



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Benzene (99.8% Purity) obtained from Carlo Erba
- Ethanol (99.8% Purity) obtained from Carlo Erba
- Alumina source ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) from Ajax Finechem
- Tetrapropylammonium bromide (TPABr) from Sigma-Aldrich
- Ludox (40%wt SiO_2) from Sigma-Aldrich
- Sodium hydroxide (NaOH) from Carlo Erba
- Ammonium fluoride (NH_4F) from Merck Chemicals
- Distilled water

3.1.2 Gases

- N_2 (99.99 % Purity)
- H_2 (99.99 % Purity)
- He (99.99 % Purity)
- Air Zero (99.99% Purity)

All gases were obtained from Thai Industrial Gas Co., Ltd.

3.2 Equipment

The equipment used in this work is listed below.

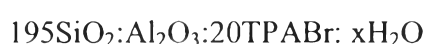
- Fixed-bed continuous flow reactor system
- Agilent Technologies model 5890N gas chromatograph with a flame ionization detector and HP-5 column for detecting the alkylated aromatic hydrocarbons
- Catalyst characterization instruments e.g. BET, XRD, TPO, TPD, SEM and XRF.

3.3 Methodology

3.3.1 Catalyst Preparation

3.3.1.1 HZSM-5 catalyst synthesized by NaOH

This technique used NaOH as a mineralizing agent. HZSM-5 samples were synthesized from hydrogel solutions via hydrothermal synthesis with the following molar composition



where $x = 3900, 4875, 5850, \text{ and } 7800$.

First, Ludox and 4/5 of the distilled water were stirred at 350 rpm. Under stirring, aqueous solution of NaOH was slowly dropped into the Ludox solution to obtain a pH value of 10.5. The obtained mixture was stirred for 1 h at room temperature while controlling the pH value at 10.5.

The rest of the distilled water and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed together until $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was completely dissolved. The $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution and TPABr were placed in the Ludox solution beaker followed by conditioning the pH value to 10.5 with NaOH solution. The mixture was stirred at 350 rpm for 24 h while controlling the pH value at 10.5.

The gel was placed into an autoclave for hydrothermal and heated in an oven at various conditions. After the hydrothermal synthesis, the autoclave was cooled down to room temperature. The gel forms powder after hydrothermal. Next the powder was washed for reducing pH from 10.5 to 7 by distilled water. And then the powder was dried at 80 °C overnight, and calcined to remove the precursor at 550 °C for 5 h.

After first calcination, the as-synthesized ZSM-5 was exchanged with 1 M NH_4NO_3 solution for three times at 80 °C, and then washed with distilled water to remove the nitrate ions. The resultant zeolite was dried overnight at 80 °C and calcined in flowing dry air at 550 °C for 5 h to obtain the acidic form of the zeolite (HZSM-5).

3.3.1.2 *HZSM-5 catalyst synthesized by NH₄F*

This technique used NH₄F as a mineralizing agent. First, TPABr was placed into the distilled water and stirred at 700 rpm. After that, NH₄F, alumina source and silica source were introduced in this order and allowed to mix by using this molar composition with 195SiO₂:Al₂O₃:24TPABr:312NH₄F:xH₂O where x = 4875, and 6435. Then, the mixture solution was stirred at 700 rpm for 24 hours at room temperature. The gel was brought into an autoclave and allowed to proceed at various hydrothermal conditions. The powder was washed by distilled water to remove the fluoride ions. After that it was dried at 80 °C overnight and calcined to remove the precursor at 550 °C for 5 h to obtain the acidic form of the zeolite (HZSM-5).

3.3.2 Catalyst Characterization

3.3.2.1 *X-ray Diffraction (XRD) Measurements*

The crystalline phase of catalyst was analyzed by a Rigaku Dmax X-Ray diffractometer, RINT-2200 with Cu tube for generating CuK α radiation (1.5406 Å). The system consists of a voltage generator of 40 kV. The 2 θ (degree) is in the range between 5° and 35° with a scanning rate of 5°C/min. This analysis is generally performed based on the fact that an x-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of different samples, the higher intensity indicates the higher content.

3.3.2.2 *Temperature Programmed Oxidation (TPO) Technique*

The spent catalyst approximately 0.05 g was packed into the quartz tube reactor supported with quartz wool before introduced to the TPO reactor. The calibration was done by injecting the exact amount of CO₂ pass through the methanator unit to convert CO₂ to CH₄ and then detected by FID detector. The analysis process utilizing 2% O₂ in He as oxidizing agent flew through the reactor with flow rate of 40 ml/min. The outgoing gas was pass the methanator unit before go to the detector as same as the calibration step. The reactor was heated from 30 to

900 °C with heating rate 10 °C/min. The received area was then converted to the carbon amount by using the calibration factor obtained from the CO₂ calibration.

3.3.2.3 Temperature Programmed Desorption (TPD) Technique of Isopropylamine

The catalyst was weighed approximately 0.05 g and then packed into the quartz tube reactor supported with quartz wool before introduced to the TPD reactor. The sample was treated in helium flow 65 ml/min to 350 °C with heating rate 10 °C/min. The sample was then cooled to 30 °C for the isopropylamine adsorption process. Isopropylamine 5 µL was injected to the reactor in continuously helium flow, the injection was done every 30 minutes for 4 times. In analysis process, the reactor was heated from 30 to 800 °C with heating rate 20 °C/min. The desorbed gas was detected by mass spectrometer, the mass of 41 represented to propylene was considered. The area of desorbed propylene in TPD profile was integrated to calculate the amount of Brønsted acid by using the calibration factor of propylene.

3.3.2.4 Scanning Electron Microscopy (SEM) with Energy Dispersive Spectrometer (EDS)

Scanning Electron Microscope (SEM), Hitachi S4800, was utilized to identify the microstructure and capture the micrograph of catalyst morphology. Energy Dispersive Spectrometer (EDS), Oxford Model 6111, was utilized to identify the presence of elements (from characteristic x-ray) in the catalyst region being examined. The catalyst sample was placed on a stub and coated by platinum in sputtering device before being placed in the sample holder of SEM.

3.3.2.5 Surface Area Analyzer

The surface area of the fresh and spent catalysts was measured using a BET surface area analyzer (Quantachrome/Autosorb 1 MP). The glass tube was outgased at 150 °C for 30 minutes before weighed and used. The sample approximately 0.06-0.10 g was placed into the glass tube. Then the sample was outgased at 250 °C around 6 to 20 hours depended on the sample. The outgased sample was weighed again to obtain the exact weight before introduce into the analysis station. The measurement was performed at the liquid nitrogen temperature (-196 °C), using relative pressure (P/P_0) in the range of 0.001 to 0.999 with a number

of adsorption equal to 21 points and desorption 20 points. The surface area was calculated by using 7 points BET method with P/P_0 in the range of 0.05 to 0.3.

3.3.2.6 *The Compositions of Liquid Produced*

The composition of produced liquid was analyzed by a gas chromatograph (Manual System GC, HP 5890 Series II), with under the condition as shown below:

- Column: HP-5 capillary column (30 m × 0.32 mm × 0.25 μm)
- Oven temperature: 50 °C to 150 °C at 5 °C/min. (hold 10 min.)
- Injector temperature: 250 °C
- Detector: Flame Ionization detector at 250 °C
- Carrier gas: Helium

3.3.2.7 *X-ray Fluorescence Spectroscopy (XRF)*

X-ray fluorescence spectroscopy was used to determine the actual Si, Al, and Na content of the catalysts. With a primary X-ray excitation source from an X-ray tube, the X-ray can be absorbed by the atom, and transfer all of its energy is transferred to and innermost electron. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable conditions, electron from the outer shells are transfer to the inner shells, and this process gives off a characteristic X-ray, whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The intensities of observed lines for a given atom vary according to the amount of that atom present in the specimen.

3.3.3 Catalytic Activity Testing

The synthesized HZSM-5 zeolite catalysts were tested for the catalytic activity of the ethylation of benzene in different reaction conditions using a fixed-bed continuous down-flow reactor having 12 mm in outside diameter and 37 cm in length. 0.2 g of catalyst was loaded into the middle of the reactor and supported in the both

sides with a thin layer of glass wool. Prior to the catalytic measurements, the catalyst was purged at temperature 300 °C for an hour under flowing nitrogen.

The temperature of catalyst bed was monitored and controlled by a PID temperature controller (Shinko) equipped with a K-typed thermocouple. The reaction was carried out at atmospheric pressure. The reactant mixture of benzene and ethanol was fed using a syringe pump and preheated before entering the reactor. The nitrogen as a carrier gas was controlled at a flow rate of 40 ml/min by a mass flow controller (Sierra C100L). The product was allowed to flow through a condenser attached to the end of reactor. The liquid product was attained and collected for sampling every 70 minutes on stream. The liquid products were chromatographically analyzed using a gas chromatograph (HP 5890 Series II) equipped with an FID detector and an HP-5 column. A schematic diagram of the system is shown in Figure 3.1.

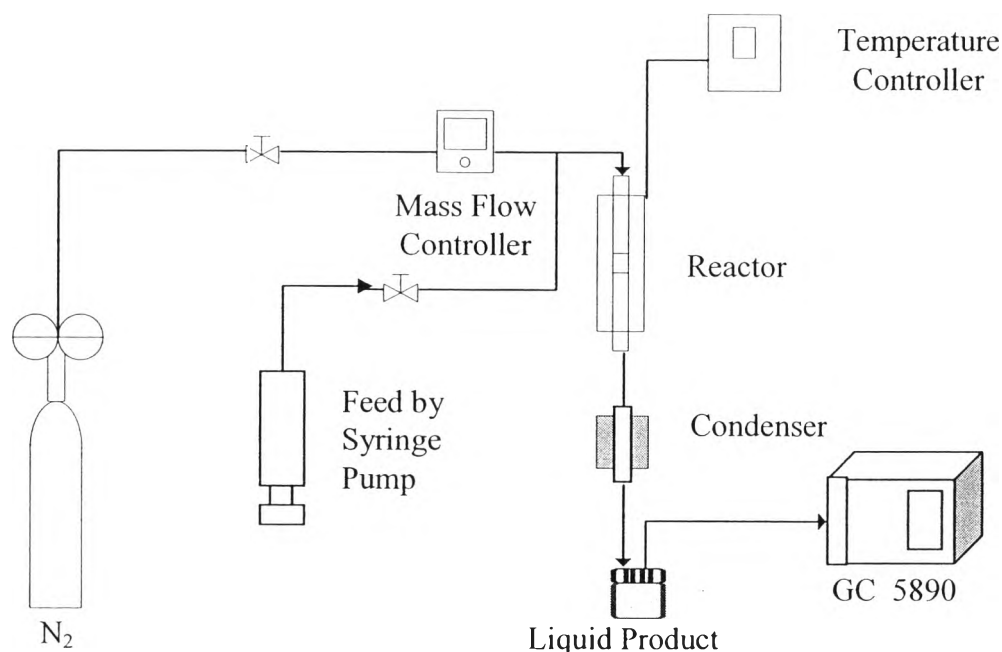


Figure 3.1 Schematic of the experimental system.

Benzene conversion, ethanol conversion, and ethylbenzene selectivity were calculated according to the following formulae:

$$\% \text{ Benzene conversion} = \frac{(C_6H_6^{\text{feed}} - C_6H_6^{\text{out}})}{C_6H_6^{\text{feed}}} \times 100 \quad (3.1)$$

$$\% \text{ Ethanol conversion} = \frac{(C_2H_5OH^{\text{feed}} - C_2H_5OH^{\text{out}})}{C_2H_5OH^{\text{feed}}} \times 100 \quad (3.2)$$

$$\% \text{ Ethylbenzene selectivity} = \frac{EB^{\text{formed}}}{\text{All products formed}} \times 100 \quad (3.3)$$

where

| | | |
|--------------------------|---|-------------------------------------|
| $C_6H_6^{\text{feed}}$ | = | Weight of C_6H_6 fed |
| $C_6H_6^{\text{out}}$ | = | Weight of C_6H_6 out |
| $C_2H_5OH^{\text{feed}}$ | = | Weight of C_2H_5OH fed |
| $C_2H_5OH^{\text{out}}$ | = | Weight of C_2H_5OH out |
| EB^{formed} | = | Weight of ethylbenzene formed |
| All products formed | = | Total weight of all products formed |