

CHAPTER III

EXPERIMENTS

3.1 Equipment and apparatus

3.1.1 Pressure reactors and furnaces

Crystallization of the gels was carried out in Teflon lined stainless steel autoclave and rotated at 70 rpm at a temperature of 140°C. Organic template was removed from MCM-22 channels by calcination at 540°C for 8 h using a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

3.1.2 X-ray powder diffractometer

The MWW structure of synthesized zeolite was identified using a Rigaku D/MAX-2200 Ultima+ X-ray diffractometer (XRD) equipped with Cu target X-ray tube at 2theta angle between 2 to 40 degree.

3.1.3 Surface area analyzer

The specific surface area and pore volume of catalysts were identified using a BEL Japan, BELSORP-mini instrument. The sample weight was about 40 mg and weighed exactly after pretreatment at 400°C for 3 h before each measurement.

3.1.4 Scanning electron microscope

Morphology and particle sizes of catalysts were examined using JEOL JSM-5410 LV and JEOL JSM-6480 LV scanning electron microscope. All samples were coated with spluttering gold under vacuum.

3.1.5 ICP-AES spectrometer

The chemical compositions of the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

3.1.6 AAS spectrometer

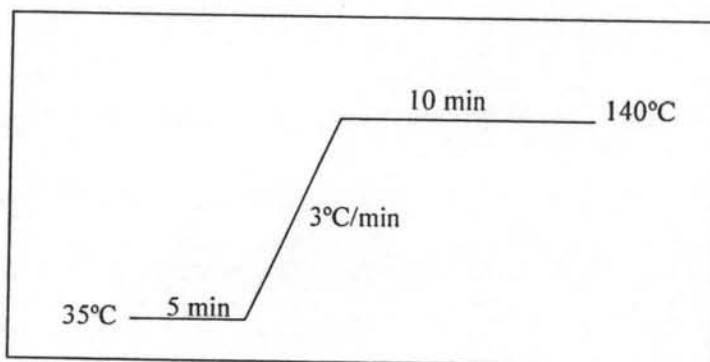
Sodium contents in the catalysts were analyzed using the Varian, 280FS atomic adsorption spectrometer (AAS).

3.1.7 ^{27}Al -NMR spectrometer

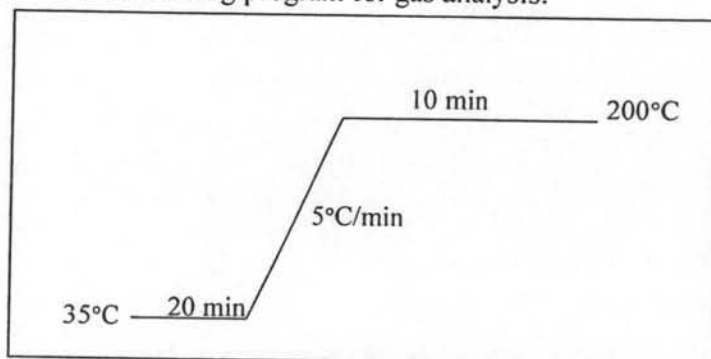
Solid state ^{27}Al -NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer.

3.1.8 Gas chromatograph

Hydrocarbon gases were analyzed using a Varian, GC CP 3800 model, gas chromatograph equipped with a 50 m length \times 0.53 mm inner diameter Alumina-PLOT column. Liquid products were also analyzed using the same instrument but equipped with a 30 m length \times 0.25-mm inner diameter CP-sil 5 column (equivalent to DB-1 column). All GC detectors are flame ionization detectors (FID). The GC heating programs for gas and liquid analysis were shown in Scheme 3.1. and 3.2., respectively.



Scheme 3.1 The GC heating program for gas analysis.



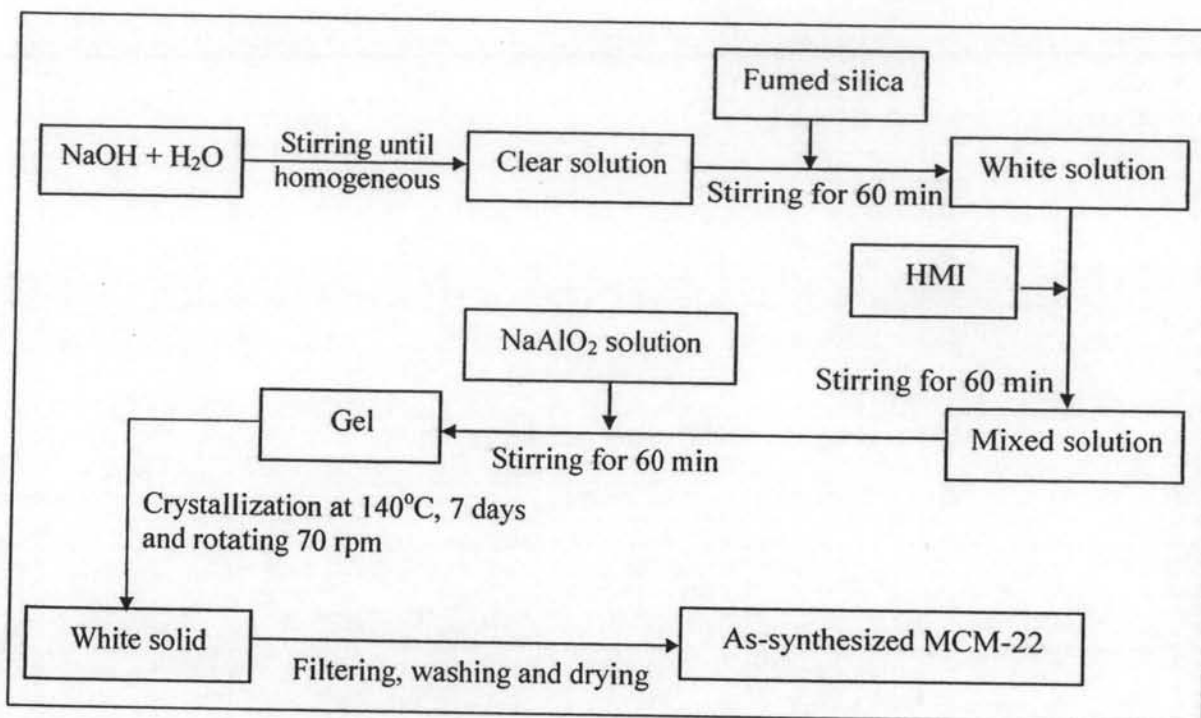
Scheme 3.2 The GC heating program for liquid analysis.

3.2 Chemicals and gases

1. Fumed silica (Cab-osil[®]M-5) (Riedel-de Haën)
2. Sodium aluminate, NaAlO_2 (Riedel-de Haën, reagent grade)
3. Hexamethyleneimine, HMI ($\geq 97.0\%$, Fluka)
4. Sodium hydroxide, NaOH ($\geq 99\%$, Lab-Scan)
5. Ammonium chloride, NH_4Cl (Fluka, reagent grade)
6. Cetyltrimethylammonium bromide, CTMABr ($\geq 96.0\%$, Fluka)
7. Tetrapropylammonium hydroxide, TPAOH (1.0 M in water, Aldrich)
8. Hydrochloric acid, HCl (37%, Carlo Erba)
9. Hydrofluoric acid, HF (48%, Merck)
10. Nitric acid, HNO_3 (65%, Lab-Scan)
11. Standard gas mixture for GC analysis was kindly obtained from PTTCHEM.
12. Standard gas liquid was obtained from RESTEK.
13. Nitrogen gas was obtained from Thai Industrial Gases (TIG), highly pure grade.

3.3 Synthesis of MCM-22 [34, 35]

The layer MCM-22 (P) precursor was prepared using hexamethyleneimine (HMI) as the directing agent (SDA), fumed silica (SiO_2 : Cab-osil[®]M-5), sodium aluminate (NaAlO_2 : 40-45 wt% Na_2O , 50-56 wt% Al_2O_3 , 0.05 wt% Fe_2O_3), sodium hydroxide (NaOH) and deionized water. Apparatus for gel preparation was shown in Figure 3.1. More specifically a sample with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ was prepared in the following way: To a mixture containing 25.04 g of fume silica, 3.53 g of NaOH and 150 g of H_2O was added 37.19 g of HMI dropwise under vigorous stirring. A solution of 2.65 g of NaAlO_2 in 150 g of water was added dropwise after 1 h and the mixture was stirred continuously until producing a homogenous gel with a molar composition of $\text{SiO}_2 : 0.15 \text{ Na}_2\text{O} : 0.033 \text{ Al}_2\text{O}_3 : 0.9 \text{ HMI} : 40 \text{ H}_2\text{O}$. The resulting gel was transferred into a Teflon lined stainless-steel autoclave, rotated at 70 rpm and heated at 140°C for 7 days. The solid product was filtered, washed with deionized water until the pH was below 9, and subsequently dried at 80°C overnight to obtain lamellar precursor of MCM-22. Then MCM-22 (P) was calcined in air at 540°C for 8 h to remove SDA and the yield was MCM-22. The procedure for MCM-22 preparation was shown in Scheme 3.3.



Scheme 3.3 Preparation diagram for MCM-22.

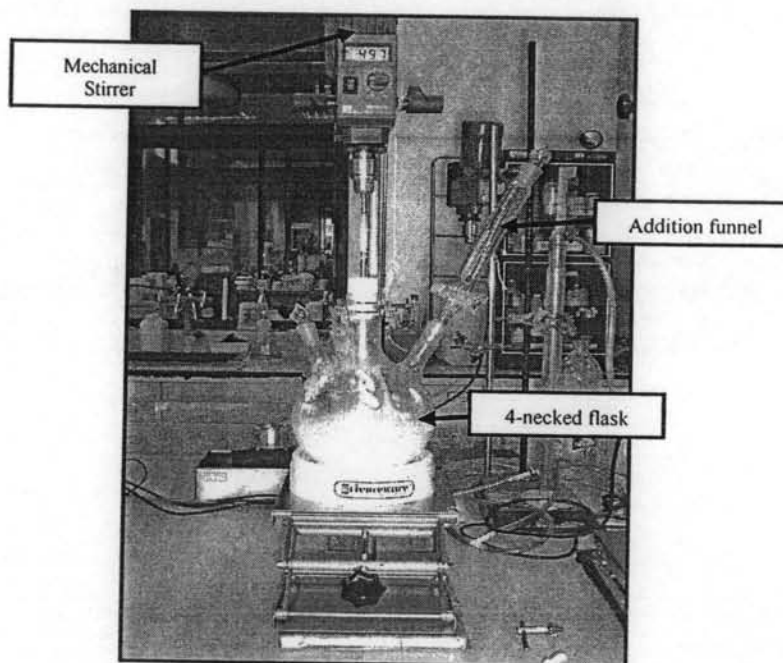


Figure 3.1 Apparatus for synthesis of MCM-22.

3.3.1 Preparation of MCM-22 with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios

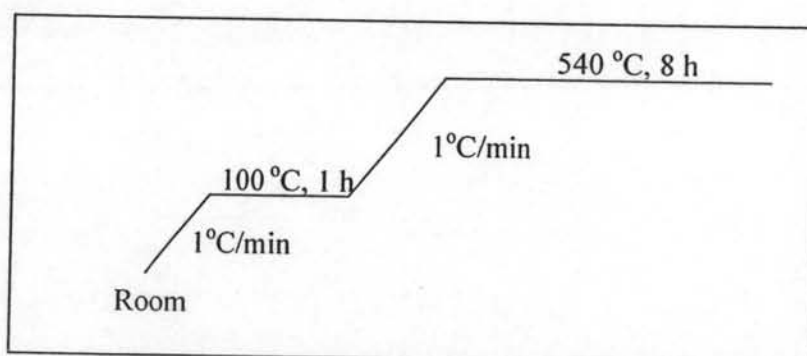
The samples with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in gel of 30, 60, 120, 250 and 400 using the similar method which was described in Section 3.3. Different amount of required aluminum for each sample was indicated in Table 3.1. The MCM-22 samples were characterized using XRD, SEM, ^{27}Al -MAS-NMR, ICP-AES and nitrogen adsorption-desorption instruments.

Table 3.1 Required amounts of sodium aluminate in the preparation of MCM-22 samples with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in gel

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios in gel	NaAlO_2 dissolved in 150 g H_2O (g)
MCM-22 (30)	30	2.65
MCM-22 (60)	60	1.36
MCM-22 (120)	120	0.67
MCM-22 (250)	250	0.32
MCM-22 (400)	400	0.20

3.4 Organic template removal

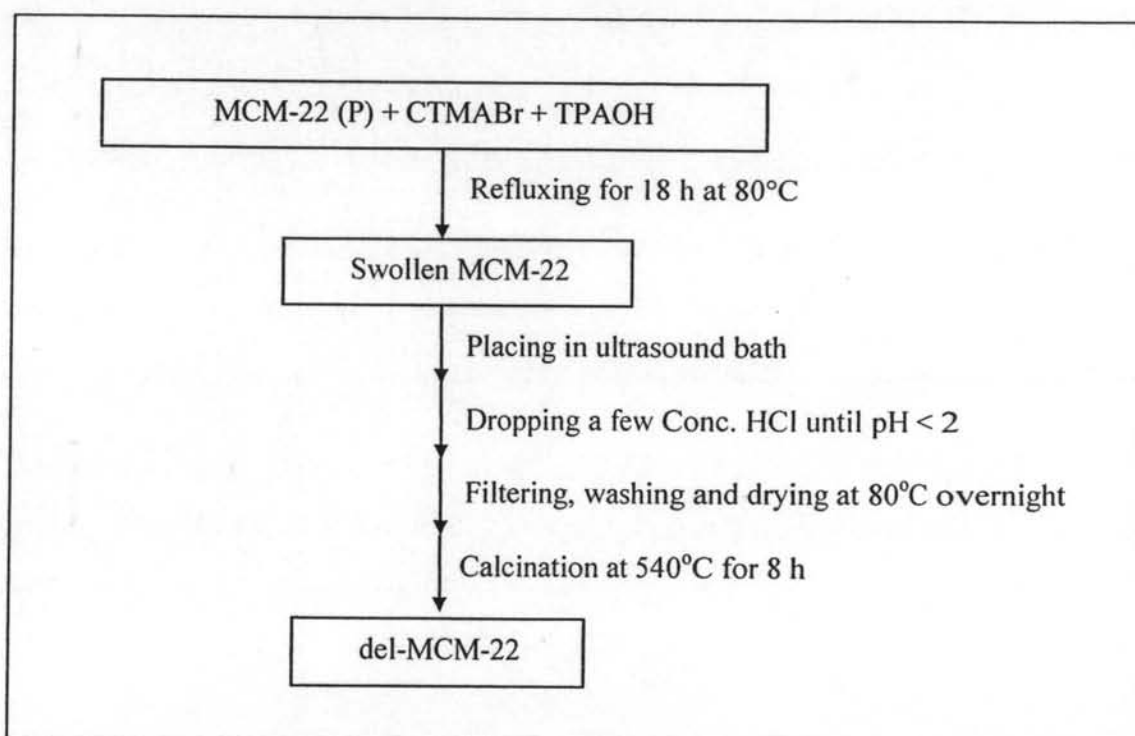
To remove the template, hexamethyleneimine (HMI), the solid sample was calcined in a muffle furnace from room temperature to 540°C for 8 h as shown in Scheme 3.4.



Scheme 3.4 A heating program for removal of organic template from the pores of MCM-22.

3.5 Preparation of delaminated MCM-22

Del-MCM-22 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) was obtained by swelling the MCM-22 (P) with hexadecyltrimethylammonium bromide (CTMABr). Typically, 1 g of MCM-22 (P) was mixed with 5.64 g of surfactant, 12.02 g of an aqueous solution of 20 wt% tetrapropylammonium hydroxide and 11.92 g of deionized water and refluxed for 16 h at 80°C . The layers in the swollen MCM-22 (P) were stripped apart by placing the slurry in an ultrasound bath for 1 h. Subsequent addition of a few drops of concentrated hydrochloric acid, until the pH below 2, allowed harvesting of the solid by centrifuging. Then, removal of the organic material by calcination at 540°C yields del-MCM-22. The procedure for preparing the del-MCM-22 and conditions of del-MCM-22 preparation were shown in Scheme 3.5 and Table 3.2., respectively.



Scheme 3.5 Preparation diagram for del-MCM-22.

Table 3.2 Conditions of del-MCM-22 preparation [36-39,73]

Sample Code	Composition (g)				Sonication time (h)
	Precursor	H ₂ O	CTMABr	TPAOH	
D1	1.00	0.89	3.89	1.22	1
D2	1.00	11.36	5.60	6.00	1
D3	1.00	45.94	19.44	6.11	1
D4	1.00	11.90	5.64	12.02	3
D5	1.00	32.36	5.60	2.40	5

3.6 Ion exchange of MCM-22 and del-MCM-22 sample.

MCM-22 zeolite was converted into H-form by following procedure: MCM-22 (P) and 1 M NH₄Cl solution (20 ml/g) were placed in a round bottom flask fitted with an air condenser. The mixture was stirred at 80°C for 18 h. Then the material was filtered under suction and washed with distilled water. The filtered material was dried at 80°C overnight. The dried material was once again treated with 1 M NH₄Cl by adopting the same procedure. This cycle was repeated four times in order to achieve maximum exchange into H-form by calcination in air at 540°C for 8 h. The product was characterized using ²⁷Al-MAS-NMR instrument.

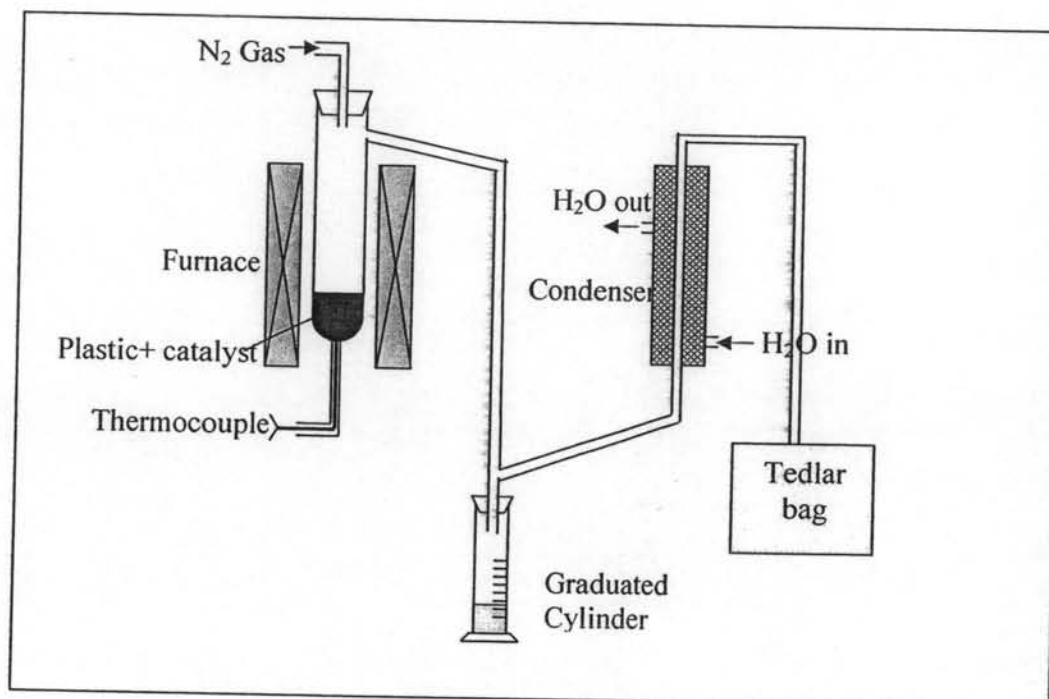
3.7 Sample preparation for ICP-AES analysis

Elemental analysis was performed to determine SiO₂/Al₂O₃ in catalyst. The sample solution was prepared by soaking 0.0400 g of a calcined catalyst with 10 cm³ of 6 M HCl. Then 10 cm³ of 48% hydrofluoric acid was added dropwise to the mixture to get rid off silica in the form of volatile SiF₄ species. The sample was heated on a hot plate until dryness and the fluoride treatment was repeated twice more. An amount of 10 cm³ of a mixture of 6 M HCl : 6 M HNO₃ at a ratio of 1:3 was added slowly and warmed until dried again. After that 10 cm³ deionized water was added to and warmed for 5 min. The sample solution was transferred to a 50 cm³ polypropylene volumetric flask. The solution in the flask was brought to the mark with 1,000 ppm KCl solution. The flask was capped and shaken before transferred into a plastic bottle. The sample solution was determined by ICP-AES technique.

3.8 Catalytic cracking of polypropylene waste over MCM-22

3.8.1 General procedure in catalytic cracking of PP waste

Catalytic cracking was carried out in glass reactor by batch operation as shown in Scheme 3.6.



Scheme 3.6 Apparatus for plastic cracking.

In each experiment, a 5.0 g of PP waste and 0.5 g of catalyst were loaded and mixed into the reactor. The pure nitrogen gas was purged through reactor with a flow rate of 20 ml/min during the experiment to remove the air. The reactor was heated to a required temperature with heating rate 20°C/min using a split-tube furnace equipped with a programmable temperature controller and a thermocouple. The temperature was maintained constant at the reaction temperature for 40 min. The gas fraction which flowed from the reactor with the nitrogen stream was passed through a condenser which cooled at 1°C. 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 cm³ 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 that were gases, liquid hydrocarbon and residue. The gas products were analyzed by a gas chromatography. The percentage of gaseous product was estimated by subtracting the weight of liquid products and residues from the plastic. Liquid fraction obtained from the reaction was distilled under vacuum as shown in Figure 3.2. 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 residue consisted of both coke and wax remaining in the catalytic line. The % coke was determined by the weight loss upon calcination of the used catalyst after washed with excess amount of hexane. The calcination heating program for de-coke was shown in Scheme 3.4.

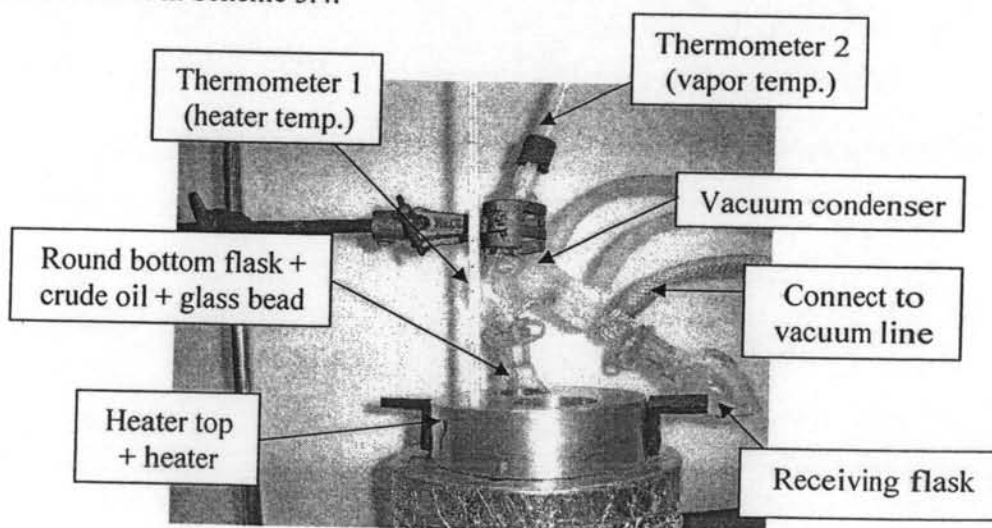
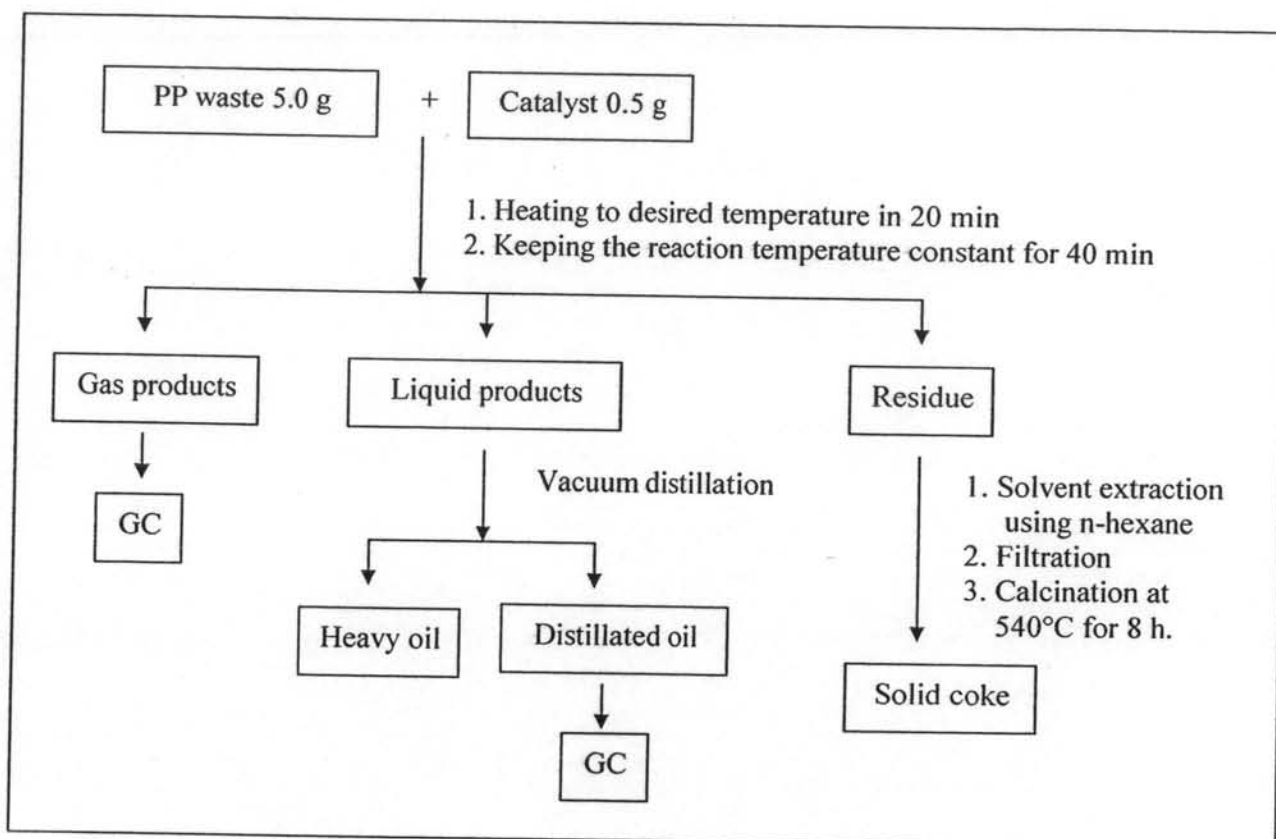


Figure 3.2 Apparatus for vacuum distillation.



Scheme 3.7 Catalytic cracking of PP waste using MCM-22 as catalyst.

3.8.1.1 Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in catalyst

The degradation of PP waste was compared with using all $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of Na-MCM-22 and H-MCM-22 catalysts. The reaction was performed in the similar way to what described in Section 3.8.1. The experiments were set up at reaction temperature of 380°C.

3.8.1.2 Thermal cracking and catalytic cracking over MCM-22

The thermal cracking of PP waste was investigated and compared with cracking over MCM-22 at the reaction temperature of 350°C, 380°C and 400°C.

3.8.1.3 Study on the effect of reaction temperature

The effect of temperature on cracking of PP waste was studied in the same way to general procedure, but the reaction temperature was varied to 350, 380, and 400°C.

3.8.1.4 Study on the effect of polypropylene waste to catalyst ratio

The catalytic cracking reaction was carried out according to the procedure above in Section 3.7.1, but the amount of catalyst (MCM-22) was changed to 5 wt%, 10wt%, and 15wt% catalyst of plastic.

3.9 Catalyst regeneration

The spent catalyst ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 120) was subjected to regeneration. They were washed with the excess amount of hexane after the first run, dried at 80°C overnight and regenerated by calcination in air at 540°C for 8 h. It was denoted as regenerated type I catalyst. In addition, the regenerated type I catalyst was treated with 1 M NH_4Cl solution for 2 h, filtered and repeated 5 times then washed with DI water (remove Cl), dried at 80°C overnight and calcined at 540°C for 8 h. It was denoted as regenerated type II catalyst. Regenerated catalysts were characterized by XRD, SEM and test activity by catalytic cracking of PP waste at reaction temperature 380°C . The reaction was performed in the similar way to what described in Section 3.8.1.