CHAPTER V
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

- Toluene (99.5 % purity) obtained from Carlo Erba
- Methanol (99.8 % purity) obtained from Carlo Erba
- Tetraethyl orthosilicate (TEOS) (Aldrich, USA)
- Cyclohexane (RCI Labscan)
- Oxalic acid anhydrous (Merck)
- Commercial ZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of 23, 50, 80 and 280 (Zeolyst international)

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 an FID and installed with HP–PLOT/Al_2O_3S and HP-INNOWAX columns
- Rigaku X-ray Diffractometer (XRD), Model : D8-Discover
- Quantachrome Surface Area Analyzer, Model : Autosorb-1 MP
- Thermo Finnigan TPD/R/O 1100 equiped with flame ionization

detector

- PANalytical analysis instrument with AXIOS&SUPERQ version 4.0 systems

- Scaning electron microscopy (SEM), Model : TM300

- NMR 500 MHz with CP/MAS solid probe and Nano probe Varian model INOVA

- Mass flow controller (BROOKS 5850E)

3.3 Methodology

3.3.1 Catalyst Preparation

For preparing the catalysts modified by CLD, about 1 g of HZSM-5 zeolite with SiO_2/Al_2O_3 mole ratio of 280 was mixed with a desired amount of TEOS (varied from 0.2 to 2 ml) in 10 ml cyclohexane for 7 h with mildly stirring. After that, the solid was filtered out and dried in an oven followed by calcination in air at 550 °C for 4 h (Hui *et al.*, 2011). The cycle of CLD treatment was altered to investigate its effect on the activity of catalysts. The prepared sample was designated as CLD(x)-HZ-5, where x represents the desired amount of TEOS by CLD treatment.

For preparing the catalysts modified by dealumination, about 10 g of HZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of 280 was mixed with 50 mL oxalic acid solution (0.5 mol) with mildly stirring, and then, the mixture was heated under reflux for 10 h. Subsequently, the solid was filtered out and washed repeatedly with deionized water. After being dried at 120 °C for 8 h in an oven, the sample was calcined in air at 550 °C for 4 h. The prepared sample was designated as DeAl-HZ-5.

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 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 is in the range between 5 and 50 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 Microscope (SEM)

Scaning electron microscopy (SEM) was used to study morphology and crystal size of the catalyst on a TM300. The catalyst sample was placed on stub and coated by platinum in sputtering device, then the sample was placed in the sample holder in SEM.

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

The surface area of catalyts was 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 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 is established. This volume-pressure data was used to calculate the BET surface area.

3.3.2.4 Temperature Programmed Desorption of Isopropylamine (TPD- IPA)

The Brønsted acid site of catalysts were characterized by temperature program desorption of isopropylamine (TPD-IPA). Firstly, 50 mg of sample was pretreated at 400 °C under He flow for 1h. The sample was cooled down to 30 °C and then 5.0 µl of isopropylamine was injected over the sample, then the excess of isopropylamine 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 44, 41, and 17 were monitored to determine the evolution of isopropylamine, propylene, and ammonia, respectively.

3.3.2.5 Temperature Programmed Desorption of Ammonia (TPD- NH₃)

The acidity of catalyst was characterized by temperature program desoption of ammonia (TPD-NH₃). Firstly, 50 mg of sample was pretreated at 400 °C under He flow for 1h. 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 was 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 was analyzed on-line by a TPDRO/MS 1100 TCD detector as a function of temperature.

3.3.2.7 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.

3.3.2.8 Solid state ^{27}Al MAS Nuclear Magnetic Resonance Spectrometer (^{27}Al MAS NMR)

Solid state ^{27}Al MAS NMR spectroscopy has become an efficient method to determine the coordination state of the aluminum species in zeolites by NMR 500 MHz with CP/MAS solid probe and Nano probe Varian model INOVA. The non-equivalent positions of identical aluminum coordination states may strongly overlap, but the resonances of tetrahedral and octahedral environments are sufficiently resolved to determine the Al(IV)/Al(VI) ratio, respectively.

3.3.3 Catalytic Activity Testing

The catalytic activity for the catalysts on methylation of toluene with methanol was carried out at atmospheric pressure, temperature of 400 °C, WHSV of 24 h^{-1}, toluene to methanol ratio of 4, using a fixed-bed continuous down-flow reactor. The reactor has an inside diameter of 6 mm and a length of 37 cm. The catalyst was loaded into the middle of reactor and supported with thin layers of glass

wool. Before the reaction, the catalyst was activated at 400 °C for 0.5 h in flowing nitrogen. The temperature of the reactor was monitored and controlled using a PID temperature controller (Shinko FCR-13A) equipped with a K-typed thermocouple. The reactant mixture of toluene and methanol which was fed into the reactor using a syringe pump was preheated before entering the reactor by a heating wire. Nitrogen was used as a carrier gas and controlled at a flow rate of 40 ml/min using a mass flow controller (BROOKS 5850E). The gas and liquid products were analyzed using a gas chromatograph (HP 6890) equipped with an FID and installed with HP–PLOT/Al$_2$O$_3$S and HP-INNOWAX columns every 60 min on stream for 6 h.
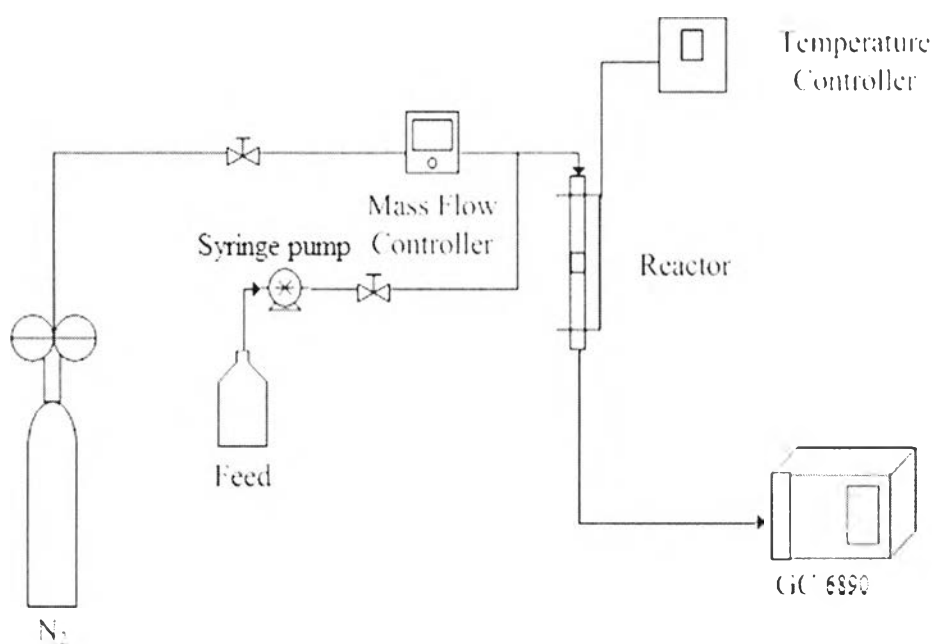

Figure 3.1 Schematic of the catalytic activity testing system.

3.3.4 Product Analysis

For the gas and liquid products were analyzed using a gas chromatograph (HP 6890) equipped with an FID and installed with HP–PLOT/Al$_2$O$_3$S and HP-INNOWAX columns

The GC operating condition was inlet temperature at 250 °C, detector temperature: at 250 °C. The oven initial temperature was at 35 °C, and program temperature as follows

Table 3.1 Oven condition

Oven Ramp	Ramp rate (°C/min)	Temperature (°C)	Hold 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:

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

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

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

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