

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Toluene (99.5 % Purity) obtained from (RCI Labscan)
- Ethanol (99.8 % Purity) obtained from (RCI Labscan)
- Alumina source ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (Ajax Finechem)
- Tetrapropylammonium bromide (TPABr) (Sigma-Aldrich)
- Ludox (40%wt SiO_2) (Sigma-Aldrich)
- Sodium hydroxide (NaOH) (Carlo Erba)
- Tetraethyl orthosilicate (TEOS) (Aldrich, USA)
- Cyclohexane (RCI Labscan)
- Commercial $\text{NH}_4\text{ZSM-5}$ zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 23, 80, and 280) obtained from Zeolyst, USA.

3.1.2 Gases

- N_2 (99.99 % Purity)
- H_2 (99.99 % Purity)
- He (99.995 % Purity)
- Air Zero (99.99% Purity)

All gases were obtained from TIG 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
- X-Ray diffractometer (RINT-2200)
- Surface Area Analyzer (Quantachrome/autosorb 1 MP)
- Scanning Electron Microscope (Hitachi S4800)
- Thermo Finnigan TPD/R/O 1100 equipped with flame ionization detector
- X-ray fluorescence spectroscope (XRF, Bruker SRS 3400)
- Furnace (Carbolite)

3.3 Methodology

3.3.1 Preparation of Catalysts

3.3.1.1 Preparation of Synthesized HZSM-5 Catalysts

HZSM-5 catalysts with initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 195 were synthesized by hydrothermal technique using Ludox, aluminium nitrate and tetrapropylammonium bromide (TPABr) as Si source, Al source, and templating agent respectively. The TPABr/ SiO_2 molar ratio was employed at 0.1026 along with that of $\text{H}_2\text{O}/\text{SiO}_2$ at 40. Ludox and 4/5 of the desired distilled water were stirred. 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 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the rest of distilled water and TPABr were placed into the Ludox solution beaker followed by stirring 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 days for hydrothermal treatment. After that, the autoclave was cooled down to room temperature. The resulting powder was washed

by distilled water for reducing its pH from 10.5 to neutral. Then the powder was dried at 110 °C overnight, and calcined 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 HZSM-5.

3.3.1.2 Preparation of Modified HZSM-5 Catalysts

Commercial $\text{NH}_4\text{ZSM-5}$ zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios of 23, 80, and 280) were calcined at 550 °C at a rate of 10 °C/min for 4 h yielding the unmodified HZSM-5 catalysts. For preparing chemical liquid deposition (CLD) modified catalysts, 1 g of HZSM-5 zeolite was mixed with a given amount of TEOS (varied from 0.2 to 2 ml) in cyclohexane 10 ml for 7 h. After that it was filtered and dried at 110 °C overnight, followed by calcination in air at 550 °C at a rate of 10 °C/min for 4 h. The CLD treatment was repeated in its procedure, if desired.

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Diffraction (XRD)

The structure of the catalysts was characterized by using X-ray Diffraction (XRD) technique by a Rigaku Dmax X-Ray diffractometer, RINT-2200 with Cu tube for generating $\text{CuK}\alpha$ radiation (1.5418 Å). The system consists of a voltage generator of 40 kV. The 2θ is in the range between 5 and 40 with a scanning rate of 5°C/min. Due to the x-ray diffraction pattern is unique for each crystalline substance, XRD can be used to identify or confirm the structure of unknown crystalline materials.

3.3.2.2 Surface Area Measurement

The surface areas of catalysts were characterized by using surface area analyzer (Quantachrome/autosorb 1 MP). The sample was degassed to remove water and other volatile materials under vacuum at 300 °C for 12 h before the analysis, then N_2 was purged to adsorb by physical adsorption on the surface of catalyst, measuring the quantity of gas adsorbed or desorbed from their solid surface at some equilibrium vapor pressure by static volumetric method. The solid sample

was maintained at a constant temperature of the sample cell until the equilibrium is established. This volume-pressure data was used to calculate the total surface area of catalyst.

3.3.2.3 Scanning Electron Microscope (SEM)

The morphology and crystal size were characterized by using scanning electron microscope, Hitachi S4800. The catalyst sample was placed on stub and coated by platinum in sputtering device, after that the sample was placed in the sample holder in SEM.

3.3.2.4 Temperature Programmed Desorption of Isopropylamine (IPA-TPD)

The acid properties of catalysts were characterized by temperature program desorption of isopropylamine (TPD-IPA). To clean the surface of catalyst, 50 mg of catalyst was placed in a quartz tube and heated with rate of 10 °C/min under He flow with the flow rate of 10 ml/min up to 300 °C for 1 h. After cleaning, the reactor was cooled to 30 °C, then isopropylamine was injected over the sample, after that He was purged with the flow rate of 10 ml/min for 20 min to eliminate non adsorbed isopropylamine, the sample was heated with the flow rate of 10 °C/min to 550 °C under the He atmosphere, m/e 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, ammonia.

3.3.2.5 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.

3.3.2.6 X-ray fluorescence method (XRF)

The composition of materials was determined by the X-ray fluorescence method (XRF) using the PANalytical analysis instrument with AXIOS&SUPERQ version 4.0 systems. IQ+ program was used to measure and analyze the samples. In the analysis procedure, the scans were first searched for peaks. The found peaks were identified and analyzed quantitatively using fundamental parameter.

3.3.3 Catalytic Activity Testing

3.3.3.1 Ethylation of toluene with ethanol

Catalytic activity was studied at 300 °C to 500 °C, WSHV of 5-20 h⁻¹ and toluene to ethanol molar ratio of 1-5, using a fixed-bed continuous down-flow reactor. The reactor has an inner diameter of 8.5 mm and a length of 37 cm. About 0.2 g of catalyst having a particle size of 20-40 mesh was loaded into the reactor and supported with a thin layer of glass wool. Before the reaction, the catalyst was activated at temperature 300 °C for an hour under flowing nitrogen. The nitrogen used as a carrier gas, was controlled at a flow rate of 26 ml/min. The product was condensed using a condenser at the end of reactor. The liquid product was collected and analyzed using a gas chromatograph (HP 5890) equipped with an FID and a capillary HP-5 column. A schematic diagram of the system is shown in figure 3.1.

3.3.3.2 *o*-Xylene isomerization

In order to investigate catalytic properties at external acid sites, catalytic activity of *o*-Xylene isomerization was studied at 350 °C, WSHV of 20 h⁻¹, using the same fixed-bed continuous down-flow reactor. About 0.2 g of catalyst was loaded into the reactor and supported with a thin layer of glass wool. The catalyst was activated at temperature 300 °C for an hour under flowing nitrogen before the reaction. The nitrogen used as a carrier gas, was controlled at a flow rate of 26 ml/min. The product was condensed using a condenser at the end of reactor. The liquid product was collected and analyzed using a gas chromatograph (HP 6890) equipped with an FID and a capillary HP-Innowax column.

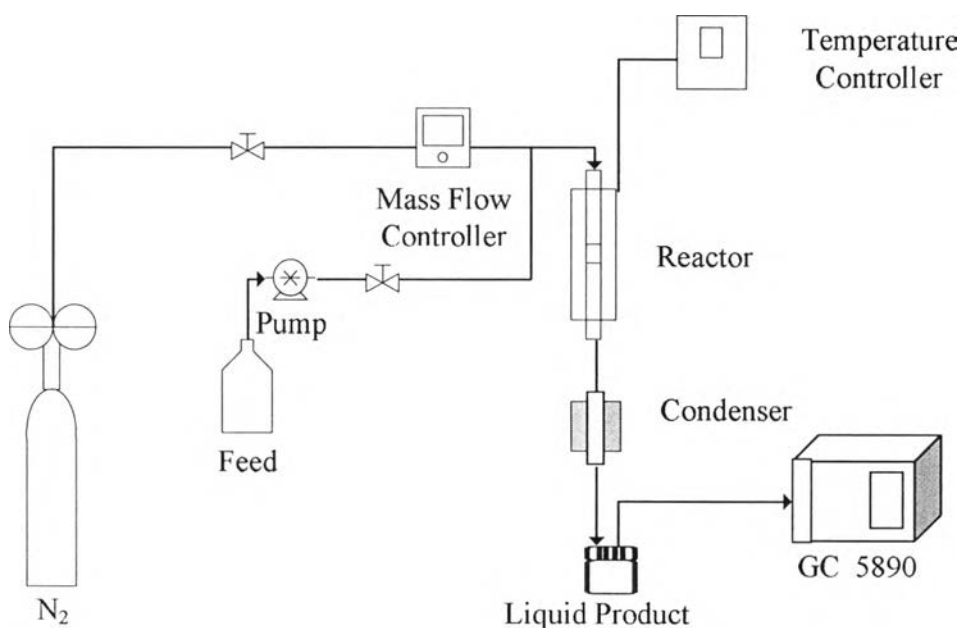


Figure 3.1 Schematic of the experimental system.

3.3.4 Product Analysis

For ethylation of toluene with ethanol, the liquid product was analyzed using a gas chromatograph (HP 5890) equipped with an FID and a capillary HP-5 column. The GC operating condition was summarized as follows:

Injector temperature: 250 °C

Detector temperature: 280 °C

Carrier gas: He

Column type: Capillary HP-5 column

The oven initial temperature was at 40 °C, and heat at a rate of 3 °C/min to 280 °C.

For *o*-xylene isomerization, the liquid product was analyzed using a gas chromatograph (HP 6890) equipped with an FID and Innowax column. The GC operating condition was summarized as follows:

Injector temperature: 250 °C

Detector temperature: 250 °C

Carrier gas: He

Column type: Capillary HP-Innowax column

The oven initial temperature was at 40 °C, and heat at a rate of 5 °C/min to 150 °C.

The toluene, ethanol, and *o*-Xylene conversion, and *p*-ET selectivity are defined as follows:

$$\text{Toluene conversion (\%)} = \frac{(\text{moles of toluene fed} - \text{moles of toluene out})}{\text{moles of toluene fed}} \times 100 \quad (3.1)$$

$$\text{Ethanol conversion (\%)} = \frac{(\text{moles of ethanol fed} - \text{moles of ethanol out})}{\text{moles of ethanol fed}} \times 100 \quad (3.2)$$

$$p\text{-ET selectivity in products (wt \%)} = \frac{\text{weight of } p\text{-ET formed}}{\text{weight of all liquid products formed}} \times 100 \quad (3.3)$$

$$o\text{-Xylene conversion (\%)} = \frac{(\text{moles of } o\text{-Xylene fed} - \text{moles of } o\text{-Xylene out})}{\text{moles of } o\text{-Xylene fed}} \times 100 \quad (3.4)$$