

CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Bio-ethanol concentration 99.5% (Sapthip Co., Ltd.)
2. SAPO-34 catalyst (Tianjin Chemist Scientific Ltd.)
3. NH₄-ZSM-5 zeolite (SiO₂/Al₂O₃ = 40)
4. Deionized water
4. Quartz Wool
5. Alumina Ball
6. Helium gas (High purity)
7. Gallium (III) nitrate hexahydrate (Ga(NO₃)₃•6H₂O)
8. Germanium (IV) oxide
9. Tin (II) chloride (SnCl₂•2H₂O)
10. Antimony Trichloride (SbCl₃)
11. Carbon disulfide (CS₂)

3.2 Equipment

1. Isothermal fixed bed stainless steel U-tube reactor
2. Agilent Technologies 6890, Gas Chromatography (GC)
3. Varian CP-3800, Simulated Distillation Gas Chromatography (SIMDIST GC)
4. Agilent© 7890, Gas Chromatography-Mass Spectrometry, Time of Flight (GC-TOF)
5. X-Ray Fluorescence spectrophotometer (XRF)
6. Thermo Finnigan Sorptomatic 1990, Surface Area Analyzer (SAA)
7. Oxford/6111, Scanning Electron Microscope (SEM)
8. Condensing flask
9. Hydraulic pellet machine
10. Sieves, Mesh 20-40

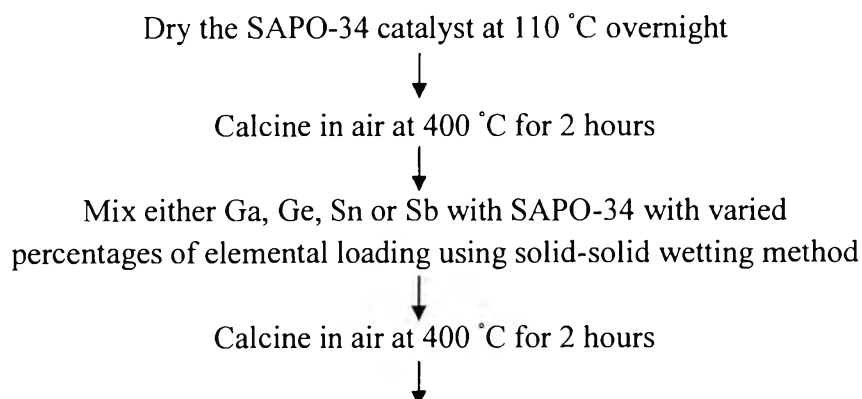
11. Rigaku, X-ray Diffraction Spectroscopy (XRD)
12. Mass flow controller
13. Temperature program controller
14. Syringe pump
15. Tedlar bag

3.3 Methodology

3.3.1 Catalyst preparation

The catalyst preparation of this research work was divided in two main parts. The first one is on the oxides of Ga, Ge, Sn, and Sb loaded on a SAPO-34 catalyst by solid-solid wetting method. The second part was on the HZSM-5 catalyst treated with KOH solutions at various concentrations.

First of all, the SAPO-34 catalyst used in this work was supplied from Tianjin Chemist Scientific Limited. It was dried overnight at 110 °C and calcined with the heating rate of 10 °C/min to reach 400 °C and kept at this temperature for 2 hours in order to remove impurities from the catalyst. An appropriate amount of GaCl₂, GeCl₂, SnCl₂ or SbCl₃ was individually mixed with SAPO-34 by physical mixing method to obtain the elemental loading percentages of 3%, and 5%. Then, the catalysts were calcined at 400 °C for 2 hours. Before being used in the reactor, the catalysts were pelletized by a hydraulic pelletizer machine. Afterwards, the pellets were crushed and sieved in the range of 20 to 40 meshes. The catalyst preparation procedure can be simplified into the diagram as shown below;



Pelletize the catalysts using a hydraulic pelletizer machine
 ↓
 Crush and sieve the pellets in the range of 20-40 meshes

For the second part, a HZSM-5 catalyst was modified by alkaline treatment. The treatment steps consisted of ion-exchanging 10 g of commercial HZSM-5 catalysts ($\text{SiO}_2/\text{Al}_2\text{O}_3=40$, molar ratio) with 150 ml of KOH solutions with various concentrations (0.1 M, 0.5 M, and 0.9 M) and stirring at 80 °C overnight. After that, the slurry was rapidly cooled to room temperature, filtered, and then washed with distilled water. The remaining solid was dried overnight at 110 °C and calcined, with the heating rate of 10 °C/min, upto 500 °C and kept at this temperature for 5 hours. Finally, HZSM-5 catalysts treated with KOH solutions were pelletized by a hydraulic pelletizer machine, and then the pellets were crushed and sieved in the range of 20 to 40 meshes. The preparation procedure can be simplified into the diagram as shown below;

Treat the HZSM-5 catalyst with a KOH solution
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 Stir at 80 °C and keep overnight
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 Cool the slurry rapidly to room temperature, filter,
 and wash the catalyst with distilled water
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 Dry the catalyst at 110 °C overnight
 ↓
 Calcine in air at 500 °C for 5 hours
 ↓
 Pelletize the catalyst using a hydraulic pelletizer machine
 ↓
 Crush and sieve the pellet in the range of 20-40 meshes

3.3.2 Catalytic reaction

The catalytic reaction was carried out in an isothermal fixed-bed stainless steel U-tube reactor at atmospheric pressure. Three grams of a catalyst sample was loaded into the middle part of the reactor and held in place using quartz wool support. The bio-ethanol was fed into the helium stream flow passing through

the catalyst bed using a syringe pump at LHSV 0.5 h^{-1} and for 45 minutes. The reaction temperature was controlled at $400 \text{ }^{\circ}\text{C}$ by temperature controllers. The reaction products were passed through a condenser in order to drop the liquid components. The gaseous products leave from the reactor was kept in a gas sampling bag were analyzed by a gas chromatography with a flame ionization detector (FID). Moreover, the oils were extracted from the aqueous liquid products using 2 ml of carbon disulfide (CS_2). After that, the extracted oils were analyzed by using the SIMDIST GC and GC-TOF.

3.3.3 Product analysis

3.3.3.1 *Gas Chromatography (GC)*

The gaseous product leaving from the reactor was kept in a gas sampling bag and then analyzed by a gas chromatograph (Agilent Technologies 6890 Network GC system) using an HP-PLOT Q column (30 m x 0.32 mm ID and 20 μm film thicknesses) equipped with a flame ionization detector (FID) to determine hydrocarbon gases; namely, CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , C_4H_{10} , and C_4H_8 . A DBWAX column installed in parallel and also equipped with the FID was employed to determine oxygenate components.

3.3.3.2 *Simulated Distillation Gas Chromatography (SIMDIST GC)*

All maltenes and their petroleum fractions (gasoline, kerosene, gas oil, light vacuum gasoil, and heavy vacuum gas oil) were analyzed by a Varian CP-3800 simulated distillation gas chromatography (SIMDIST GC), conformed with ASTM D2887 method for true boiling point curves. A liquid sample was injected to the SIMDIST GC after dilution with carbon disulphide (CS_2). The conditions were set as follows: initial temperature of $30 \text{ }^{\circ}\text{C}$, time at initial temperature of 0.01 min, heating rate of $20^{\circ}\text{C}/\text{min}$, final temperature of $320 \text{ }^{\circ}\text{C}$, and 8.50 minute holding time.

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

The oils and aqueous products from the catalytic dehydration were identified for their compositions using a Gas Chromatography 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 minute, 4 °C/min heating rate, final temperature of 270 °C held for 5 minutes, and split ratio at 1:50.

3.3.4 Catalyst characterization

3.3.4.1 *Surface area analyzer (SAA)*

The Brunauer-Emmett-Teller (BET) technique was performed to determine the specific surface area, the total pore volume, and the pore size of catalysts by using a Thermo Finnigan/Sorptomatic 1990 surface area analyzer, which is based on the physical adsorption of nitrogen gas. A sample was initially out-gassed to remove the humidity and volatile components adsorbed on the catalyst surface under vacuum at 300 °C for at least 18 hours prior to analysis. 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.

3.3.4.2 *Scanning Electron Microscope (SEM)*

The microstructure of a catalyst sample was examined using a Scanning Electron Microscope (SEM: JEOL/JSM 5200). The SEM takes the advantage of electrons that are backscattered or emitted from the specimen surface. The samples were placed on a stub and coated with gold by using an ion sputtering device. The specimen was scanned with a narrow beam of electrons, and the back-scattered electrons were measured by an electron detector. The intensity of a second any electron beam was modulated, and the image was formed on a TV screen.

3.3.4.3 *X-ray Diffraction Spectroscopy (XRD)*

The oxide of catalyst was analyzed by a Bruker X-Ray diffractometer system (D8 Advance) equipped with a 2.2 kW Cu anode long fine focus ceramic X-ray tube for generating a CuK α radiation (1.5405 Å). The detector scanned the peak position from the sample as a function of 2θ by starting at the 10° to 50° (2θ) range and a scan speed of 0.02° (2θ)/0.6 second. The data from XRD were analyzed and recorded by an on-line computer.

3.3.4.4 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 ground samples was generally needed special preparation-although materials should be presented to the spectrometer in a homogeneous, reproducible form. 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 m of collimator, angle of 10.0002 degree, gas flow 0.90 l/h, and gas pressure of 1020.8 hPa.