CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Bio-ethanol concentration 99.5 % (Sapthip Co., Ltd.)
2. H-Beta zeolite ($Si/Al_2 = 37$, CP811C-300 grade. Zeolyst company)
3. HZSM-5 zeolite ($Si/Al_2 = 30$. CBV28014 grade. Zeolyst company)
4. Deionized water
5. Helium gas (High purity)
6. Quartz wool
7. Alumina ball
8. Carbon disulfide (CS_2)
9. Aluminum tri-sec-butoxide ($Al\text{-}(i\text{-}BuO)_3$)
10. Tetraethylammonium hydroxide (TEAOH)
11. Tetrapropylammonium hydroxide (TPAOH)
12. Tetraethylorhosilicate (TEOS)
13. Cetyltrimethylammonium bromide (CTAB)
14. Fumed silica
15. Ammonium nitrate

3.2 Equipment

1. Isothermal fixed bed stainless steel U-tube reactor
2. Electrical furnace
3. Syringe pump
4. Mass flow controller
5. Condensing flask
6. Ice-water cooling system
7. Hydraulic pellet machine
8. Sieves (20 - 40 mesh)
9. Riguku, X-Ray Diffraction Spectroscopy (XRD)
10. Thermo Finnigan Sorptomatic 1990, Surface Area Analyzer (SAA)

11. Thermo Finnigan 1100, Temperature Programmed Desorption (TPD-NH_3)

12. Agilent Technologies 6890, Gas chromatography (GC)

13. A Gas Chromatography-equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent© 7890 with 2D dimension mode

14. A Varian CP-3800 Simulated Distillation Gas Chromatography (SIMDIST-GC), conformed with ASTM D2887

15. Perkiln Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)

16. X-ray Photoelectron Spectroscopy (XPS)

17. Transmission Electron Microscope (TEM)

3.3 Experimental Procedure

3.3.1 Catalyst Preparation

3.3.1.1 Synthesis of MSU-S_{BEA}

To prepare the BEA-seed solution, a mixture of Al-(i-BuO)$_3$ (0.02 mol) and TEOS (0.98 mol) were added to a stirred solution of aqueous TEAOH (35 wt%, 0.37 mol) in H_2O (20 mol). After aging about 2 hours, the solution was transferred into a Teflon-line autoclave and hydrothermal treatment at 100 °C for 3 hours to form BEA-seeds. After that, the seed solutions was added to a solution of CTAB (0.25 mol) in H_2O (127 mol). The solution was adjusted to a pH 9.0 by sulfuric acid (0.17 mol). The resulting synthesis gel was hydrothermally treated in a Teflon-lined autoclave at 150 °C for 2 days to form the mesostructure. The solution was filterd, washed, dried, and calcined at 2 °C/min to 550 °C for 4 hours to obtain the MSU-S_{BEA} catalysts. (Liu *et al.*, 2001; Triantafyllidis *et al.*, 2007).

3.3.1.2 Synthesis of MSU-S_{ZSM-5}

10.2 g of tetrapropyl ammonium hydroxide (TPAOH, 40 %wt) was mixed with 79.26 g of deionized water. Then, 6.0 g of fumed silica and 0.34 g of sodium aluminate as a silicon and aluminum source were sequentially added into the solution of TPAOH and deionized water. The solution was then stirred at 50 °C for 18 hours to form the ZSM-5-seed containing solution. After that, 9.44 g of CTAB were mixed with 100 g of deionized water, and mixed with the solution of ZSM-5-seed. The final gel was kept in a Teflon-lined autoclave for the hydrothermal treatment at 150 °C for 2 days to form the mesoporestructure. Then, the final gel was filtered, washed, and dried. The obtained white powder was ion exchanged with 0.1M NH_4NO_3 in 96 % ethanol at 80 °C reflux temperature for 2 hours. The final catalyst was dried, and calcined at 1 °C/min to 550 °C kept for 10 hours (Liu *et al.*, 2001; Rashidi *et al.*, 2013). Then, the calcined MSU-S_{ZSM-5} was pelletized, crushed, and sieved into 20 - 40 mesh particles before use in the reactor.

3.3.1.3 Commercial Zeolites

HZSM-5 zeolite (MFI, NH_4-form, SiO_2/Al_2O_3 = 30 mol/mol, BET surface area = 340 m^2/g, Zeolyst International, USA), and HBeta zeolite (BEA, NH_4-form, SiO_2/Al_2O_3 = 37 mol/mol, BET surface area = 502 m^2/g, Zeolyst

International, USA) were calcined at 500 °C, 10 °C/min for 4 hours, and 550 °C, 2 °C/min for 6 hours to get the H-form zeolite. Then, they were pelletized, crushed, and sieved to 20-40 meshes before use in the reactor.

3.3.2 Catalysts Characterization

3.3.2.1 X-Ray Diffraction Spectroscopy (XRD)

Rigaku TTRAX III was used to investigate the crystallographic spectra of the catalysts for the SAX mode, the detector scanned 2θ from 1° to 7° range and scan speed of 1°/min with step of 0.01°. For the wide-angle mode, Rigaku Smartlab® was used to determine the crystallographic spectra from 5° to 50° with scan speed of 5°/min with step of 0.01°.

3.3.2.2 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 10 hours prior to analysis steps. The specific surface area and the pore size of catalyst were obtained from the forty-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the B.J.H. and H.K. method.

3.3.2.3 Temperature Programmed Desorption Analyzer (NH_3-TPD)

Acid properties such as acid strength, and acidity were determined by Thermo Finnigan 1100. 0.2 g of a catalyst was treated by nitrogen flow at 300°C for 3 hours. Then, after the catalyst was cooled down to room temperature, it was added with 10 % v/v NH_3 of helium balance with a flow of 20 ml/min. The NH_3-TPD profiles were obtained by heating the reactor at 10 °C/min up to 800 °C with helium flow of 20 ml/min. After that, the desorbed gases were analyzed by TCD detector.

3.3.2.4 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The coke formation on catalysts was determined by a TG/DTA machine. The spent catalysts were weighed and placed in a Pt pan followed by heating from 50 to 900 °C with the heating rate of 10 °C /min. Nitrogen and oxygen flow rate were controlled at 100 ml/min and 200 ml/min, respectively.

3.3.2.5 X-ray Photoelectron Spectroscopy (XPS)

XPS was used to determine the Si/Al ratio on the surface of the fresh and spent catalysts. The scan pass energy was 160 kV for wide scan and 40 kV for narrow scan. The electron source was Al Kα 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.

3.3.2.6 Transmission Electron Microscopy (TEM)

The mixture of a catalyst powder and ethanol was sonicated for 20 min. After that, the mixture was dropped onto copper grid with a Formvar support, and then dried. Hitachi H-7501 SS in TEM high-resolution (HR) mode took images using a voltage of 100 kV.

3.3.2.7 X-Ray Fluorescence (XRF)

X-ray fluorescence spectrometry (AXIOS PW4400) was used to determine the bulk Si/Al ratio of the fresh and spent catalysts. 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.

3.3.3 Catalytic Reaction

3.3.3.1 The Two Consecutive Layers of Catalysts

The stainless steel U-tube fixed bed reactor was filled by alumina balls, and then, quartz wool was placed on alumina balls to secure the catalysts. Afterwards 1.5 g of a commercial zeolite (H-Beta, or HZSM-5) was placed in the first layer. After the quartz wool was put on the commercial zeolite, 1.5 g of the MSU-S was placed in the second layer and covered with the quartz wool. Helium used as a carrier gas was mixed with bio-ethanol fed by a syringe pump with 0.5 h^{-1} LHSV. The reaction was conducted at 450 °C for 8 hours

3.3.3.2 Catalytic Activity as a Function of Time-on-Stream

The stainless steel U-tube fixed bed reactor was filled by alumina balls. and then. quartz wool was on alumina balls to secure the catalysts. Afterwards 3 g of a catalyst (H-Beta, HZSM-5. MSU-S with Beta and ZSM-5 seeds) was placed. Helium as a carrier gas was mixed with bio-ethanol fed by a syringe pump with 0.5 h^{-1} LHSV. The reaction was performed at 450 °C for 4 days. and the data were collected every 4 hours.

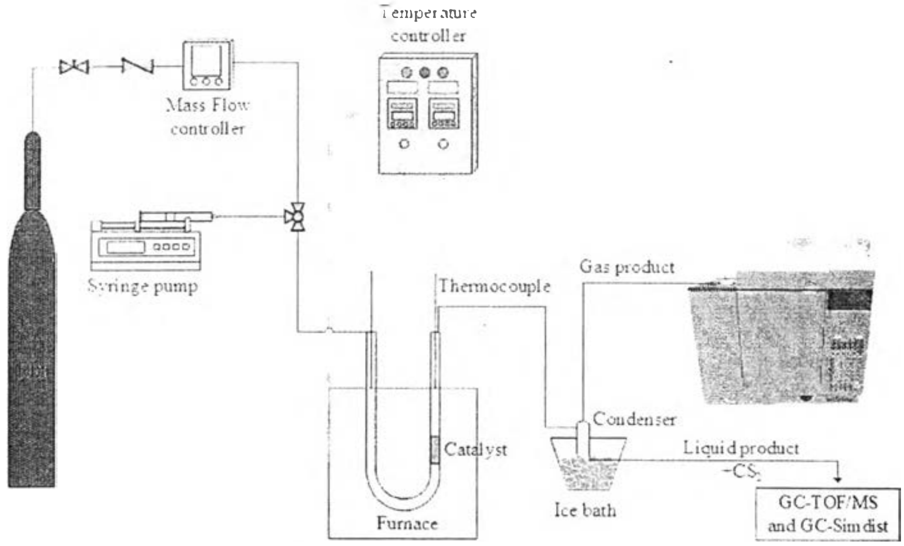

Figure 3.1 Experimental set-up of bio-ethanol dehydration.

3.3.4 Product Analysis

3.3.4.1 Gaseous Product Analysis

The gaseous products from the reactor 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). Gas chromatograph was composed of 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 oxygenated compounds (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.

3.3.4.2 Liquid Product Analysis

The liquid products from the reactor were analyzed by a Gas Chromatograph equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent 7890 with 1D dimension mode by using helium as the carrier gas. The conditions were set as follows: initial temperature of 50 °C, time at initial temperature of 30 minutes, 2 °C/min heating rate to 120 °C, held for 5 minutes. After that, use heating rate of 10°/min to final temperature of 310 °C, and split ratio of 5.

In addition, to identify the petroleum fraction, a Varian CP-3800 Simulated Distillation Gas Chromatograph (SIMDIST-GC) was used. Conformed with ASTM D2887 method for true boiling point curves. The different boiling point used to classified 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 (CS_2) 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.