

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

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

3.1.2 Gases

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

All the gases were obtained from Thai Industrial Gas Public Company Limited.

3.2 Equipment

- Fixed-bed continuous flow reactor system
- Temperature controller equipped with a K-type thermocouple
- Gas chromatograph (Agilent Technologies model 5890N) with a flame ionization detector and HP-5 column for detecting the alkylated aromatic hydrocarbons
- Teflon-lined stainless steel autoclave (Parr Instrument Company, USA. , 125ml)

- pH meter (Denver Instrument, Ultra Basic U10)
- Magnetic stirrer (Cole Parmer Instrument Company)
- Furnace (Carbolite)
- X-ray diffractometer (XRD, Rigaku/RINT-2200 HV)
- X-ray fluorescence spectrometer (XRF, Bruker SRS 3400)
- Thermo Finnigan TPD/R/O 1100 equipped with a flame ionization detector
- Scanning Electron Microscope (Hitachi S4800)
- Surface area analyzer (Quantachrome/Autosorb1-MP)

3.3 Methodology

3.3.1 Catalyst Preparation

HZSM-5 catalysts were synthesized by hydrothermal technique. Ludox (40 wt% SiO₂) and aluminium nitrate (Al(NO₃)₃·9H₂O) were used as Si and Al source, respectively. The initial SiO₂/Al₂O₃ molar ratios were varied in the range of 195 to 280 based on the following recipe: Tetrapropylammonium bromide (TPABr) was used as a template. The TPABr/SiO₂ molar ratio was employed at 0.1026 along with that of H₂O/SiO₂ at 40.

First, Ludox and 4/5 of the desired distilled water were mixed and stirred at 350 rpm. The pH value of the obtained mixture was controlled at 10.5 by adding aqueous solution of NaOH as being stirred for 1 h at room temperature.

The aluminium nitrate solution obtained by mixing Al(NO₃)₃·9H₂O with the rest of distilled water and TPABr were placed into the Ludox solution beaker followed by stirring at 350 rpm for 24 h while controlling its pH value at 10.5 with NaOH solution.

The gel was placed into an autoclave and heated in an oven at 140 °C for 3 or 7 days for hydrothermal treatment. After that, the autoclave was cooled down to room temperature. The resulting powder was washed with distilled water for reducing its pH from 10.5 to neutral. Then the powder was dried at 110 °C overnight, and calcined to remove the precursor at 550 °C for 5 h.

After the 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 110°C and calcined at 500°C for 4 h to obtain the acidic form of the zeolite (HZSM-5).

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Diffraction (XRD)

The crystalline phase of catalyst was analyzed by a Rigaku Dmax X-Ray diffractometer, RINT-2200 with Cu tube for generating $\text{CuK}\alpha$ radiation (1.5418 \AA). The system consists of a voltage generator of 40 kV. The 2θ (degree) is in the range between 5 and 35 with a scanning rate of $5^\circ\text{C}/\text{min}$. 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 (www.iza-structure.org/databases.)

3.3.2.2 X-ray Fluorescence Spectroscopy (XRF)

X-ray fluorescence spectroscopy technique was used to investigate the type and amounts of chemical compound of the catalysts. The X-ray from a primary X-ray excitation source in X-ray tube is absorbed by the atom, then and the energy created is transferred to an innermost electron. If the primary X-ray has sufficient energy, vacancies created from electrons are emitted from the inner shells. The vacancies present an unstable condition for the atom. The electrons from the outer shells are transferred to the inner shell while the atom returns to its stable condition. This process brings about a characteristic X-ray that its energy is the difference between the two binding energies of the corresponding shells. Since each element has a unique set energy levels, each element produces X-ray 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.

3.3.2.3 Temperature Programmed Oxidation (TPO)

The spent catalyst approximately 0.05 g was packed into the quartz tube reactor supported with quartz wool before introduced to a TPO reactor. The calibration was done by injecting the exact amount of CO₂ passing through the methanator unit to convert CO₂ to CH₄ and then detected it using on 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 passed through the methanator unit before being sent to the detector as same as the calibration step. The reactor was heated from 30 to 900 °C with a heating rate 10 °C/min. The received area was then converted into the carbon amount by the calibration factor obtained from the CO₂ calibration.

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 in SEM.

3.3.2.5 Surface Area Measurement

The surface areas of the fresh and spent catalysts were measured using a surface area analyzer (Quantachrome/Autosorb 1 MP). The glass tube was outgassed at 150 °C for 30 min before being weighed and used. The sample approximately 0.06-0.10 g was placed into the glass tube. Then the sample was outgassed at 250 °C around 6 to 20 hours depending on the sample amount. The outgassed sample was weighed again to obtain the exact weight before introducing

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 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 Products

The composition of produced liquid was analyzed using a gas chromatograph (Manual System GC, HP 5890 Series II), under the conditions 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 5 min for 50 and 150 °C, respectively.)
- Injector temperature: 250 °C
- Detector: Flame Ionization detector at 250 °C
- Carrier gas: Helium

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 370 mm in length. The 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 activated 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 on-line gas and liquid

products were chromatographically analyzed using a gas chromatograph (HP 5890) equipped with an FID and an HP-5 column. A schematic diagram of the system is shown in figure 3.1.

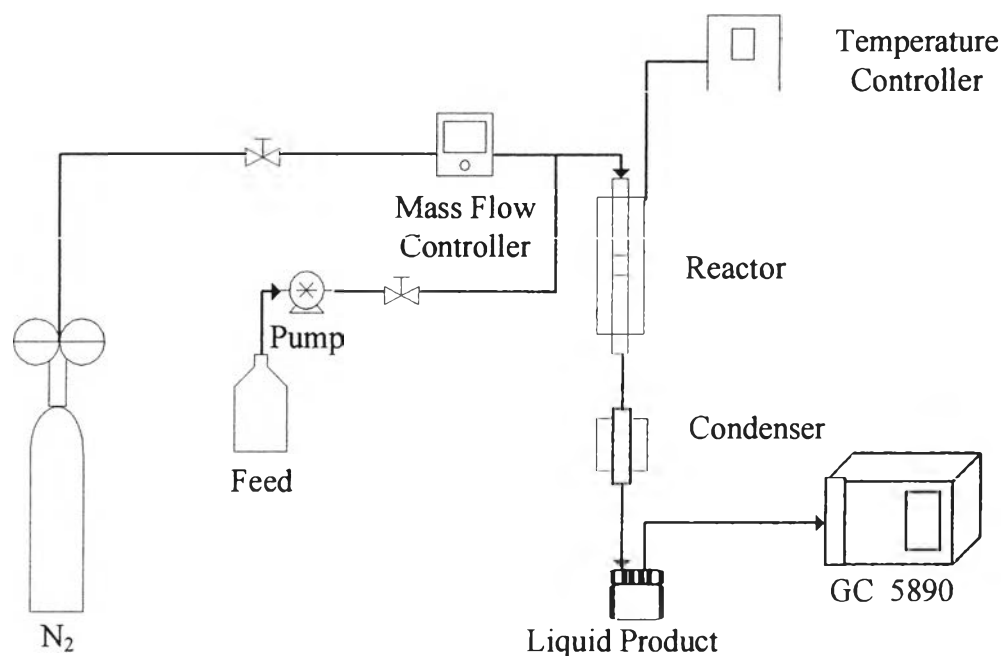


Figure 3.1 Schematic of the experimental system.

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

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

$$\text{Ethylbenzene selectivity (\%wt)} = \frac{EB^{\text{formed}} \times 100}{\text{All products formed}} \quad (3.2)$$

where

B^{feed}	= Moles of Benzene fed
B^{out}	= Moles of Benzene out
EB^{formed}	= Weight of ethylbenzene formed
All products formed	= Total weight of all products formed