

## **CHAPTER III**

### **METHODOLOGY**

#### **3.1 Materials**

Passenger car tires from Bridgestone TURANZA GR-80 were prepared by cutting machine in the size range of 20-40 mesh.

#### **3.2 Equipments**

1. Bench-scale autoclave reactor
2. Grinder machine
3. Agilent Technologies 6890, Gas chromatography (GC), Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
4. Gas Chromatography - Mass Spectrometry, Time of Flight (GCxGC-TOF/MS)
5. Rigaku D/MAX 2200H X-Ray diffractometer system (XRD)
6. Rigaku TTRAXIII diffractometer
7. Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)
8. Thermo Finigan TPDRO 1100 (Temperature Programmed Desorption/Reduction/ Oxidation)
9. Bruker DPX-300 NMR spectrometer.
10. Perkin Elmer/Pyris Diamond (Thermogravimetric/Differential Thermal Analysis, TG/DTA)
11. LECO® Elemental Analyzer (TruSpec®S)
12. Sieves (20,40 and 60 U.S. mesh (ASTM))
13. Rotary Evaporator
14. Aquariums air pump
15. Vacuum Air Pump

### 3.3 Chemicals and Solvents

1. n-pentane ( $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ , Assay  $\geq 99\%$ )
2. Carbon disulfide,  $\text{CS}_2$
3. Nitrogen gas
4. HZSM-5 (Si/Al = 15) from Tosoh Company, Singapore
5. HY (Si/Al = 7.5) from Tosoh Company, Singapore
6. HBETA (Si/Al = 14) from Tosoh Company, Singapore
7. Tetraethylorthosilicate (TEOS)
8. Aluminium isopropoxide ( $\text{Al}(\text{OH})_3$ )
9. Cetyltrimethylammonium bromide (CTAB)
10. Sodium hydroxide (NaOH)
11. Aqueous ammonia (aq.  $\text{NH}_3$ )
12. Ethanol

### 3.4 Experimental Procedures

#### 3.4.1 Catalyst Preparation

##### 3.4.1.1 *Zeolites*

$\text{NH}_4$ -BETA (Si/Al=14), HY (Si/Al=7.5), and HZSM-5 (Si/Al=15) were purchased from TOSOH Company (Singapore).  $\text{NH}_4$ -BETA was calcined at 600 °C for 2 h with 2 °C/min. HY and HZSM-5 was calcined at 500 °C for 3 h with 10 °C/min.

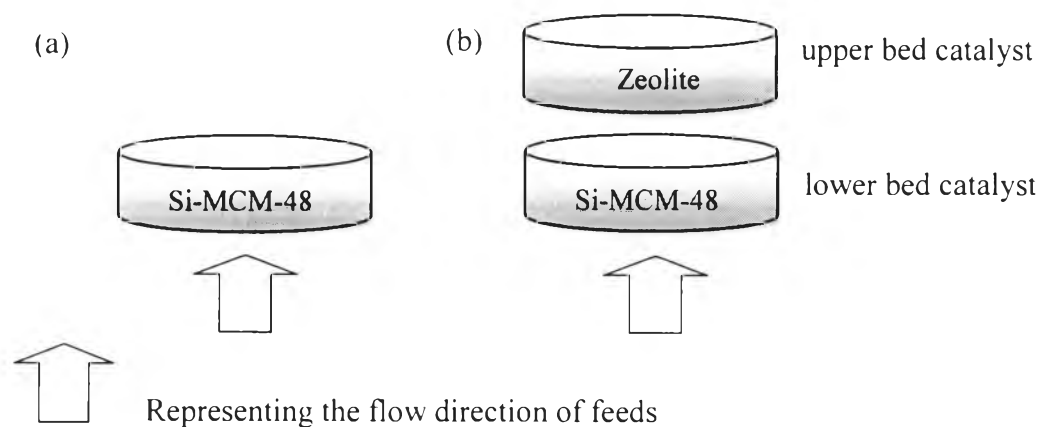
##### 3.4.1.2 *Synthesis of Si-MCM-48 and Al-MCM-48*

The Si-MCM-48 catalyst was synthesized at room temperature following the modified Stöber synthesis method (Kibombo *et al.*, 2014). The molar composition of gel was 0.41 CTAB: 11 aq. $\text{NH}_3$ : 1.0 TEOS: 53 Ethanol: 344  $\text{H}_2\text{O}$ . Ethanol (25 ml), CTAB (1.2 g), aq.  $\text{NH}_3$  (6 mL) and TEOS (1.8 mL) were sequentially added into deionized water (50 mL), and stirred for 4 h. After synthesis, the catalyst was filtrated and washed with deionized water. After that, the catalyst was dried in a 80°C oven for overnight, and calcined for 6 h in air at 540°C with heating rate 2°C/min.

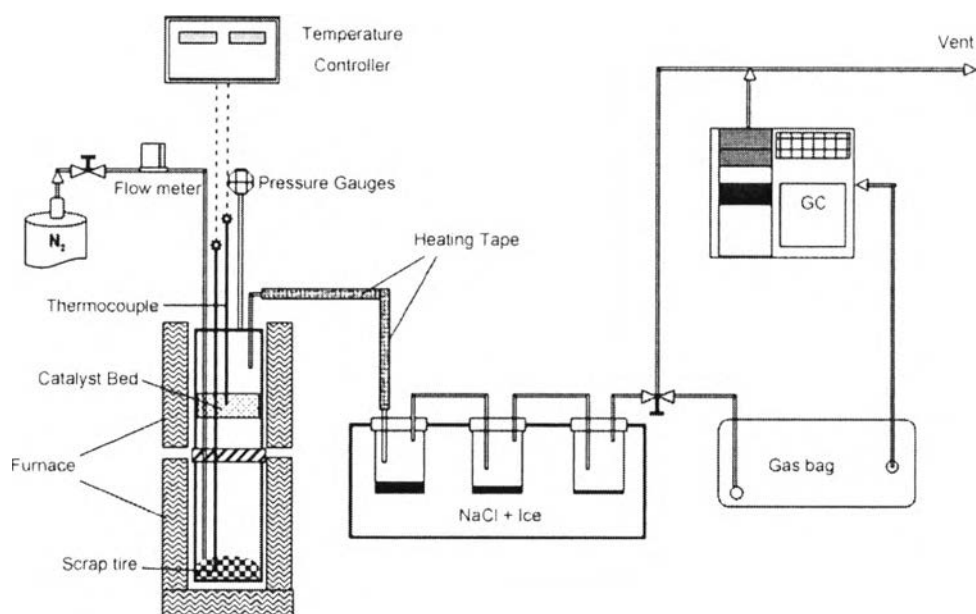
The Al-MCM-48 catalysts (starting Si/Al of precursors = 50, 75, and 200) were synthesized via hydrothermal synthesis method (Huang *et al.*, 2008) using tetraethoxysilane (TEOS), aluminum isopropoxide, and cetyltrimethylammonium bromide (CTAB) as the silica source, alumina source, and templating agent, respectively. 9.56 g of CTAB was dissolved in 170 ml of deionized water at 35°C. Then, 3.15 g of NaOH was added into the resulted solution, and stirred for 10 min. After that, 29.07 ml of TEOS and 0.13-0.55 g of alumina precursor were added and stirred for 2 h at 35 °C. Then, the gel was transferred to a Teflon-lined autoclave and heated at 120 °C for 40 h. The solid product was filtrated and washed with deionized water. Next, the catalyst was dried at 80 °C overnight and calcined at 540 °C with 2 °C/min heating rate for 6 h. Finally, the catalyst powder was pelletized, crushed, and sieved into the particle size range of 40-60 mesh.

#### 3.4.2 Pyrolysis Process

The same pyrolysis system was employed in the experiments, following the method set by Dũng *et al.* (2009b). 30 g of waste tyre sample was loaded into pyrolytic zone, and catalyst was loaded into the catalytic zone. In addition, there are two cases for placing the catalyst; that are, single bed and double bed catalyst. The upper bed catalyst was varied (HZSM-5, HBETA, and HY), and a lower bed catalyst was fixed to Si-MCM-48 as shown in Figure 3.1. Nitrogen was flown through the reactor at 30 ml/min. Heated with the heating rate of 10 °C/min from room temperature, the pyrolytic zone was operated at 500 °C, and the catalytic zone was operated at 350 °C catalytic zone. The liquid product was collected in condensers immersed in an ice bath. The gas product was collected in a gas sampling bag, whereas the solid product remained in the pyrolytic zone of reactor.



**Figure 3.1** Placement of catalysts: (a) single bed of Si-MCM-48, and (b) double bed of Si-MCM-48 and a zeolite.



**Figure 3.2** Diagram of the pyrolysis process (Dũng *et al.*, 2009b).

### 3.4.3 Gas Analysis

The pyrolytic gas products were calculated by mass balance and were analyzed by a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm ID and 20  $\mu\text{m}$  film thicknesses.

FID was a detector with Helium as the carrier gas. The temperature program was set as follows:

Initial temperature	70 °C
Time at initial temperature	8 min
Heating rate	20 °C/min to 200 °C
Hold for	16 min
Final temperature	200 °C
Holding time	0 min

#### 3.4.4 Oil Analysis

Tire-derived oil was mixed with n-pentane at the weight ratio of 40:1. Then, the mixture was shaken at room temperature for 15 min in an ultrasonic bath before leaving overnight. After that, the asphaltene was filtered out by using 0.45 µm a teflon membrane in a vacuum system. The membrane and asphaltene were dried in an oven at 80 °C for 6 hr and weighed to determine the asphaltene content. Then, the n-pentane was evaporated from the maltene solution obtained after filtering by using a rotary vacuum evaporator at 50 °C. The remained oil was analyzed by using the LECO®Elemental Analyzer for sulfur content. The maltene was also diluted with carbon disulfide before analyzing by SIMDIST-GC and GC×GC-TOF/MS.

##### 3.3.4.1 *Gas Chromatography-Mass Spectrometry, Time of Flight (GC×GC-TOF/MS)*

The compounds in maltenes were determined by using Gas Chromatography-Mass Spectrometry (Agilent® 7890A), Time of Flight (PEGASUS® 4D), with 2D dimension mode (GC×GC-TOF/MS). Helium was used as carried gas, and nitrogen was used in the cooling system. The conditions were set as follows:

1 <sup>st</sup> Column:	Rtx 5, 30 m × 0.32 mm × 1.0 µm film thickness
2 <sup>nd</sup> Column:	Rtx 17, 1.8 m × 0.18 mm × 0.2 µm film thickness
Helium flow rate	1.5 ml/min
Inlet temperature	250 °C
Time at initial temperature	2 min

Heating rate	5 °C/min to 270 °C
Hold for	5 min
Electron impact ionization energy	70 eV

#### 3.3.4.2 *Simulated Distillation Gas Chromatography (SIMDIST GC)*

The maltene was analyzed for simulating true boiling point curves using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) equipped with a 15 m × 0.25 mm × 0.25 μm WCOT fused silica capillary column and FID. The maltene was analyzed according to the ASTM D2887 method with the conditions below:

Initial temperature	30 °C
Time at initial temperature	0.01 min
Heating rate	20 °C/min
Final temperature	320 °C
Holding time	8.50 min

#### 3.4.5 Residual Char analysis

The LECO® Elemental Analyzer (TruSpec®S) is used to determine the sulfur content in residual char. The 0.1 g of residual char is added to ceramic boat. After that, the ceramic boat is heated from room temperature to 600 °C for 15 min. Finally, the ceramic boat is heated up to 1350 °C for analyzing step.

#### 3.4.6 Catalyst Characterization

##### 3.4.6.1 *Small-Angled X-ray Scattering (SAXS)*

The small-angled X-ray scattering patterns of mesoporous catalyst were obtained using a Rigaku TTRAXIII diffractometer equipped with Cu K $\alpha$  radiation at 50 kV and 300 mA. The experimental conditions were set with 0.02° of sampling width, 2°/min of scan speed, and 2.0-6.0° of scan angles.

##### 3.4.6.2 *X-ray Diffraction (XRD)*

XRD patterns of zeolites were determined using Rigaku/Rint2200 HV equipped with CuK $\alpha$  small radiation (1.5406 Å) operating at 40 kV and 30 mA. The XRD patterns were recorded from 5° to 65° of 2 $\theta$  with a step size 2 $\theta$  = 0.02° at the scanning speed of 5°/min

#### 3.4.6.3 X-ray fluorescence (XRF)

X-ray fluorescence (XRF) instrument combined with AXIOS&SUPERQ version 4.0 systems determined the Si/Al ratios of catalyst. The IQ+ program was used to analyze the elemental composition of catalysts.

#### 3.4.6.4 Thermo Finnigan Sorptomatic 1990 (Surface Area Analyzer)

Brunauer-Emmet-Teller (BET) method using Thermo Finnigan Sorptomatic 1990 was used to determine specific surface area, total pore volume, pore size distribution and isotherm

#### 3.4.6.5 Temperature-Programmed Desorption Ammonia (TPD-NH<sub>3</sub>)

Temperature-Programmed Desorption Ammonia (TPD-NH<sub>3</sub>) was used to determine acid density. The samples were pretreated at 300 °C for 3h under a Helium flow of 20 mL/min. After that, they were analyzed with 10 % NH<sub>3</sub> in Helium balance heated to 800 °C with the heating rate of 10°C/min. The desorbed gases were analyzed by TCD detector.

#### 3.4.6.6 <sup>27</sup>Al Magic Angle Spinning–Nuclear Magnetic Resonance (<sup>27</sup>Al MAS NMR)

The <sup>27</sup>Al MAS NMR spectra were analyzed by a Bruker DPX-300 NMR spectrometer to determine Brönsted and Lewis acid sites. The spectra were recorded at a frequency of 78 MHz. The experimental conditions were set as follows: 800 numbers of scan (NS), a relaxation delay of 4 second, spin rate of 5 kHz and spectral size 4 K with 2 K time domain size.

#### 3.4.6.7 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The coke formation on catalysts is determined by TG/DTA machine. The spent catalysts are weighed and placed in a sample pan followed by heating from the room temperature to 900 °C with the heating rate of 10 °C /min. Oxygen flow rate is controlled at 20 ml/min

#### 3.4.6.8 LECO® Elemental Analyzer (TruSpec®S)

Elemental analyzer (LECO, CHNS-932) is used to determine the amount of sulfur deposition on spent catalysts and in tire-derived oil.