

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Rubber particle was prepared by a cutting machine, using passenger car tire, which life time was fixed at about 50,000 km for catalytic pyrolysis process.

### 3.2 Equipment

1. Bench-scale autoclave reactor
2. Gas sampling bag
3. Cutting Tool
4. Agilent Technologies 6890, Gas chromatography (GC),
5. Liquid chromatography column (Glass), 650 mm height, 26.6 mm inside diameter
6. Varian GC-3800 simulated distillation gas chromatograph (SIMDIST GC)
7. Aquariums air pump
8. Thermo Finigan TPDRO 1100 (Temperature Programmed Reduction/Oxidation)
9. Micromeritics, TPD/TPR 2900 Analyzer
10. LECO<sup>®</sup> Elemental Analyzer (TruSpec<sup>®</sup>S)
11. Sorptomatic 1990 system

### 3.3 Chemical and Solvents

1. Benzene (C<sub>6</sub>H<sub>6</sub>, Assay ≥ 99.8%)
2. Diethyl ether ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, Assay ≥ 99.5%)
3. N-pentane (CH<sub>3</sub> (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, Assay ≥ 99%)
4. N-hexane (CH<sub>3</sub> (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), Assay ≥ 99 %)
5. Methanol (CH<sub>3</sub>OH, Assay ≥ 99.8 %)

6. Carbon disulfide, CS<sub>2</sub>
7. Silica for liquid chromatography (Particle size 0.063-0.200 ; 70-730 mesh ASTM)
8. Neutral alumina for liquid chromatography (0.05-0.15mm ; pH 7.0±0.5)
9. N<sub>2</sub> gas
10. Catalysts from Tosoh Company, Singapore : HMOR
11. Catalysts from Wongkasemjit group, MCM-48
12. Clays
  - Kaolin from Sibeco Co.
  - Bentonite from Compound Clay Co.
  - Montmorillonite from Aldrich Co.
  - Talcum from Compound Clay Co.
13. α-alumina
14. Metal precursors: Ruthenium (III) chloride hydrate (RuCl<sub>3</sub>.aq)

### 3.4 Methodology

#### 3.4.1 Catalyst Preparation

##### 3.4.1.1 *Preparation of Ru/HMOR and Ru/MCM-48-based Catalysts*

The silica MCM-48 was synthesized by silatrane. Silatrane was first synthesized using the method of Wongkasemjit's group (Longloilert *et al*, 2011). Silatrane precursor was added to hexadecyltrimethyl ammonium bromide (CTAB, purchased from Sigma Chemical Co.), and sodium hydroxide (NaOH, sigma Chemical Co.). After that, water was added with vigorous stirring, and gel was kept in an autoclave 16 hr at 140°C. The obtained crude product was filtered and washed with water to keep a white solid. The ratio of chemicals: Si/CTAB/NaOH/H<sub>2</sub>O was used as 1/0.3/0.5/62. Next, the white solid was dried at room temperature and calcined at 550 °C for 6 hours with ramping rate of 0.5°C/min to obtain mesoporous MCM-48. Then, the precursor solution of ruthenium (III) chloride hydrate was

dropped on an individual support by a spilling for 1-2 hours. 5 g. of support was loaded with 0.7%Ru, which needed 0.0719 g of Ru<sub>3</sub>Cl.

The HMOR, from Tosoh Company; Singapore, was calcined at 500°C for 3 hours with the heating rate of 10°C/min. Then, a 10 g. of support was loaded with 0.7 %wt ruthenium by using the incipient wetness impregnation technique. The precursor solution was dropped on an individual support by a spilling for 1-2 hours. After that, both of wet supports were dried in an oven at 110°C for 3 hours and calcined in a furnace at 500°C for 3 hours with the heating rate of 10°C/min to obtain the bifunctional catalysts in an oxide form. Then, the catalysts were reduced with H<sub>2</sub> at 400°C for 1-2 hours in order to convert the metal oxide form to metal element (Ru-supported HMOR zeolite and Ru-supported MCM-48).



Then, Ru/HMOR and Ru/MCM-48 with the %wt in the range of 5-20%wt were mixed of 80-95%wt of clay (kaolin) and 10 %wt  $\alpha$ -alumina in deionized water. The mixture is homogenized and extruded through a hole of 2 mm diameter. The extrudates were dried in an oven at 110°C for 3 hours and calcined in a furnace at 250°C for 2 hours with the heating rate of 10°C/min to get the catalysts for catalytic pyrolysis.

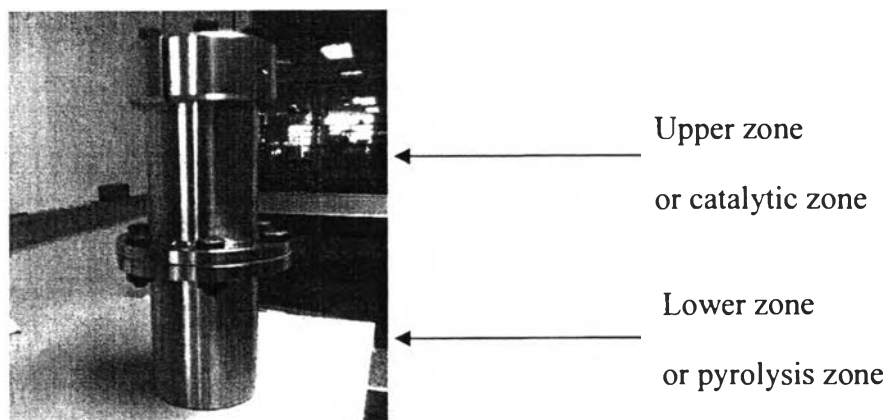
#### 3.4.1.2 Preparation of Catalyst for Studying the Effect of Matrix

The HMOR support was loaded with 0.7 %wt ruthenium by using the incipient wetness impregnation technique. The precursor solution of ruthenium (III) chloride hydrate was dropped on an individual support by a syringe for 1-2 hours. After that, the wet supports were dried in oven at 110°C for 3 hours and calcined in a furnace at 500°C for 3 hours with the heating rate of 10°C/min to obtain the bifunctional catalysts in an oxide form. Then, the catalyst was reduced with H<sub>2</sub> at 400°C for 1-2 hours in order to convert the metal oxide form to metal element (Ru-supported HMOR).

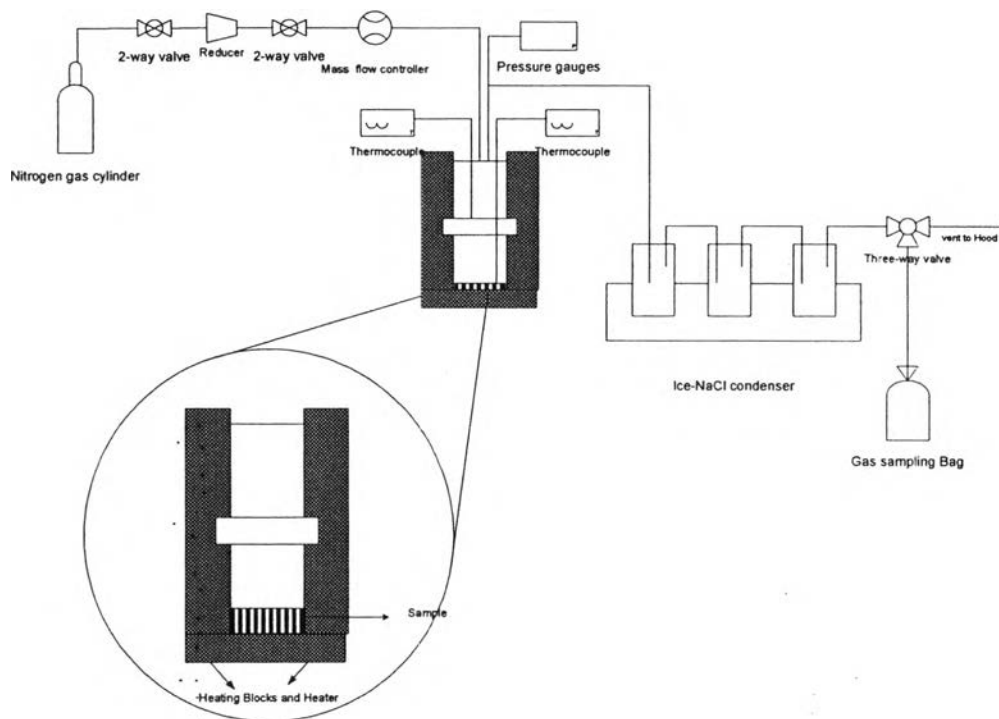
After that, an amount of Ru/HMOR in the range of 5-20%wt was mixed with 80-95%wt of a clay, which were kaolin, bentonite, talc, and montmorillonite.

### 3.4.2 Pyrolysis Experiments

The reactor was separated into 2 zones: the upper zone was the catalytic zone, and the lower zone was pyrolysis zone where tire was loaded. The temperature of lower zone was controlled at 500 °C, and that of catalytic zone was controlled at 350 °C with the ramping rate of 10 °C/min. The nitrogen was flown into the reactor in order to purge oxygen and sweep the pyrolysis product to condensers. The flow rate was controlled at 30 ml/min. The non-condensable products were collected in a gas sampling bag. Pyrolysis experiments were divided to 2 parts. The first was the catalytic pyrolysis using Ru/HMOR, and the second was the catalytic pyrolysis using Ru/MCM-48.



**Figure 3.1** The autoclave reactor used in the experiment (Mhodmonthin, 2005).



**Figure 3.2** Schematic of the pyrolysis process (Mhodmonthin, 2005).

#### 3.4.2.1 *The Catalytic Pyrolysis Using Ru/HMOR*

The upper zone was loaded with 7.5 g. Ru/HMOR-based catalyst, and the lower zone was loaded with 30 g. of tire.

#### 3.4.2.2 *The Catalytic Pyrolysis Using Ru/MCM-48*

The upper zone was loaded with 2.5 g. Ru/MCM-48-based catalyst, and the lower zone was loaded with 10 g. of tire.

### 3.4.3 Oil Product Analysis

#### *A) Asphaltene Precipitation*

The oil product was separated into maltene and asphaltene by adding n-pentane into the pyrolytic oil at the ratio of 40:1. Next, the solution was shaken in an ultrasonic bath for 15 min at 30 °C. The solution was left overnight. After that, asphaltene was filtrated out using a Teflon membrane in a vacuum system. The Teflon membrane with asphaltene precipitate was next dried in an oven at 110

°C for 6 hr. Finally, the solution which passed through membrane was evaporated at 37 °C for n-pentane removal to obtain the maltene.

### B) Liquid Chromatography

The maltene was separated into 5 fractions: saturated hydrocarbons, mono-, di-, poly-, and polar aromatic compounds. The liquid chromatography column was packed with alumina and silica. The column was pre-wetted with n-hexane overnight. After that, solvents were passed through the column to obtain saturated hydrocarbon and aromatic compounds as shown Table 3.1, respectively. The flow rate of the mobile phases was kept constant at 20 cm<sup>3</sup>/min controlled by an aquarium pump. And, then the mobile phases (solvents) were separated from the chemical fractions by using a rotary vacuum evaporator at about 60°C.

**Table 3.1** The optimized compositions and volumes of mobile phases for preparative separation of petroleum maltenes using the chromatographic column (Sebor *et al.*, 1999)

Mobile phase	Volume (cm <sup>3</sup> )	Prevailing compounds type
Hexane	600	Saturated hydrocarbons
Hexane-benzene (24:1, v/v)	500	Mono-aromatics
Hexane-benzene (22:3, v/v)	500	Di-aromatics
Benzene	500	Polya-romatics
Benzene-diethylether-methanol (1:1:3 v/v)	500	Polar-aromatic compounds

### C) SIMDIST Gas Chromatography (SIMDIST GC)

The liquid fraction was analyzed by a Varian CP-3800 stimulated distillation gas chromatography (SIMDIST GC), equipped with an FID. The condition of temperature program was as follows:

Initial temperature	30	°C
Heating rate	20	°C/min
Final temperature	320	°C
Holding time	8.50	min

#### 3.4.4 Gas Product Analysis

The gas product was analyzed by a Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm diameter and 20 µm film thicknesses. FID was used as a detector with He as the carrier gas. The conditions were as follows:

Initial temperature	70	°C
Heating rate	20	°C/min to 200 °C
Hold for	16	min
Final temperature	200	°C
Holding time	30	min

#### 3.4.5 Catalyst Characterization

##### *a. X-ray Diffraction Spectroscopy (XRD)*

X-ray diffraction (XRD) patterns was taken by using a Rigaku, Rint X-Ray diffractometer system (RINT 2200) with Cu tube for generating CuK $\alpha$  radiation (1.5406 Å) and nickel filter. In this experiment, XRD determines the structure of catalysts and crystal size on the supports. A catalyst sample was ground to be fine and homogeneous particles, and then packed in a glass specimen holder. The data from XRD were analyzed and recorded by an on-line computer.

##### *b. Thermal Programmed Reduction (TPR)*

TPR Micromeritics 2900 analyzer uses 5% H<sub>2</sub>/N<sub>2</sub> as carrier gas. It was used to determine the reduction temperature of catalysts. The instrument was connected to a TCD detector, and the detected signal was sent online to the software. 0.5 g. sample was used in the quart tube. In addition, the sample was pretreated before analysis with He at 150 °C for 30 min. The analytical temperature was increased from room temperature to 900°C with ramping rate 10 °C/min.

c. *Surface Area Measurement (BET)*

The specific surface area, the total pore volume, and the pore size of catalyst were determined by Brunauer-Emmett-Teller (BET) technique using Thermo Finnigan, Sorptomatic 1990 system. This technique was based on the physical adsorption of nitrogen gas at 77°K. Before starting, the catalyst sample was outgassed by heating under vacuum at 300°C for 6 hours in order to remove moisture. The specific surface area and the pore size of catalyst were obtained more than twenty-two-point nitrogen adsorption and desorption isotherm plot. The pore size distribution was calculated using the BET equation as shown in Equation 1.

$$\frac{1}{W\left(\frac{P}{P_0}-1\right)} = \frac{1}{W_m C} + \frac{(C-1)}{W_m C} \left(\frac{P}{P_0}\right) \quad (1)$$

Where:

W = weight of gas adsorbed at relative pressure  $P_0$

$W_m$  = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

$P_0$  = saturated vapour pressure of the liquid at the operating temperature

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction.

The surface area was calculated by Equation 2.

$$A = \frac{W_m A_{\text{nitrogen}} \times 6.02 \times 10^{23}}{MW_{\text{nitrogen}}} \quad (2)$$

Where:

A = surface area of sample

$A_{\text{nitrogen}}$  = cross-section area of one molecule nitrogen (0.162 nm<sup>2</sup> at -196°C)

$MW_{\text{nitrogen}}$  = molecular weight of nitrogen (28 g/g-mol).