CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Ludox (40%wt SiO_2) from Sigma-Aldrich
- Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$, min.98%) from Ajax Finechem
- Tetrapropylammonium bromide (TPABr, min.98%) from SigmaAldrich
- Sodium hydroxide (NaOH) from RCI Labscan
- Ammonium nitrate (NH_4NO_3, min.99%) from Ajax Finechem
- Toluene ($C_6H_5CH_3$, min.99.5%) from Carlo Erba
- Methanol (CH_3OH, min.99.8%) from Carlo Erba
- Tetraethyl orthosilicate (TEOS) from Aldrich, USA
- Cyclohexane from RCI Labscan
- Oxalic acid anhydrous from Merck

3.1.2 Gases

- N_2 (99.99 % Purity)
- H_2 (99.99 % Purity)
- He (99.95 % Purity)
- Air Zero (99.99% Purity)

All the gases mentioned 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 6890) equipped with a flame ionization detector and HP–PLOT/Al_2O_3S and HP-INNOWAX columns

Teflon-lined stainless steel autoclave

- Rigaku X-ray Diffractometer (XRD), Model: D8-Discover
- X-ray fluorescence spectroscope (PAN analytical analysis instrument with AXIIOS&SUPERQ version 4.0 systems)
- Quantachrome Surface Area Analyzer (SAA), Model: autosorb 1MP
- Scanning Electron Microscope (SEM), Model: TM300 Hitachi
- Thermo Finnigan TPD/R/O 1100 equiped with flame ionization detector
- Mass flow controller (BROOKS 5850E)

3.3 Methodology

3.3.1 Catalyst Preparation

3.3.1.1 Preparation of Synthesized HZSM-5 Catalyst

HZSM-5 samples were synthesized from hydrogel solutions with the following molar composition

$195SiO_2:Al_2O_3:20TPABr:7800H_2O$

Firstly, Ludox and 4/5 of the distilled water were mixed and stirred at 350 rpm. Then aqueous solution of NaOH was slowly dropped into the Ludox solution to obtain a pH value of 10.5. After that the mixture was stirred for 1 h at room temperature while controlling the pH value at 10.5

The rest of distilled water and $Al(NO_3)\cdot 9H_2O$ were mixed together until $Al(NO_3)\cdot 9H_2O$ was completely dissolved. The $Al(NO_3)\cdot 9H_2O$ 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 resultant gel was placed into an autoclave for hydrothermal treatment 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 treatment. The powder was washed by distilled water for reducing its pH from 10.5 to 7. Then the powder was dried at 80 °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 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 Preparation of Modified HZSM-5 Catalysts

For chemical liquid deposition (CLD) modified catalyst, HZSM-5 zeolite with ratio SiO_2/Al_2O_3 of 200 was mixed with various amounts of TEOS ranging in 0.5-2 ml in 10 ml of cyclohexane solution at room temperature for 7 h, after that HZSM-5 was filtered and dried in a vacuum oven, followed by calcination in air at 550 °C for 5 h.

For dealumination synthesized HZSM-5 zeolites with SiO_2/Al_2O_3 ratio of 200 was mixed with oxalic acid 0.5 M. with stirring and the mixture was heated at 80 °C under reflux for 6 and 8 h. Subsequently, the sample was filtered and washed repeatedly with deionized water. After being dried at 80 °C overnight, it was calcined in air at 550 °C for 5 h.

The combined treatment sample was divided into 2 methods. Firstly, silylation-dealumination sequence was prepared by CLD method which catalyst was mixed with TEOS 1ml in 10 ml of cyclohexane, then, followed by dealumination method which catalyst was mixed with 0.5 M oxalic acid with stirring and the mixture was heated at 80 °C under reflux for 6 h. The resultant material was dried at 80 °C before calcination in air at 550 °C for 5 h. Another method is The solid was separated, washed with deionized water, dried (80 °C), and calcined in air at 550 °C for 5 h. Another method is dealumination-silylation sequence. The catalysts was prepared by dealumination method, then, followed by CLD method. The solid was separated, washed with deionized water and dried at 80 °C overnight followed by calcination in air at 550 °C for 5 h.

3.3.2 Catalyst Characterization

3.3.2.1 X-ray Diffraction (XRD)

X-ray Diffraction was carried on a Rigaku Dmax X-Ray diffractometer, RINT-2200 wide-angle goniometer with Cu tube for generating CuKα radiation (1.5406 Å), a generator voltage of 40 kV, and a generator current of 30 mA was used to characterize the catalyst as XRD patterns. The 2θ was in the range between 5 and 35 with a scanning rate of 5°C/min. Due to the specific chemical composition and crystallographic structure of each material which presented on XRD patterns, XRD can be used to identify and characterize unknown crystalline materials by matching the pattern of reference and unknown.

3.3.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM), TM300 Hitachi, was used to identify the microstructure and capture the micrograph of catalyst morphology and crystal size. The catalyst sample was coated with platinum before measurement for improving conductivity of sample. A beam was passed through a series of lenses to form a magnified image of a sample that was inserted in the area of the objective lens. The image from selected area was viewed through projection onto a view of screen.

3.3.2.3 Brunauer-Emmett-Teller (BET) Surface Area Measurement

The surface area of catalyst was characterized by using surface area analyzer (Quantachrome/autosorb 1MP). The sample was degassed to remove water and other volatile materials under vacuum at 300 °C for 4 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 was established. This volume-pressure data is used to calculate the BET surface area

3.3.2.4 Temperature Programmed Desorption of Isopropylamine (TPD- IPA)

The acidity of catalysts are characterized by temperature program desorption of isopropylamine (TPD-IPA). Firstly, 50 mg of sample was pretreated at 200 °C under He flow for 1h. The sample was cooled down to 100 °C and then 4.0 μl of isopropylamine was injected over the sample, then the excess of isopropylamine was removed by purged He with the flow rate of 10 ml/min for 20, the sample was heated with the flow rate of 10 °C/min to 800 °C under the He atmosphere. Mass 44, 41, and 17 are monitored to determine the evolution of isopropylamine, propylene, and ammonia respectively.

3.3.2.5 Temperature Programmed Desorption of Ammonia

The acidity of catalyst was characterized by temperature program deposition of ammonia (NH_3-TPD). Firstly, 50 mg of sample was pretreated at 400 °C under He flow for 1 h. The sample was cooled down to 100 °C and then ammonia was flow over the sample until its reach the saturation. After that the excess of ammonia was removed by purged He with the flow rate of 30 ml/min, the sample was heated with the flow rate of 20 °C/min to 800 °C under the He atmosphere. Masses 17 were monitored to determine the evolution of ammonia.

3.3.2.6 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation is employed to analyze the amount and characteristics of coke deposited on the catalysts during reaction. 50 mg of catalyst was placed in a quartz reactor and heated with the rate of 10 °C/min under N_2 flow with the rate of 20 ml/min up to 120 °C for 30 minute in order to clean the catalyst surface. Then the reactor was cooled down to 30 °C. After that the catalyst particles were heated again to 950 °C at a heating rate of 10 °C/min under the flow of 4.99 % O_2/He with the rate of 20 ml/min. The CO_2 that was produced by the oxidation of the coke species is analyzed on-line by a TPDRO/MS 1100 TCD detector as a function of temperature.

3.3.3 Catalytic Activity Testing

The catalytic activity for the catalysts studied on methylation of toluene with methanol was carried out at atmospheric pressure using a fixed-bed continuous down-flow reactor under varied parameters including WHSV, molar ratio of toluene-to methanol, and reaction temperature. The reactor has outside diameter of 12 mm and length of 37 cm. Prior to the reaction, about 50 mg catalyst sample was packed between the thin layers of glass wool located at the middle of reactor. The reactor was placed into an electric furnace equipped with K-type thermocouples. The catalyst was purged at temperature 400 °C for an hour under flowing nitrogen. The temperature of the reactor is monitored and controlled by a PID temperature controller (Shinko) at atmospheric pressure. Then, the reactant mixture of toluene and methanol was introduced into the reactor using a syringe pump. The nitrogen was used as a carrier gas and controlled at a flow rate of 40 ml/min by a mass flow controller (BROOKS 5850E). The gaseous products were analyzed using a gas chromatograph (HP 6890) equipped with an FID and installed with HP-PLOT/Al_2O_3S and HP-INNOWAX columns every 60 min on stream for 6 h. A schematic diagram of the system is shown in Figure 3.1.

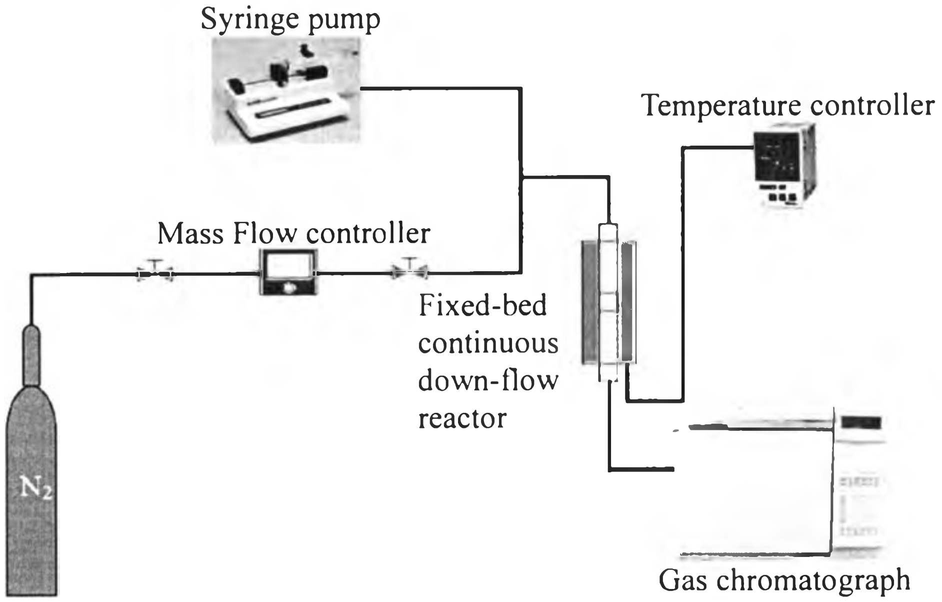

Figure 3.1 Schematic of the catalytic activity testing system.

3.3.4 Determination of Product Composition

The composition of produced was analyzed using a gas chromatograph (HP 6890) equipped with an FID and installed with HP-PLOT/Al2O3S and HP-INNOWAX columns which was operated according to the conditions present in Table 3.1 under the following conditions:

- Inlet temperature: 250 °C
- Detector temperature: 250 °C
- Initial temperature: 35 °C
- Carrier gas: Helium
- Temperature programmed steps as presented in Table 3.1

Table 3.1 Operating conditions for the GC utilized

Step	Ramp rate (°C/min)	Temperature (°C)	Holding Time (min)
Initial	-	35	2.00
Ramp 1	5	75	10.00
Ramp 2	3	100	0.00
Ramp 3	10	145	17.67

Toluene and methanol conversion, and p-xylene selectivity are defined as follows:

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

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

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