CHAPTER III
EXPERIMENTAL

3.1 Materials

1. Bio-ethanol concentration 99.5% (Sapthip Co., Ltd.)
2. NH_4-Beta zeolite (Si/Al_2 = 27 and 37, 930NHA and 940NHA grade, Tosoh company)
3. H-Beta zeolite (Si/Al_2 = 300, CP811C-300 grade, Zeolyst company)
4. Gallium (III) nitrate hexahydrate ($Ga(NO_3)_3 \cdot 6H_2O$)
5. Germanium (IV) oxide (GeO_2)
6. Deionized water
7. Alumina ball
8. Quartz wool
9. Helium gas (High purity)
10. Carbon disulfide (CS_2)
11. Aluminum tri-sec-butoxide (Al-$(i$-$BuO)_3$)
12. Tetraethylorhosilicate (TEOS)
13. Tetraethylammonium hydroxide (TEAOH)
14. Cetyltrimethylammonium bromide (CTAB)

3.2 Equipments

1. Isothermal fixed bed stainless steel U-tube reactor
2. Electrical furnace
3. Ice-water cooling system
4. Syringe pump
5. Condensing flask
6. Sieves (20 - 40 meshes)
7. Hydraulic pellet machine
8. Teflon-line autoclave
9. Riguku, X-Ray Diffraction Spectroscopy (XRD)

10. Hitachi, Transmission Electron Microscope (TEM)

11. PANalytical, X-Ray Fluorescence Spectrophotometer (XRF)

12. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)

13. Thermo Finnigan 1100, Temperature Programmed Desorption (TPD) of Ammonia (NH_3)

14. Temperature-programmed desorptions (TPD) of Isopropylamine (IPA)

15. Agilent Technologies 6890, Gas chromatography (GC)

16. A Gas Chromatography-equipped with a Mass Spectrometry of Time of Flight type (GC-TOF), Agilent© 7890

17. A Varian CP-3800 Simulated Distillation Gas Chromatography (SIM-DIST-GC), conformed with ASTM D2887

3.3 Experimental Procedures

3.3.1 Synthesis of MSU-S/H$_{BEA}$ materials

MSU-S/H$_{BEA}$ was synthesized following the steps in the literature (Triantafyllidis et al., 2007). BEA seeds were freshly synthesized. First, Al-(i-BuO)$_3$ (0.02 mol) and TEOS (0.98mol) were mixed with a solution of TEAOH (0.37 mol, 20 wt%) in H_2O. Two hours of aging step was provided under stirring. After that, the solution was transferred into a Teflon-line autoclave for hydrothermal treatment at 100 °C for 3 h to form the BEA seeds. The BEA seeds were next further grown up around a surfactant template (CTAB) to form MSU-S in the following steps. A solution of CTAB (0.25 mol) in H_2O (127 mol) was added with the BEA seeds solution. A pH was controlled at 9.0 and adjusted by sulfuric acid. The solution was hydrothermally treated again at 150 °C for 2 days. The solution was filtered, washed, and dried to get the final hexagonal MSU-H catalyst.

3.3.2 Catalyst Preparation

In the first step, 5.0 wt% of Ga or Ge was loaded to calcined zeolites, including H-Beta (Si/Al$_2$ = 27), H-Beta (Si/Al$_2$ = 37), H-Beta (Si/Al$_2$ = 300), and MSU-S/H$_{BEA}$ by the incipient wetness impregnation technique. After that the catalysts was dried overnight at 120°C and calcined at 600°C, 5 hours with the heating rate of 2°C/min for H-Beta and 550°C, 4 hours with the heating rate of

2°C/min for MSU-S/ H_{BEA} to remove impurities. Then, the prepared catalysts were pelletized using a hydraulic pelletizer machine, crushed and sieved to sizes in 20 to 40 meshes before use in the reactor.

3.3.3 Catalytic Reaction

The stainless steel U-tube reactor was prepared by starting from filling alumina balls and 3.0g of catalysts, and both were kept to stay in place by quartz wool. The U-tube reactor was assembled in a furnace. The reactor was preheated with helium stream at 450°C several hours before start. Bio-ethanol was fed into the reactor using a syringe pump at 0.5 h^{-1} LHSV with helium as a carrier gas. The reaction testing was run for 8 hours at 450°C. The product coming out from reactor was separated in two phases, which were gas and liquid. The gaseous product was passed through a condensing flask, and then analyzed by using an online gas chromatograph (GC-FID). The condensable liquid product was subsequently analyzed by using a SIMDIST-GC and a GC-TOF.

3.3.4 Catalyst Characterization

3.3.4.1 X-Ray Diffraction Spectroscopy (XRD)

The metal oxide and zeolites structures were analyzed by using the Rigaku SmartLab X-Ray Diffractometer (XRD) system equipped with with 9 kW rotating anode Cu Kα source. The detector scanned for the peak positions from the samples as a function of 2θ by starting at the 5° to 100° (2θ) range with a scanning speed of 5° (2θ)/min. The data from XRD were recorded by the SmartLab Guidance software and analyzed by PDXL software.

3.3.4.2 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 %. The powder samples were hydraulically pressed to a flat surface. The conditions were set as follows: the 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.

3.3.4.3 Surface Area Analyzer (SAA)

The Brunauer-Emmett-Teller (BET) technique was employed to determine the specific surface area and the total pore volume, 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 h prior to analysis steps. The specific surface area and the pore size of catalyst were obtained from many points nitrogen adsorption and desorption isotherm plot. The micro-pore size distribution was calculated using the Horvath-Kawazoe (HK) method. Moreover, the meso-pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method.

3.3.4.4 Temperature Programmed Desorption Analyzer of Ammonia (NH_3-TPD)

Acid properties, acid strength, acidity and etc. were determined by Thermo Finnigan 1100. 0.3 g of each catalyst were cleaned by flowing helium at 500°C for 3 h. After cooled down to room temperature, catalyst was added with 5% v/v NH_3 of helium balance with a flow of 30 ml/min. The NH_3-TPD profiles were obtained by heating the reactor at 5°C/min up to 900°C in 30 ml/min helium flow.

3.3.4.5 Temperature Programmed Desorptions of Isopropylamine (IPA-TPD)

The acid density and acid strength of Lewis and Bronsted acid sites were characterized using TPD-IPA. 50 mg of catalyst was packed inside a 1/4 inch quartz tube reactor, which was assembled and connected to an online MS detector (MKS Cirrus). For the first step, catalyst pretreatment was performed at 500°C in a flow of He for 1 h. After that, the sample was cooled in He to 30°C and then 5 μl pulses of isopropylamine were injected over the sample, until the sample was saturated. Mass spectrometry was used to confirm the saturation of isopropylamine adsorption. Then, He was paused to remove excess isopropylamine for 30 min, followed by constant heating to 800°C with a heating rate of 20°C/min.

The MS signal of mass 17, 41, and 44 were monitored to determine the ammonia, propylene, and isopropylamine desorption, respectively. The amount of desorbed propylene (Mass = 41) was calibrated with a 2 ml pulse of 2 % propylene in He.

3.3.4.6 Transmission Electron Microscopy (TEM)

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

3.3.5 Product Analysis

3.3.5.1 Gas Chromatography (GC)

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) was composed of a thermal conductivity detector (TCD) to detect hydrocarbons by using the HP-PLOT Q column and a flame ionization detector (FID) to detect oxygenates by using the DB-WAX Column. 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.

3.3.5.2 Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)

The extracted oil was analysed by using a gas chromatograph equipped with a Mass Spectrometry of Time of Flight type (GC×GC-TOF/MS), Agilent 7890. 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 min, 4°C/min heating rate, final temperature of 270°C held for 5 min, and split ratio at 1:50.

3.3.5.3 Simulated Distillation Gas Chromatography (SIMDIST GC)

The petroleum fractions were obtained by using a Varian CP-3800 Simulated Distillation Gas Chromatograph (SIMDIST-GC) conformed with ASTM D2887 method for true boiling point curves. The different boiling point ranges were used to classify petroleum fractions; namely, 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.