

## CHAPTER III

### EXPERIMENTS

#### 3.1 Instruments and Apparatus

##### Ovens and Furnaces

During the synthesis course, the starting mixture was heated in a Memmert UM-500 oven. Heating of any solid sample at 100°C was carried out using the same oven. Calcination of the solid catalysts at 540°C was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

##### X-ray Powder Diffractometer (XRD)

The structure of synthesized mesoporous materials was identified by using a Rigaku, Dmax 2200/ultima plus X-ray powder diffractometer with a monochromator and Cu K $\alpha$  radiation (40 kv, 30 mA). The 2-theta angle was ranged from 1.5 to 8.0 degree with scan speed of 5 degree/min and scan step of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, and 0.15 mm, respectively.

##### ICP-AES spectrometer

Aluminum content in the catalysts was analyzed by using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

##### Scanning Electron Microscope (SEM)

JEOL JSM-5410LV scanning electron microscope was used to examine the morphology and particle size of Al-MCM-41. All samples were coated with sputtering gold under vacuum.

##### NMR Spectrometer

Solid state  $^{27}\text{Al}$ -MAS-NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer.

### Nitrogen Adsorptometer

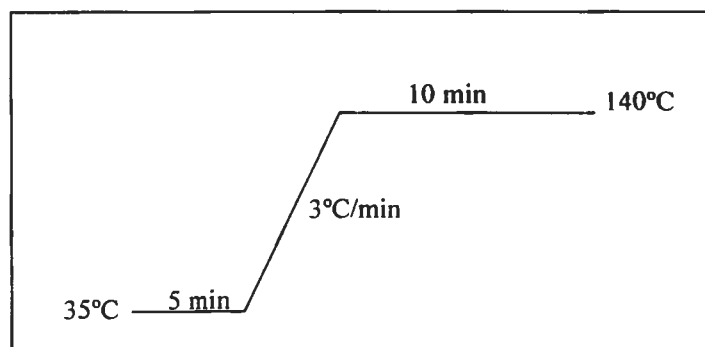
Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts was carried out using a BELSORP-II instrument. The sample weight was near 40 mg and weighted exactly pretreatment at 400°C 3h before each measurement.

### NH<sub>3</sub> TPD Machine

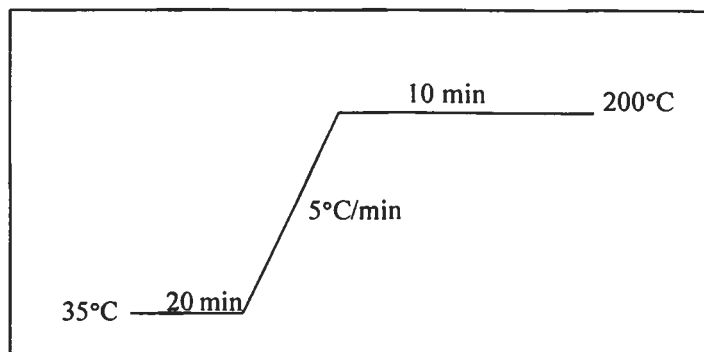
Acid strength of catalysts was determined using the BEL-CAT Japan instrument. The sample weight was near 200 mg and weighted exactly pretreatment at 400°C 20 min before each measurement.

### Gas Chromatograph

Hydrocarbon gases were analyzed using a Varian CP-3800 gas chromatograph equipped with a 50-m long and 0.53-mm inner diameter Alumina-PLOT column. Liquid samples were analyzed using a Varian CP-3800 gas chromatograph equipped with a 30-m long and 0.25-mm inner diameter CP-sil 5 (0.25  $\mu\text{m}$  film thickness) column. All GC detectors are flame ionization detectors (FID). The GC heating programs for 3.00- $\mu\text{l}$  gas and 1.00- $\mu\text{l}$  liquid analysis are shown in Schemes 3.1 and 3.2, respectively.



**Scheme 3.1** The GC heating program for gas analysis.



**Scheme 3.2** The GC heating program for liquid analysis.

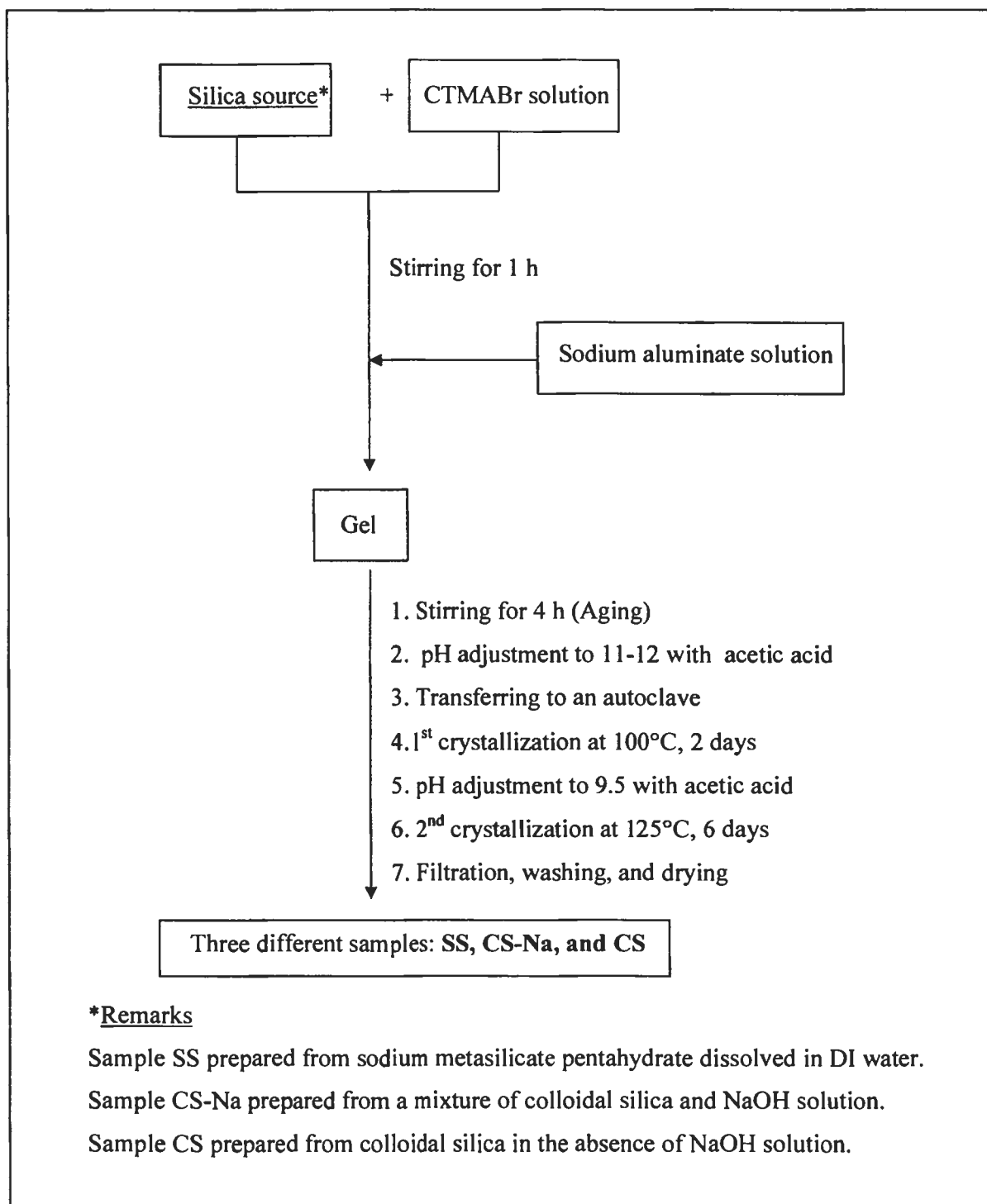
### 3.2 Chemicals and Gases

1. Colloidal silica (Ludox AS-40) (Aldrich)
2. Sodiummetasilicate pentahydrate,  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  (Fluka, reagent grade )
3. Cetyltrimethylammonium bromide,  $\text{C}_{16}\text{TMABr}$  (CTAB, reagent grade)
4. Sodium aluminate,  $\text{NaAlO}_2$  (Riedel-de Haën, reagent grade)
5. Sodium hydroxide,  $\text{NaOH}$  (Lab-scan, reagent grade)
6. Ammonium chloride,  $\text{NH}_4\text{Cl}$  (Fluka, reagent grade)
7. Glacial acetic acid,  $\text{CH}_3\text{COOH}$ (Lab-scan, reagent grade)
8. Standard gas mixture and liquid mixture for GC analysis were kindly obtained from PTT Chemical Public Company Limited.
9. Nitrogen gas,  $\text{N}_2$  (Thai Industrial Gases (TIG), highly pure grade )
10. Ammonia gas,  $\text{NH}_3$  (Linde Gas Thailand, highly pure grade)

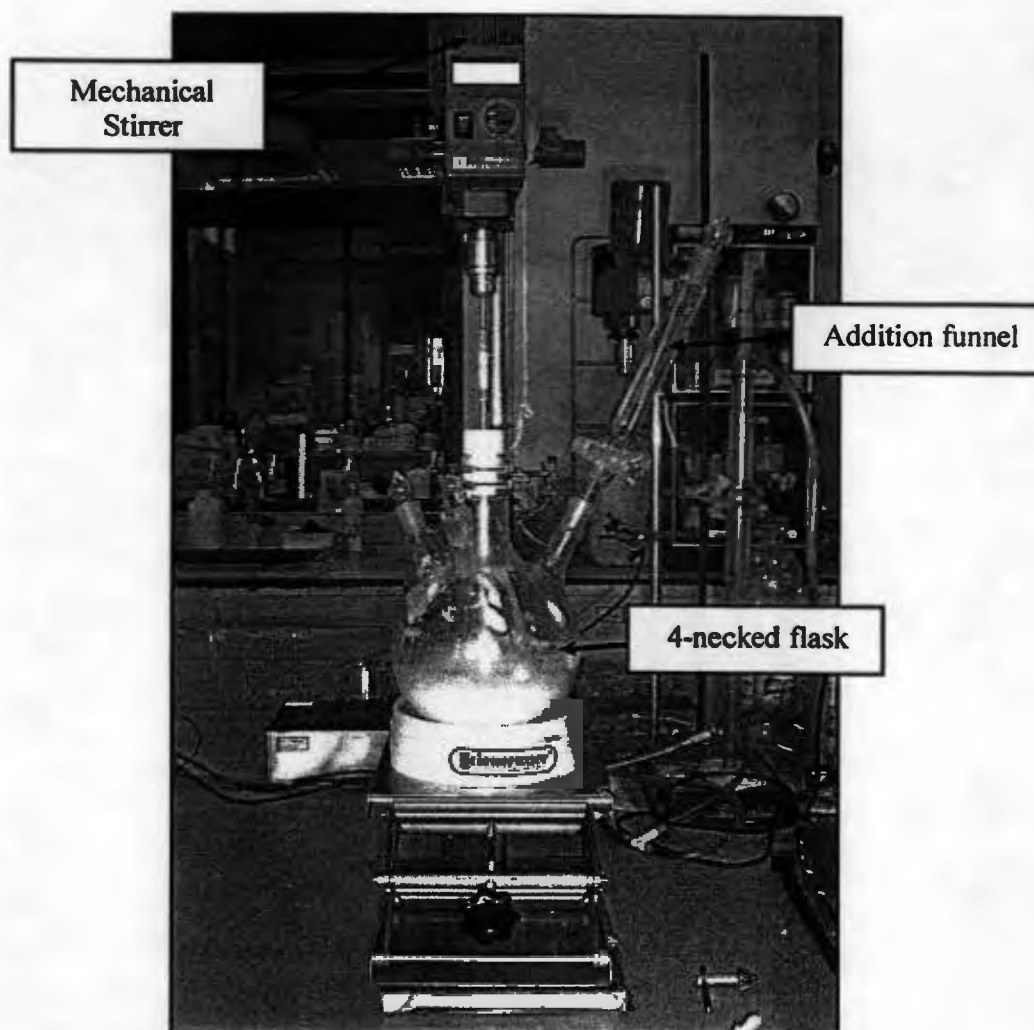
### 3.3 Preparation Methods of Al-MCM-41

This method was performed using different silica sources: sodium metasilicate pentahydrate, 40% colloidal silica, and a mixture of colloidal silica and 32% sodium hydroxide solution. Into a  $500\text{-cm}^3$  4-necked round bottom flask containing 47.69 g of a 15% solution of cetyltrimethylammonium bromide in water, an amount of silica source (16.70 g sodium metasilicate solution containing 29.20%  $\text{Na}_2\text{O}$ , 28.30%  $\text{SiO}_2$ , and 42.50%  $\text{H}_2\text{O}$  or 11.83 g of 40% colloidal silica or a mixture of 11.83 g colloidal silica and 6.55 g of a 32% sodium hydroxide solution) was added dropwise with stirring using a mechanical stirrer. Apparatus for gel preparation was shown in Figure 3.1. The mixture was stirred vigorously at room temperature for 1 h to obtain a

homogeneous milky suspension. To the suspension a solution of 0.32 g of sodium aluminate in 10.00 g distilled water was added dropwise. The mixture with the molar ratio of  $\text{SiO}_2 : 0.025$  or  $0.36 \text{ Na}_2\text{O} : 0.025 \text{ Al}_2\text{O}_3 : 0.25 \text{ CTAB} : 80 \text{ H}_2\text{O}$ , was then aged by stirring at room temperature for 4 h. Acetic acid was used to lower the pH of gel from 13 to a range of 11-12. The milky suspension became viscous white slurry. The gel was transferred into a stainless steel vessel lined with Teflon and heated in an oven at  $100^\circ\text{C}$  for 2 days without pH adjustment. After that the gel was heated at  $125^\circ\text{C}$  for 6 days with pH adjustment every day. The schematic diagram of this whole procedure is shown in Scheme 3.3. The white solid sample was filtered, washed and dried in the oven. The samples are denoted as SS, CS-Na and CS. (Sample SS prepared from sodium metasilicate pentahydrate dissolved in DI water, sample CS-Na from a mixture of colloidal silica and sodium hydroxide solution and sample CS from colloidal silica in the absence of). The white solid product was characterized using XRD, ICP-AES, SEM,  $^{27}\text{Al}$ -MAS-NMR,  $\text{NH}_3$ -TPD, and nitrogen adsorption-desorption instruments.



**Scheme 3.3** Diagram of the synthesis procedure of Al-MCM-41 with different silica sources.



**Figure 3.1** Apparatus for synthesis of Al-MCM-41.

### 3.4 Preparation of Al-MCM-41 with Various Si/Al Ratios

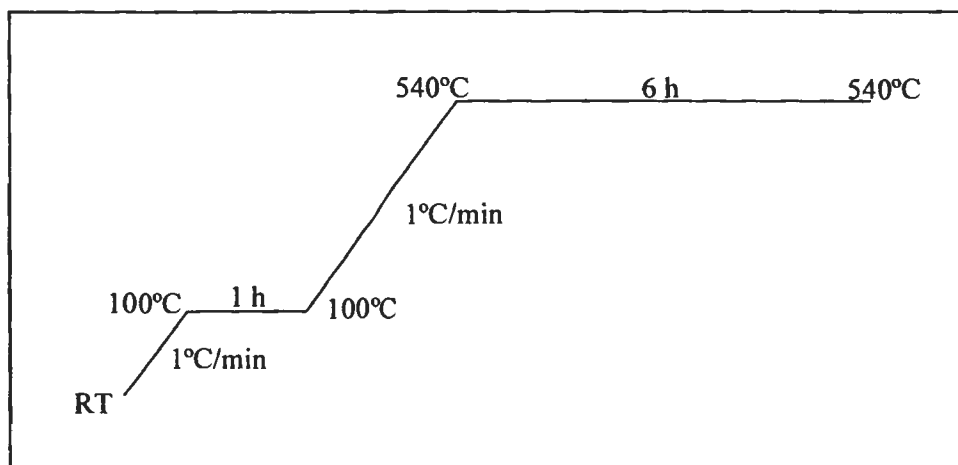
The CS-Na samples with various Si/Al ratios in gel of 20, 40 and 80 using the similar method to that described in Section 3.3. Different amounts of aluminum required for each sample were used as indicated in Table 3.1. The Al-MCM-41 samples were characterized using XRD, ICP-AES, SEM,  $^{27}\text{Al}$ -MAS-NMR,  $\text{NH}_3$ -TPD, and nitrogen adsorption-desorption instruments.

**Table 3.1** Required amounts of sodium aluminate in the preparation of CS-Na samples with various Si/Al ratios in gel of 20, 40 and 80

Sample	Si/Al molar ratio in gel	NaAlO <sub>2</sub> dissolved in 10.00 g H <sub>2</sub> O (g)
CS-Na-20	20	0.32
CS-Na-40	40	0.16
CS-Na-80	80	0.08

### 3.5 Removal of Organic Template from the Al-MCM-41 Catalysts

To make room in the catalyst structure, the organic template must be removed by oxidation to carbon dioxide at elevated temperature. An as-synthesized Al-MCM-41 was calcined in a muffle furnace using the heating program for the template removal as shown in Scheme 3.4. The calcined sample was kept in a desiccator prior to use.



**Scheme 3.4** A heating program for removal of organic template from the pores of Al-MCM-41.

### 3.6 NH<sub>4</sub><sup>+</sup>-Exchange Treatment

One gram of calcined Na/Al-MCM-41 was dispersed in 20 ml of an aqueous solution of NH<sub>4</sub>Cl and heated at the boiling temperature for 1, 3 and 6 h with stirring. Samples are denoted as CS-Na-T, for example, CS-Na-T-20 means ammonium chloride treated CS-Na-20. The solid was filtered, dried and calcined at 540°C in air for 6 h. A series of experiments have been done using different concentration of NH<sub>4</sub>Cl (0.01, 0.03, 0.05, 0.1 and 1M). The product was characterized using <sup>27</sup>Al-MAS-NMR instrument.

### 3.7 Elemental Analysis

Elemental analysis was performed to determine Si/Al in catalyst. The content of silica (SiO<sub>2</sub>) was obtained by difference of catalyst weight and Al<sub>2</sub>O<sub>3</sub> weight calculated from ICP-AES. Aluminum (Al) was determined by ICP-AES. The sample solution was prepared by soaking 0.0400 g of a calcined catalyst with 10 cm<sup>3</sup> of 6 M HCl added. Then 10 cm<sup>3</sup> of 48% hydrofluoric acid was added dropwise to the mixture to get rid off silica in the form of volatile SiF<sub>4</sub> species. The sample was heated but not boiled until it was dried on a hot plate. Then the fluoride treatment was repeated twice before 10 cm<sup>3</sup> of a mixture of 6 M HCl: 6 M HNO<sub>3</sub> at a ratio of 1:3 was added slowly and warmed until dried again. After that 10 cm<sup>3</sup> deionized water was added to and warmed for 5 min. The sample solution was transferred to a 50-cm<sup>3</sup> polypropylene volumetric flask. The solution in the flask was brought to the mark with DI water. The flask was capped and shaken before transferred into a plastic bottle. The sample solution was determined by ICP-AES technique. The standard solution of 1000-ppm aluminum in HNO<sub>3</sub> (from BDH) was diluted to 5, 10, 15 and 20 ppm to obtain a calibration curve.

## 3.8 Activity of Various Al-MCM-41 Catalysts in HDPE Cracking

### 3.8.1 Effect of Temperature

Degradation of plastic polymer was carried out in glass reactor (4.4 cm. i.d. and 37 cm. length) under atmospheric pressure by batch operation as shown in Figure 3.2 and Scheme 3.5. A total of 5g of waste plastic (HDPE) and 0.5 g of catalyst were loaded into the reactor. In a typical run, the reactor was set up, and purged with N<sub>2</sub> at flow rate of 20 ml/min to remove the air. The reactor was heated to



a required temperature (380°C or 400°C) in 20 min (20°C/min) using a split-tube furnace equipped with a programmable temperature controller and a K-type thermocouple. The temperature was maintained constant at the reaction temperature for 30 min. The gas fraction which flowed from the reactor with the nitrogen stream was passed through a condenser cooled by cold water. The gas fraction was collected into a Tedlar bag since the start of heating while the liquid fraction was condensed and collected in a 10-cm<sup>3</sup> graduated cylinder. After completion of the reaction, the reactor was cooled down to room temperature and weighed. The values of %conversion and % yield were calculated based on the equations as follows:

$$\% \text{ Conversion} = \frac{\text{mass of liquid fraction} + \text{mass of gas fraction} \times 100}{\text{mass of plastic}}$$

mass of gas fraction = mass of the reactor with plastic and catalyst before reaction –  
mass of the reactor with residue and used catalyst after reaction

$$\% \text{ Yield} = \frac{\text{mass of product fraction} \times 100}{\text{mass of plastic}}$$

The degradation products were classified into three groups: gas fraction (products which were not condensed at water cooling temperature), liquid fraction and residue. The gas products were analyzed by a gas chromatography. The liquid fraction was distilled under vacuum as shown in Figure 3.3. The distilled oil was analyzed by a GC. The values of retention time of components in the distilled oil in the GC column were compared to the boiling point range of reference in form of n-paraffins. The value of %coke formed was determined by the weight loss upon calcination of the used catalyst after leaching out of waxes by n-hexane. The heating program for regeneration of the used catalyst is shown in Scheme 3.4.

### 3.8.2 Effect of Si/Al Ratios in Catalyst

The degradation of HDPE waste was carried out using Al-MCM-41 catalysts with treated and nontreated NH<sub>4</sub>Cl with various Si/Al ratios (20, 40, and 80).

### 3.9 Activity of Various Al-MCM-41 Catalysts in PP Cracking

#### 3.9.1 Effect of Temperature

The degradation of PP waste was carried out using treated Al-MCM-41 catalysts Si/Al ratio of 20 with various temperature reactions. The reaction was performed in the similar way to what described in Section 3.8.1. and the experiments were set up at the reaction temperature of 380°C and 400°C.

#### 3.9.2 Effect of Si/Al Ratios in Catalyst

The degradation of PP waste was carried out using treated Al-MCM-41 catalysts with various Si/Al ratios (20, 40, and 80) as catalysts. The reaction was performed in the similar way to what described in Section 3.8.1. and the experiments were set up at the reaction temperature of 380°C and 400°C.

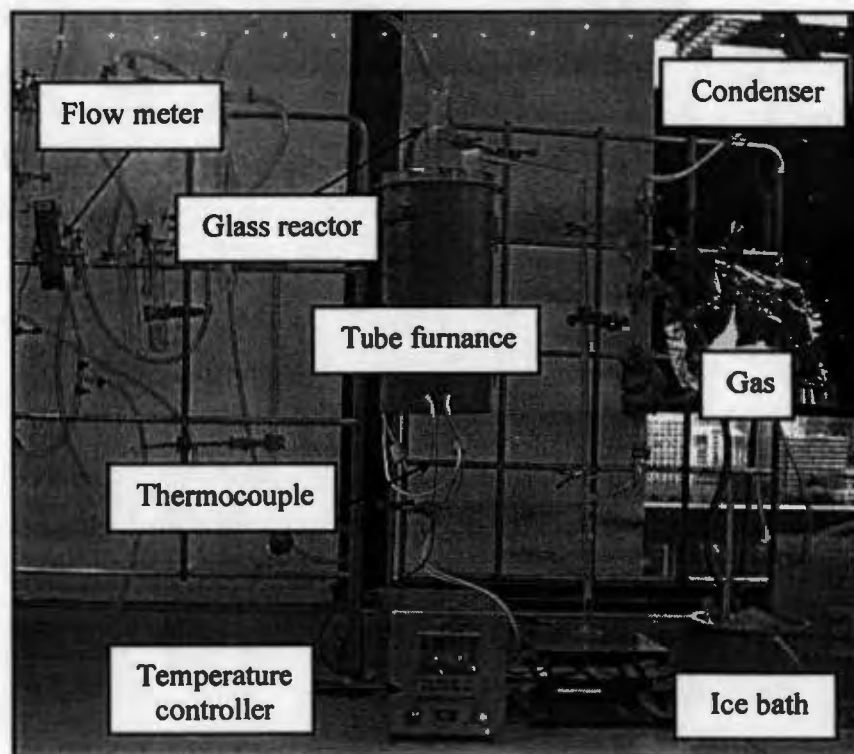
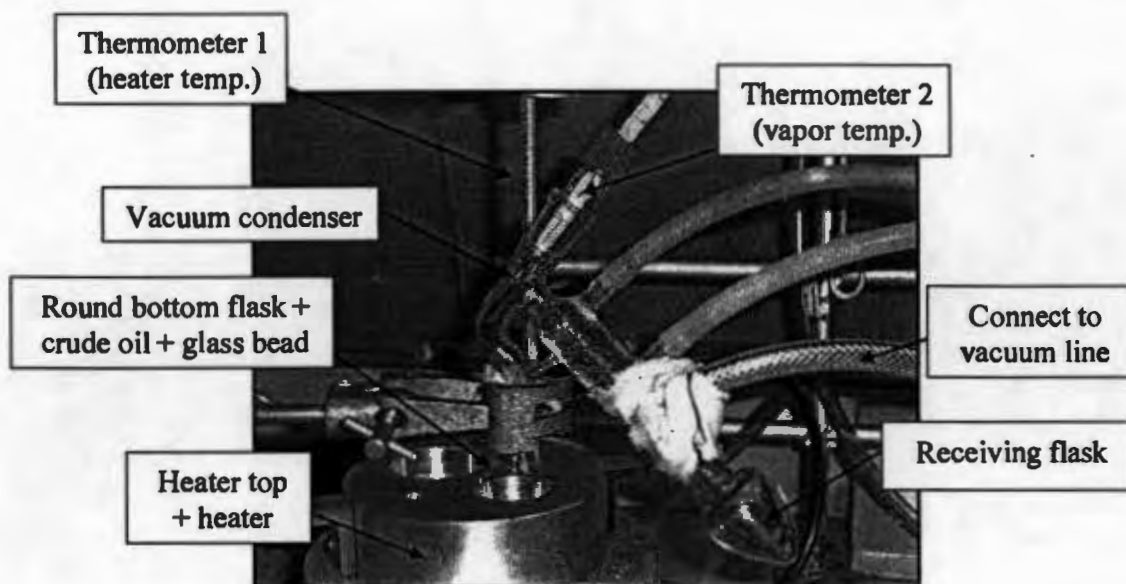
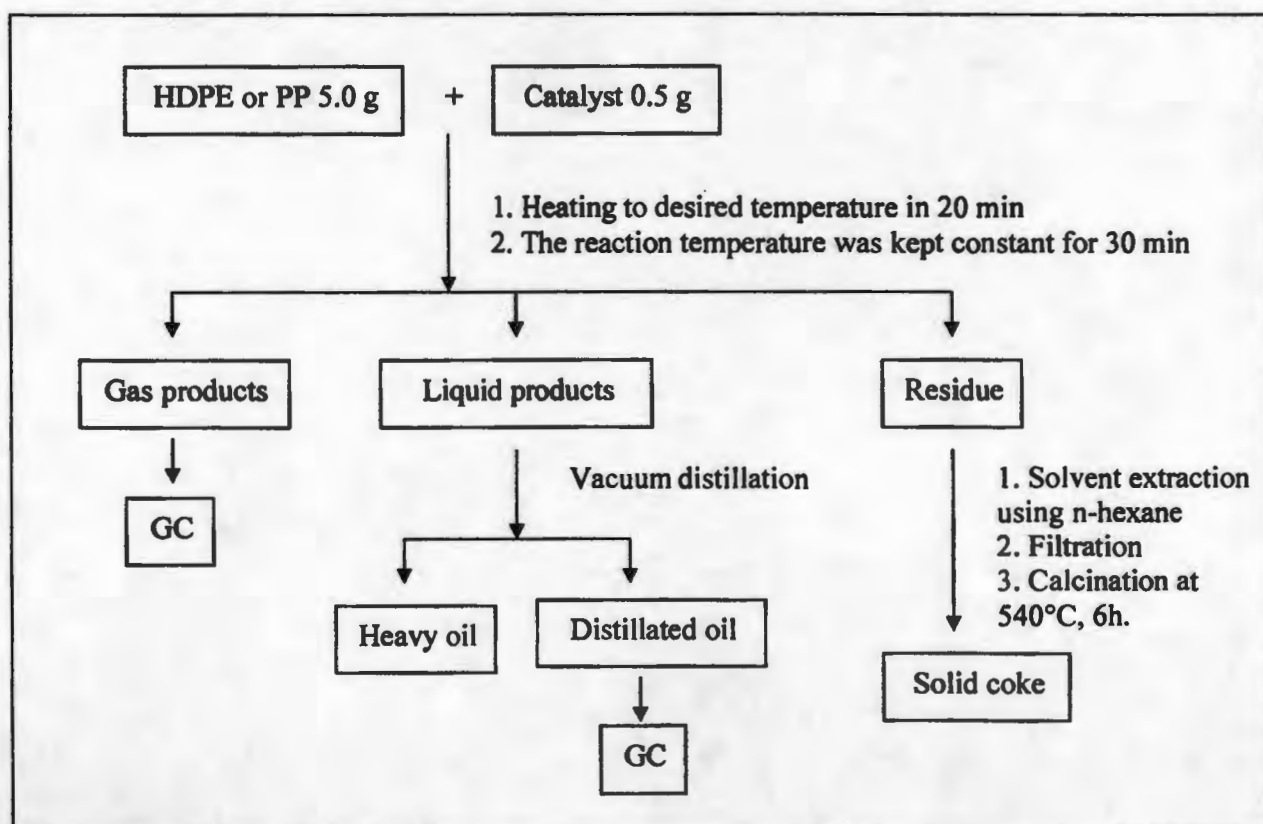


Figure 3.2 Apparatus for catalytic cracking.



**Figure 3.3** Apparatus for vacuum distillation.



**Scheme 3.5** Catalytic cracking of HDPE and PP using Al-MCM-41 as catalyst.

### **3.10 Catalyst Regeneration**

The spent catalysts of single use (Si/Al = 20) were subjected to regeneration. They were regenerated by calcination in air at 540°C for 6 h. The regenerated catalysts were characterized by XRD, SEM and test activity by catalytic cracking of PP at reaction temperature 400°C. The reaction was performed in the similar way to what described in Section 3.8.1.