

CHAPTER III

EXPERIMENTAL

3.1 Materials

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

3.2 Equipment

1. Bench-scale U-tube reactor
2. Electrical furnace
3. Ice-water cooling system
4. Oven
5. Syringe pump
6. Sieves, Mesh 20-40
7. Agilent Technologies 6890, Gas chromatography (GC)
8. Grinder machine
9. Hydraulic pellet machine
10. Condensing flask
11. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
12. X-Ray Fluorescence (XRF)
13. Raman Spectroscopy (PerkinElmer, Spectrum GX)
14. Scanning Electron Microscope (SEM)
15. A Varian CP-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC), conformed with ASTM D2887
16. 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. di-Ammonium Hydrogen Phosphate ((NH₄)₂HPO₄)
3. Antimony Trichloride (SbCl₃)
4. Bismuth (III) Chloride (BiCl₃)

5. Helium gas
6. Gallium (III) nitrate hexahydrate 99.9 % ($\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$)
7. NH_4 -ZSM-5 zeolite (Si/Al = 20, 840NHA grade, Tosoh company)
8. Na-X zeolite (Si/Al = 3.5, F-9 grade, Tosoh company)
9. NH_4 -Beta zeolite (Si/Al = 13.5, 930NHA grade, Tosoh company)
10. H-Y zeolite (Si/Al = 7, 360HUA grade, Tosoh company)
11. Carbon disulfide (CS_2)

3.4 Experimental Procedures

3.4.1 Catalyst Preparation

3.4.1.1 *The Two Consecutive Layers of Catalytic Systems*

To prepare the catalyst used in the first layer, the nitrate solution of gallium (99.9 %) was used as the source of Ga. Ga_2O_3 -modified HZSM-5 catalysts were prepared by the incipient wetness impregnation technique. An appropriate amount of gallium nitrate solution was loaded on the calcined HZSM-5 support (Si/Al = 20, 840NHA grade, Tosoh company) to reach 2.0 wt % Ga element. After impregnation, the wet catalyst was dried in an oven at 120°C overnight, followed by calcination at 550 °C for 5 hours. Then, the calcined 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.

To prepare the catalysts used in the second consecutive layer, Na-X zeolite (Si/Al = 3.5, zeolum F-9 grade, Tosoh company), H-Y zeolite (Si/Al = 7, 360HUA grade, Tosoh company), and NH_4 -Beta zeolite (Si/Al = 13.5, 930NHA grade, Tosoh company) were initially dried in an oven at 120°C overnight, followed by calcination at 550 °C for 5 hours to obtain the proton form of H-X, H-Y, and H-Beta zeolite catalysts.

3.4.1.2 *HZSM-5 Modified with Oxides of Group VA Elements*

The catalysts studied were prepared from a commercial NH_4 -ZSM-5 zeolite (Si/Al = 20, 840NHA grade, Tosoh company). NH_4 -ZSM-5 was initially dried in an oven at 120°C overnight, followed by calcination at 550 °C for 5

hours to obtain the proton form of HZSM-5 zeolite catalyst. The diammonium hydrogen phosphate ((NH₄)₂HPO₄), antimony trichloride (SbCl₃), and bismuth chloride (BiCl₃) solution were used as the source of P, Sb, and Bi, respectively. A solution of these compounds was individually loaded on the HZSM-5 support using the incipient wetness impregnation technique with the loading amount that finally gave 1.0 wt %, 2.0 wt %, 3.0 wt %, and 4.0 wt % of each element on the support. After impregnation, the wet catalyst was dried in an oven at 120°C overnight, followed by calcination at 550 °C for 5 hours. Then, the calcined 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 *Surface Area Analyzer (SAA)*

The Brunauer-Emmett-Teller (BET) technique was employed to determine the specific surface area, the total pore volume and the pore size of catalyst, using Thermo Finnigan/Sorptomatic 1990, which is based on the physical adsorption of nitrogen gas. The sample was initially out-gassed to remove the humidity and volatile 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 BJH method.

3.4.2.2 *X-Ray Fluorescence (XRF)*

X-ray fluorescence spectrometry (AXIOS PW4400) is a non-destructive analytical technique used to identify and determine the concentrations of elements present in the solid and powder samples. XRF is capable of measuring all elements from beryllium to uranium and beyond, at trace levels often below one part per million and up to 100 %. A little amount of sample is needed, or no special preparation is required although materials should be presented to the spectrometer in a homogeneous, reproducible form. The powder samples were hydraulically pressed to give a flat surface. The conditions were set as follows: internal flow of 4.10 l/min,

external flow of 2.49 l/min, cabinet temperature of 29.97 °C, primary temperature of 19.00 °C, vacuum of 10.10 Pa, x-ray generation of 50 kV (60 mA), 150 µm of collimator, angle of 10.0002 degree, gas flow 0.90 l/h, and gas pressure of 1020.8 hPa.

3.4.2.3 Raman Spectroscopy

Raman spectroscopy (PerkinElmer, Spectrum GX) is used for oxide identification of each catalyst. The powder of a catalyst was placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10d and 50d objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a charge coupled device (CCD). Raman spectra were recorded using a 1064 nm laser at a resolution of 8 cm⁻¹ in the range between 200 and 3500 cm⁻¹ and the number of scans of 500. Repeated acquisition using the highest magnification was accumulated to improve the signal-to-noise ratio. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer.

3.4.2.4 Scanning Electron Microscope (SEM)

The microstructure of the sample was identified by the scanning electron micrographs (JEOL/JSM 5200). The SEM uses the electrons that are backscattered or emitted from the specimen surface. The samples were placed on a stub and coated with gold by using ion sputtering device. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scatters or emit as the primary beam bombards each successive point of the metallic specimen surface will be measured by electron detector and used to modulate the intensity of a second electron beam and forms an image on a TV screen.

3.4.3 Catalytic Activity Testing

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 the two consecutive layers of catalytic systems, 3.0 g of 2.0 wt % Ga₂O₃-modified HZSM-5 catalyst was packed as the first layer, and one of these zeolites; H-X, H-Y, and H-Beta weighed 3.0 g was consecutively packed as the second layer. For investigating the effects of acidic

oxides of P, Sb, and Bi, 3.0 g of the modified HZSM-5 was individually loaded in a U-tube reactor. These catalysts were preheated at 500 °C for 1-2 hours in helium steam prior to the reaction, and the reaction runs were conducted at 500 °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 later as shown in Figure 3.1.

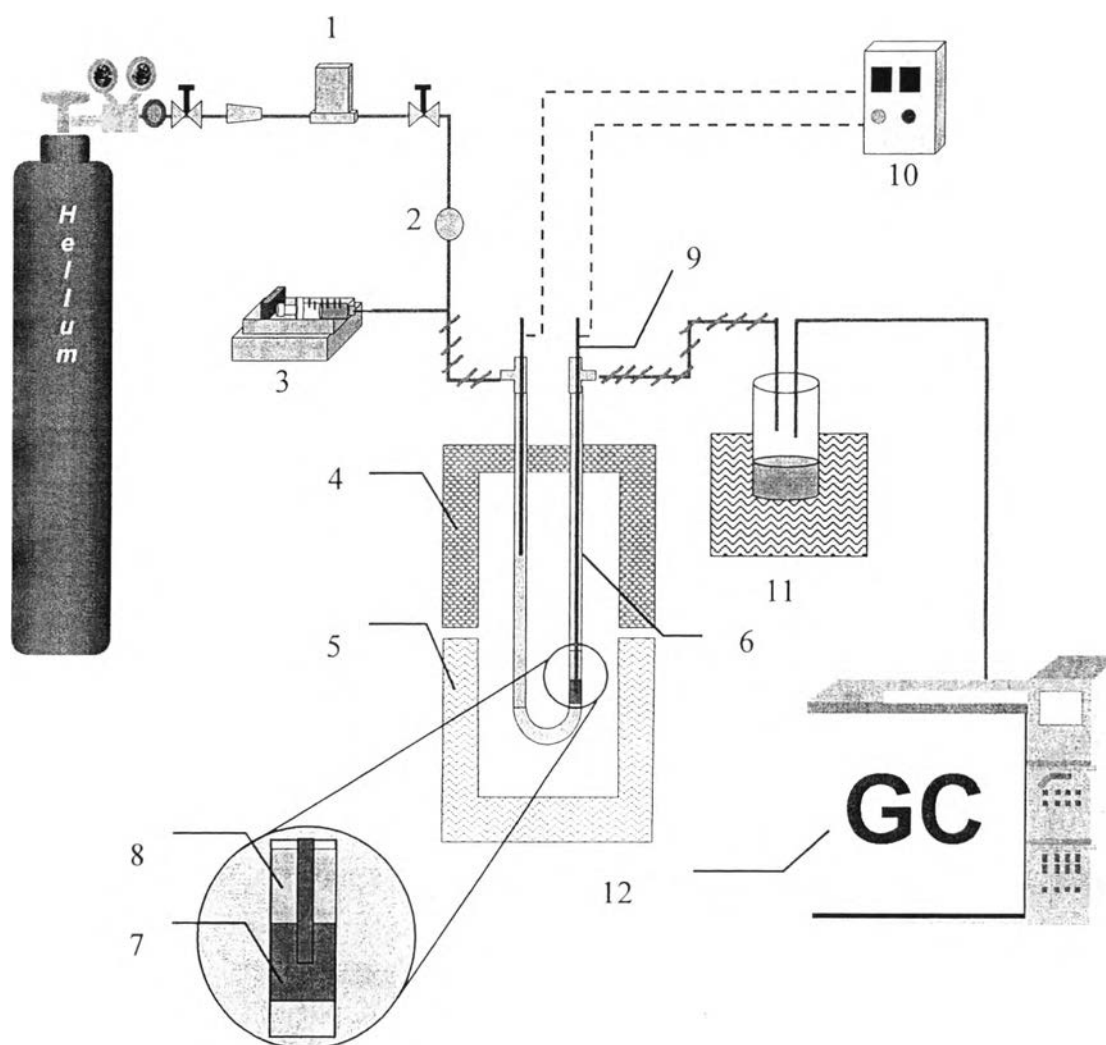


Figure 3.1 Schematic of experimental set-up: 1 = Flow meter, 2 = Pressure gauge, 3 = Syringe pump, 4 = Upper electric furnace, 5 = Lower electric furnace, 6 = U-tube reactor, 7= First Catalytic layer, 8= Second Catalytic layer, 9 = Thermocouple, 10 = Temperature programmed controller, 11 =Cooling unit, 12 = 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 kept at $-5\text{ }^{\circ}\text{C}$. The liquid product consisted of oil and aqueous solution that were weighed and separated for further analysis. 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.