

CHAPTER III

EXPERIMENTAL

3.1 Materials

The bio-ethanol for catalytic dehydration was received from Saphip Company Limited at the concentrations of 95% for run.

3.2 Equipment

1. Bench-scale U-tube reactor
2. Electrical furnace
3. Ice-water cooling system
4. Laboratory Oven
5. Syringe pump
6. Sieves, Mesh 20-40
7. Agilent Technologies 6890, Gas chromatography (GC)
8. Mortar
9. Hydraulic pellet machine
10. Condensing flask
11. Magnetic stirrer
12. Teflon-lined autoclave
13. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
14. X-Ray Fluorescence (XRF)
15. X-Ray Diffraction spectroscopy (XRD)
16. Scanning Electron Microscope (SEM)
17. A Varian CP-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC), conformed with ASTM D2887
18. A Gas Chromatography-equipped with a Mass Spectrometry of Time of Flight type (GCxGC-MS/TOF), Agilent© 7890
19. X-Ray photoelectron spectroscopy (XPS)

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, Air Zero, Nitrogen, Hydrogen
6. NH₄-Beta zeolite (SiO₂/Al₂O₃ = 27, 930NHA grade, Tosoh company)
7. H-Y zeolite (SiO₂/Al₂O₃ = 30, 360HUA grade, Zeolyst company)
8. NH₄-HZSM-5 zeolite (SiO₂/Al₂O₃ = 30, Zeolyst International)
9. NH₄-HZSM-5 zeolite (SiO₂/Al₂O₃ = 80, Zeolyst International)
10. Carbon disulfide (CS₂)
11. Ammonium hydroxy (NH₄OH)
12. Tetrabutylammonium tribromide 98% (TBABr)
13. LUDOX HS-30 colloidal silica, 30 wt% SiO₂
14. Sodium aluminate (NaAlO₂)
15. Sodium hydroxy (NaOH)

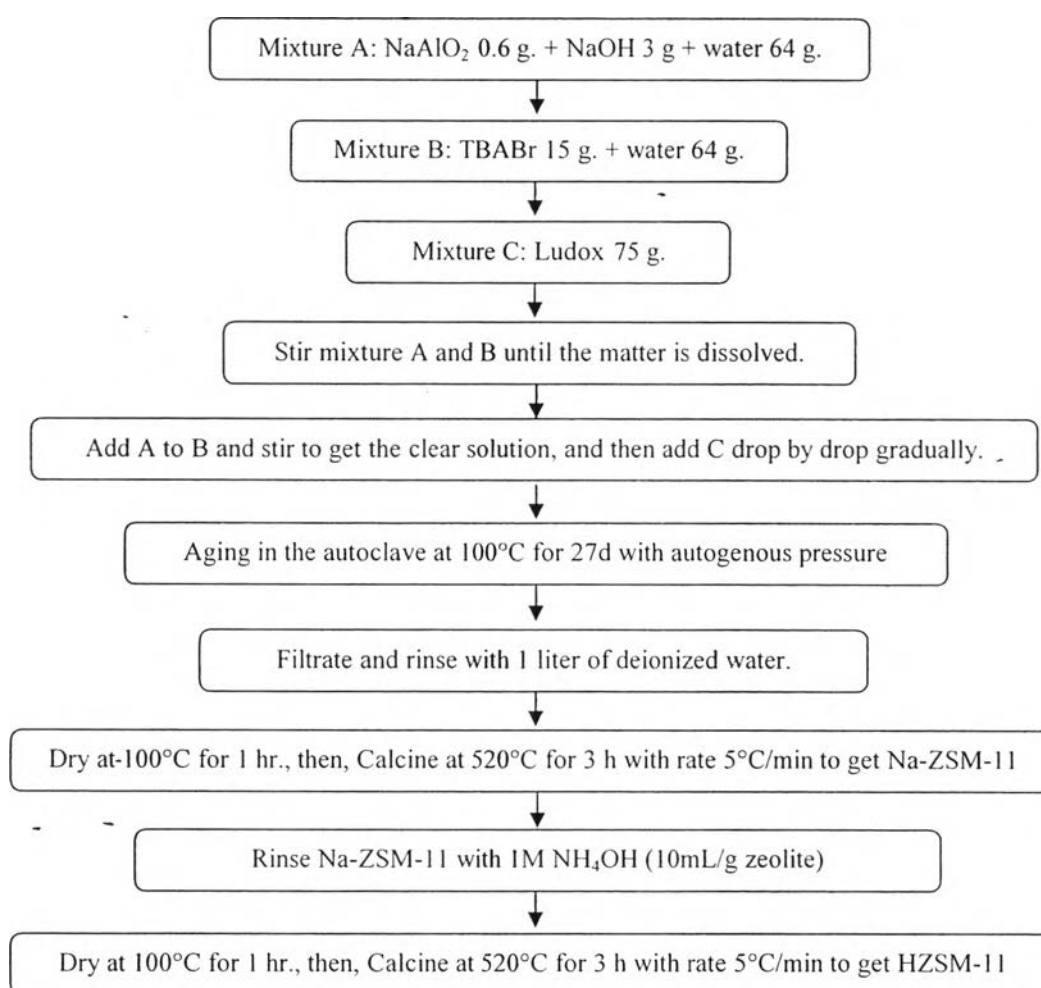
3.4 Experimental Procedures

3.4.1 Catalyst Preparation

3.4.1.1 *Synthesis of HZSM-11*

The HZSM-11 was prepared by the method in a patent (Chu *et al.*, 1973). The synthesis gel was prepared at the molar ratio $0.9 \pm 0.3 M_{2/n}O : Al_2O_3 : 20-90SiO_2 : 6-12H_2O$ where M is a cation with n valence. NaAlO₂ was used as the aluminium source, and 0.15 mol LUDOX HS-30 colloidal silica (30 wt% SiO₂) was used as the silica source. Tetrabutylammonium tribromide (TBABr) was used as the template. Two mixtures were first prepared as proposed. Mixture A was the mixture of sodium aluminate (NaAlO₂), NaOH, and water. Mixture B contained TBABr and water. Mixture C contained LUDOX HS-30 colloidal silica, a mixture of 30 wt% SiO₂, and water. Mixtures A and B were stirred separately to dissolve matter, and then the clear solution of Mixture A was added slowly with stirring using a magnetic

stirrer to Mixture B until homogeneous phase was formed. Then, Mixture C was added to the Mixture of A and B gradually to form the opaque sol-gel. Then the sol gel solution was aged in an autoclave at 100°C for 27 days at autogenous pressure. Subsequently, the obtained zeolite was washed with deionized water until the pH was neutral. The zeolite was in the Na form in this step, so ion-exchange with NH₄OH and calcination at 520°C for 3 h were necessary to change the zeolite into an H-form. The steps of HZSM-11 preparation with 1 mol SiO₂ basis is shown below.



3.4.1.2 Group 5A Oxide-loaded HZSM-11, HBeta, and HY Catalysts

The catalysts were prepared from a commercial H-Y zeolite (Si/Al = 7, 360HUA grade, Tosoh company), and NH₄-Beta zeolite (Si/Al = 13.5, 930NHA grade, Tosoh company), HZSM-5 (SiO₂/Al₂O₃ = 30 and 80, Zeolyst International, USA), and the as-prepared HZSM-11. The NH₄-Beta zeolite was

initially dried in an oven at 110°C 1 h, followed by calcination at 600 °C for 5 hours rate 2°C/min to obtain the proton form of HBeta zeolite. HY and NH₄-ZSM-5 was initially dried in an oven at 110°C 1 h, followed by calcination at 500 °C for 3 hours rate 5°C/min. Diammonium hydrogen phosphate ((NH₄)₂HPO₄), antimony trichloride (SbCl₃), and bismuth chloride (BiCl₃) were used as the source of P, Sb, and Bi, respectively. A solution of these compounds was individually loaded on the zeolite support using the incipient wetness impregnation technique with the final loading amount of 5.0 wt % of each element on the support. After impregnation, a wet catalyst was dried in an oven at 100°C for 1 hr, 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 Analyser (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-gased 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 Horvath Kawazoe (HK) 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 powder samples. XRF can detect all elements from beryllium to uranium and beyond at a long range of concentrations from part per million (ppm) to pure substances. 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 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 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 K α 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.

3.4.2.4 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 dock and coated with gold by using ion sputtering device. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattering or emit as the primary beam bombards each successive point of the metallic specimen surface was measured by an electron detector, and the intensity of a second electron beam was modulated then forms an image was formed on a TV screen.

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 effects of pore size and channel structure of HY HBeta and HZSM-11 incorporated with P₂O₅, Sb₂O₅, and Bi₂O₅, 3.0 g of a modified catalyst 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 was 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.

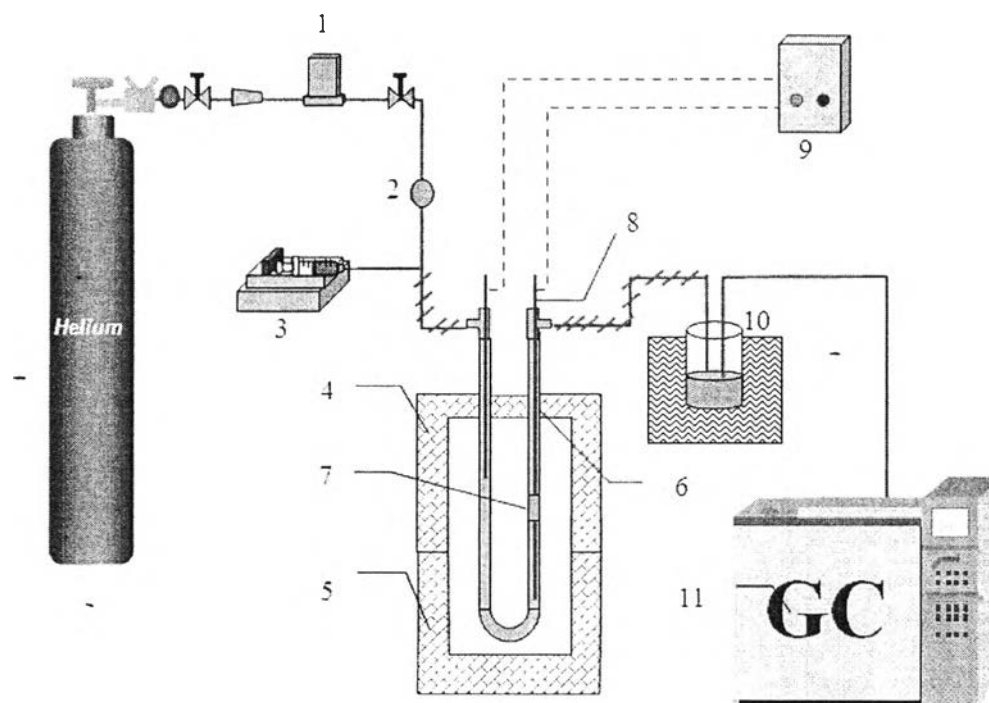


Figure 3.1 Schematic of experimental set-up: 1 = Flow meter, 2 = Pressure gauge, 3 = Syringe pump, 4 = Upper electric furnace, 5 = Lower electric furnace, 6 = U-tube reactor, 7= Catalytic layer, 8 = Thermocouple, 9 = Temperature programmed controller, 10 =Cooling unit, 11 = Gas chromatograph.

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.

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 $-5\text{ }^{\circ}\text{C}$. The liquid product consisted of oil and aqueous solution that were weighed and separated for further analysis. 3 ml of CS_2 can was used to extract the oil product out. 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. Helium was

used as the carried gas, and nitrogen was used in the cooling system. The conditions were set as follows: the initial temperature was set at 35°C, the oven temperature was set at 1 °C/min in range 35-150 °C and 20 °C/min in range 150-320 °C with split ratio of 20. 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). 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.