pellets. Subsequently, the pellets were crushed and sieved to 20 - 40 mesh particles before it was loaded into the reactor.

3.4.2 Catalyst Characterization

3.4.2.1 *X-ray Diffraction (XRD)*

The structure of catalysts and metal dispersion on the alumina support were obtained from XRD patterns using Rigaku/Rint2200 HV. For characterization procedures, the catalyst sample in powder form was packed in a glass specimen holder that was placed in the goniometer using $\text{CuK}\alpha$ small radiation (1.5406 Å) operating at 40 kV and 30 mA. The XRD patterns were recorded with a step size $2\theta = 0.01$ degrees at the scanning speed of 5 degree/min

3.4.2.2 *Surface Area Analyzer (SAA)*

The Brunauer-Emmett-Teller (BET) technique was used to determine the specific surface area, the total pore volume and the pore size of catalyst, using model Thermo Finnigan/Sorptomatic 1990, which is based on the physical adsorption of nitrogen gas. The sample was initially de-gassed to remove the moisture and unsettled adsorbents adsorbed on the catalyst surface under vacuum at 300 °C at least 18 hours prior to analysis steps. The specific surface area and the pore size of catalyst were obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the Barret-Joyner-Halendar (BJH) method.

3.4.2.3 *X-ray Photoelectron Scanning (XPS)*

XPS was used to determine the oxidation states of metal oxides dispersed in zeolites. The scan pass energy was 160 eV for wide scan and 40 eV for narrow scan. The electron source was Al $\text{K}\alpha$ that gave 10 mA of emission and 15 kV of anode HT. The neutralizer was set at 1.8 A of filament current, 2.6 V of charge balance, and 1.3 V of filament bias.

3.4.3 Catalytic Reaction

The catalytic dehydration of bio-ethanol to liquid hydrocarbons was performed in a continuous U-tube fixed-bed reactor (10 mm, inside diameter and 45.8 cm, length) under atmospheric pressure. For investigating the possibility of ethylene chain growth over metal-promoted catalysts, 3.0 g of the prepared catalyst was individually loaded in a U-tube reactor. These catalysts were preheated at 400 °C for 1-2 hours in helium steam prior to the reaction and the reaction are conducted

at 400 °C for 8 hours. The liquid bio-ethanol (99.5 % purity) was fed by a syringe pump into the U-tube reactor with a flow rate of 1.97 ml/h. It was heated to vaporize before being contacted with the catalyst bed maintained at the desired reaction temperature. The high purity helium gas was used as a carrier gas. The effluent coming out of the U-tube reactor was condensed in a cooling condensing flask to collect the condensable products while the non-condensable products were passed from the cooling condensing flask to an online gas chromatograph.

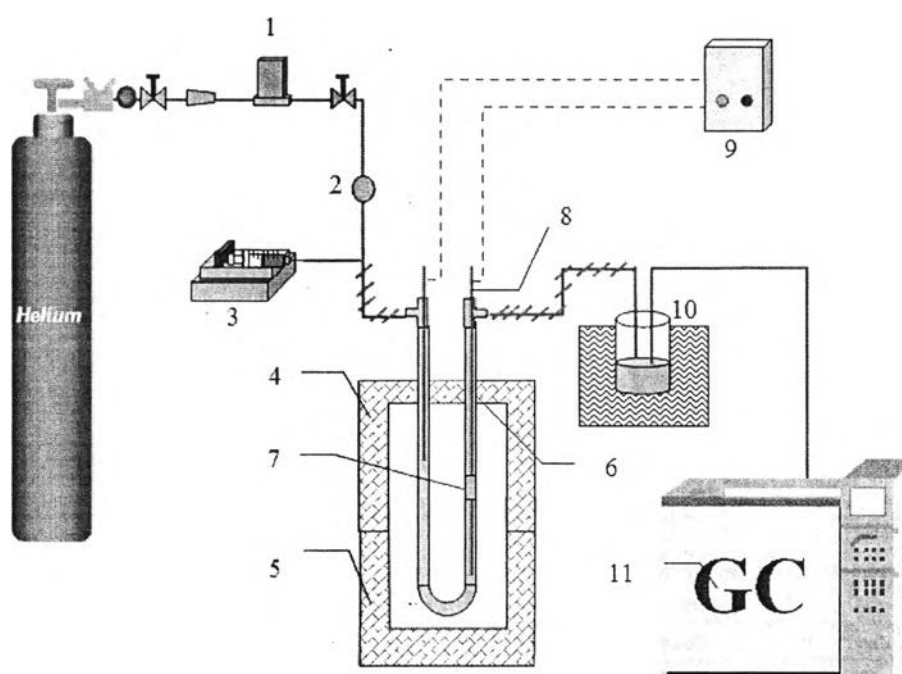


Figure 3.1 Schematic of experimental set-up: 1 = Flow meter, 2 = Pressure gauge, 3 = Syringe pump, 4 = Upper electric furnace, 5 = Lower electric furnace, 6 = U-tube reactor, 7= Catalytic layer, 8 = Thermocouple, 9 = Temperature programmed controller, 10 =Cooling unit, 11 = Gas chromatograph.

3.4.4 Product Analysis

3.4.4.1 *Liquid Product Analysis*

The liquid products formed during the catalytic reactions were collected in the condensing flask at -5 °C. The liquid product consisted of oil and aqueous solution that were weighed and separated for further analysis. CS₂ can be

used if the liquid product does not separate. The obtained oil was analyzed to determine the fraction of BTEX by using a Gas Chromatograph equipped with a Mass Spectrometry of “Time of Flight” type (GC-TOF), Agilent© 7890 with 2D dimension mode. Helium was used as the carried gas, and nitrogen was used in the cooling system. The conditions were set as follows: initial temperature of 80 °C, time at initial temperature of 2 minutes, 4 °C/min heating rate, final temperature of 270 °C held for 5 min, and split ratio at 1:50. In addition, a Varian CP-3800 Simulated Distillation Gas Chromatograph (SIMDIST-GC), conformed with ASTM D2887 method for true boiling point curves, was employed to identify the classification of petroleum fractions such as Gasoline (<149 °C) , Kerosene (149-232 °C), Gas oil (232-343 °C) , Light Vacuum Gas oil (LVGO, 343-371 °C), and Heavy Vacuum Gas Oil (HVGO, >371 °C). An oil sample was injected to the SIMDIST-GC after dilution with carbon disulphide (CS₂) at a ratio of 1:100. The conditions were set as follows: initial temperature of 30 °C, time at initial temperature of 0.01 min, heating rate of 20 °C/min, final temperature of 320 °C, and 8.50 min holding time.

3.4.4.2 Gaseous Product Analysis

The gaseous products formed during the catalytic reaction were analyzed by an online gas chromatograph (Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20 µm film thicknesses, and DB-WAX column: 30 m x 0.32 mm ID and 20 µm film thicknesses). The gas chromatograph was provided with a thermal conductivity detector (TCD) to detect hydrocarbons as well as carbon dioxide (HP-PLOT Q Column), and a flame ionization detector (FID) to detect oxygenate components (DB-WAX Column), and helium was used as the carrier gas. The conditions were set as follows: initial temperature of 40 °C, time at initial temperature of 10 min, Ramp 1: heating rate of 10 °C/min, final temperature of 120 °C, 10 min holding time, Ramp 2: heating rate of 10 °C/min, final temperature of 200 °C, 10 min holding time, and Ramp 3: heating rate of 10 °C/min, final temperature of 220 °C, 2 min holding time.