



CHAPTER III EXPERIMENTAL

3.1 Materials and Equipment

Chemicals:

Fumed silica
Aluminium hydroxide hydrate
Triethanolamine
Triisopropanolamine
Tetraethoxysilane
Ethylene glycol
Sodium hydroxide
Lithium hydroxide
Tetra-propyl ammonium bromide
Acetonitrile
Methanol
Ammonium hydroxide solution
Silicone oil
Toluene
Distilled water

Equipment:

Microwave
Thermogravimetric Analyzer (TGA)
Fourier Transform Infrared Spectrometer (FTIR)
Positive Fast Atomic Bombardment Mass Spectrometer (FAB⁺-MS)
Scanning electron microscopy (SEM)
X-ray diffraction (XRD)
Temperature programmed desorption (TPD)
Surface area analyzer (BET)
X-ray fluorescence (XRF)
Gas chromatography (GC)

Reactors

Syringes

Vials

3.2 Experimental Methods

3.2.1 Silatrane Synthesis

Following the method of Wongkasemjit [13, 15], alumatrane and silatrane were synthesized directly from inexpensive and widely available starting materials via the Oxide One Pot Synthesis (OOPS) process, which is the one step reaction.

Silatrane (tris(silatranyloxy-ethyl)amine or SiTEA) was synthesized by heating a mixture of 0.125 mol of TEA, 0.1 mol of SiO₂ and 100 ml of EG at 200°C under nitrogen atmosphere. The reaction was complete within 10 hr and the mixture was cooled down to room temperature before distilling excess EG under vacuum (8 mmHg) at 110°C for 6 hr. The white solid was washed three times with dried acetonitrile to remove unreacted TEA and EG out. The silatrane product was dried under vacuum desiccator overnight and characterized using TGA, FAB⁺-MS and FT-IR.

3.2.2 Alumatrane Synthesis

Alumatrane (tris(alumatranyloxy-i-propyl)amine or AlTIS) was synthesized using the same method and condition as silatrane synthesis by mixing 0.125 mol of TIS and 0.1 mol of Al(OH)₃ in 100 ml of EG. EG was removed after completion of the reaction by vacuum distillation (8 mmHg) at 110°C until dried crude product was obtained. Pale-yellow solid was washed three times with dried acetonitrile to obtain fine white powder. The purified product was characterized using TGA, FAB⁺-MS and FT-IR techniques.

3.2.3 Zeolite Catalyst Preparation

Silicalite-1, ZSM-5 and FAU zeolite samples with different SiO₂/Al₂O₃ ratios in the range of 50-250 were prepared using sol-gel process and

microwave technique for hydrothermal treatment. Silatrane and alumatrane were used as precursors, and the molar starting material compositions including synthesis conditions were given in Table 3.1.

Table 3.1 Molar starting compositions of the synthesis mixtures and conditions for zeolite synthesis

Zeolite	SiO ₂ /Al ₂ O ₃ ratio	SiO ₂	Al ₂ O ₃	TPA	NaOH	H ₂ O	Aging time (hr)	Heating time (hr)	Heating temp (°C)
Sil-1	α	1	-	0.1	0.4	114	90	15	150
ZSM-5	50	1	0.02	0.1	0.4	114	90	15	150
ZSM-5	100	1	0.01	0.1	0.4	114	90	15	150
ZSM-5	150	1	0.007	0.1	0.4	114	90	15	150
ZSM-5	200	1	0.005	0.1	0.4	114	90	15	150
ZSM-5	250	1	0.004	0.1	0.4	114	90	15	150
FAU	2	1	0.5	-	2*	410	72	5	110

* Use of LiOH in place of NaOH

After finishing the crystallization step, the zeolite samples were calcined at 550°C with heating rate of 1°C/min to decompose organic template out from the channels. Then, the samples were refluxed in 2M ammonium hydroxide solution for 2 hr and calcined again with the same procedure to exchange into an active form. The zeolite products were characterized using XRD, SEM, BET, TPD and XRF techniques.

3.2.4 Material Characterization

FTIR spectroscopic analysis was conducted using Bruker Instrument (EQUINOX55) with a resolution of 2 cm⁻¹ to measure functional groups of materials. The solid samples were mixed and pelletized with dried KBr. Mass spectrometry was studied using VG Autospec model 7070E from Fison Instruments with VG data system, the positive fast atomic bombardment (FAB⁺-MS) mode and glycerol as a matrix. CsI was used as a reference, while a cesium gun was used as an initiator. The mass range used was from m/e = 20 to 3,000. Thermogravimetric analysis

(TGA) was carried out using Perkin Elmer TGA7 analyzer with heating rate of 10°C/min over room temperature until 750°C under nitrogen atmosphere. Hydrothermal treatment step using microwave heating technique for zeolite synthesis was done using MARS, CME Corporation. The crystallinity and crystal structure were identified using Rigaku X-Ray diffractometer (XRD) using the scanning speed of 0.5 and 5 degree/sec, CuK α as a radiation and a filter. The working range was 5-90 theta/2 theta with 1 degree and 0.3 mm setting of divergent for scattering and receiving slit, respectively. The crystal morphology was observed using JEOL 5200-2AE scanning electron microscope (SEM). The sample mixture was heated in a Teflon vessel using power of 300 W to set point at 150°C with ramp to temperature program. Surface area and pore volumes of zeolite samples were measured using Autosorb-1 surface analyzer. Acidity and acid strength of zeolites were determined using Thermofinigan TPD/R/O 1100 instrument. The ammonia and 4-methyl quinoline were used as a basic probe to measure total acidity and external acidity, respectively. The parameters used for the TPD study are listed in Table 3.2. The actual amount of Si/Al ratio was measured using Philips 2400 X-Ray Fluorescence (XRF). Boric acid (HBO₃) was used as a matrix binder for sample blending. The reactor effluent in both of CVD and reaction procedures was examined using fixed-volume sample loop Agilent 6890N Gas chromatography (GC) equipped with a 30 m long polyethylene glycol column (DB-WAX).

Table 3.2 TPD parameters for acidity measurement

TPD Parameters	Pyridine	4-MQ
Catalyst mass (g)	0.25	0.4
Adsorption temp (°C)	Room temp	Room temp
Adsorption time (h)	1	1
Helium flowrate (ml/min)	20	20
Desorption temp (°C)	RT-900	RT-900
Heating rate (°C /min)	10	10

3.2.5 Zeolite Modification Techniques

3.2.5.1 Seeding Technique

The synthetic ZSM-5 zeolite having the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 100 can be obtained during hydrothermal treatment using microwave technique with a molar composition of $\text{SiO}_2:0.01\text{Al}_2\text{O}_3:0.1\text{TPABr}:0.4\text{NaOH}:114\text{H}_2\text{O}$. Silicalite-1, the stable aluminium-free zeolite, was used for coating the surface of ZSM-5 by seeding technique. Samples were prepared by a two-step crystallization procedure using synthetic ZSM-5 seeds produced from silatrane and alumatrane. To obtain a silicalite-1 shell coated on the ZSM-5 crystals, the ZSM-5 seeds were re-immersed in secondary synthesis mixtures containing no aluminium. The procedure of secondary synthesis was similar to the ZSM-5 synthesis. The ratio between core and shell was equal to one. The synthesis at different conditions were studied to determine the optimal condition for modification. The effect of dilution at constant pH was the preliminary study to investigate the possibility in dissolution of the crystals. The molar compositions of the secondary synthesis mixtures are given in Table 3.3.

Table 3.3 Molar compositions of the secondary synthesis mixtures and conditions for seeding

Synthesis	SiO_2	TPABr	NaOH	H_2O	Aging time (hr)	Heating time (hr)	Heating temp ($^\circ\text{C}$)
Seed 1.A	1	0.1	0.4	114	-	15	150
Seed 2.A	1	0.1	3.51	1000	-	15	150
Seed 3.A	1	0.1	17.55	5000	-	15	150
Seed 4.A	1	0.1	0.7	200	-	15	150
Seed 5.A	1	0.1	0.88	250	-	15	150

3.2.5.2 Chemical Vapor Deposition (CVD)

The surface modification on ZSM-5 zeolites by the CVD technique was performed at 3 different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, 200°C using 6.38% TEOS by volume in methanol solvent at space velocity of 5 h^{-1} , and nitrogen as a carrier gas in a vacuum line. The amount of silica deposited was controlled by the deposition time of TEOS. In order to find the optimal deposition time, the CVD

procedure was firstly scanned for 50 min. The amount of unconverted TEOS was measured using gas chromatography (GC). After finishing the deposition, the TEOS feed stream was replaced with nitrogen gas at the flow rate of 30 ml/min to remove physisorbed TEOS for 30 minutes. The catalyst bed was then calcined under air atmosphere at 500°C with heating rate of 2°C/min for 6 hr to decompose TEOS into silica layer coated on the surface. The modified catalysts were characterized to compare the properties with unmodified catalysts.

3.2.6 Toluene Disproportionation Experiment

The catalytic activity testing of zeolites by toluene disproportionation reaction was performed in a fixed bed, continuous down flow quartz reactor with 10 mm o.d. and a length of 0.6 m. The toluene reactant was introduced using a syringe pump with space velocity in the range of 2.5-100 hr⁻¹ to determine the suitable condition for the reaction. Before feeding toluene, the catalyst was treated in a nitrogen stream at 500°C for 1 hr to remove the moisture out. 1 Mole nitrogen equivalent to toluene fed was used as a carrier gas. The gas and liquid mixture was preheated at 200°C before entering to the reactor. The reaction was done under ambient pressure and two different temperatures of 400°C and 500°C. The effluent products from the reactor were analyzed using GC. The schematic flow diagram of reaction was shown in Figure 3.1.

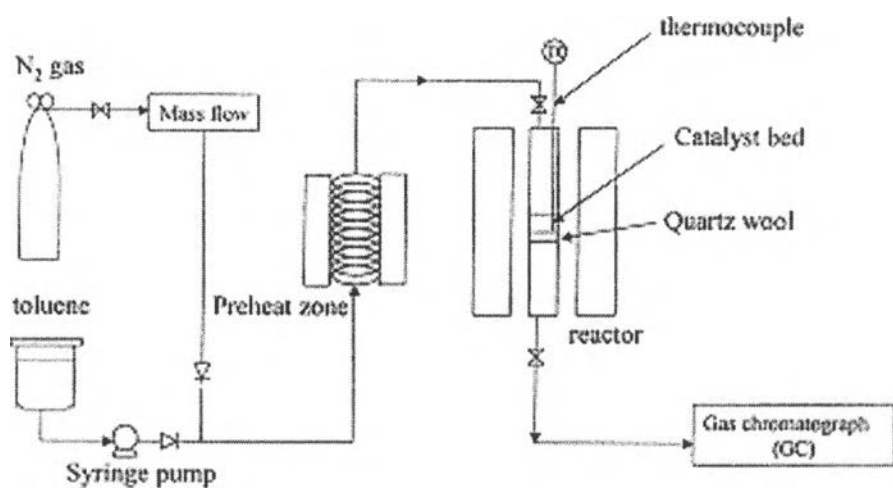


Figure 3.1 Schematic flow diagram of toluene disproportionation reaction.