

CHAPTER III

EXPERIMENTAL

3.1 Chemicals and gases

Silica source, tetraethyl orthosilicate (98% TEOS), was commercially available from Fluka. Alumina source, Aluminum isopropoxide (AIP) was obtained from Merck. Organic template for Zeolite beta, tetraethylammonium hydroxide was commercially available from Fluka and hexadecylamine (HDA) organic template for Al-HMS was obtained from Fluka. Standard gas mixture for GC analysis was kindly obtained from PTTCHEM. Polypropylene pellets (density = 0.91 g/cm³ melting point = 163°C) were obtained from Thai Polypropylene Co., LTD. High density polyethylene pellets (density = 0.966 g/cm³ melting point = 132°C) were obtained from Thai polyethylene Co., LTD. Other chemicals were provided from Merck or Fluka, otherwise specially identified.

3.2 Instruments, apparatus and analytical techniques

Oven and furnace

Zeolite beta was hydrothermally synthesized in a Memmert UM-500 oven at 135°C for 1 day. Moreover, the catalysts were dried at 110°C in the oven. The calcination was performed on a Carbolite RHF 1600 muffle furnace in order to remove moisture and organic templates from the catalyst. As-synthesized zeolite beta was heated to 100°C with a heating rate of 1°C/min and the temperature was maintained at 100°C for 1 h. Then the temperature was raised to 550°C with the same heating rate and maintained at that temperature for 6 h. After calcinations, zeolite beta was named as “calcined zeolite beta”. Similar to zeolite beta as synthesized Al-HMS was calcined at 120°C for 2 h and 550°C for 10 h with the heating rate of 1°C/min. After calcinations Al-HMS was named as “calcined Al-HMS”.

Ultrasonic irradiation

Gel mixture of zeolite beta was sonicated using a SONICS, VC 505 irradiation. It consists of a power supply (net power output: 500 watts, frequency : 20 KHz), sealed converter (piezoelectric lead zirconate titanate crystals) and a titanium

alloy probe (13-mm-diameter tip). The mixture was subjected to ultrasound irradiation with a set amplitude of 40% for 30 min.

Powder X-ray diffraction (XRD)

The XRD pattern and d-spacing of zeolite beta and Al-HMS catalysts were determined by a Rigaku, Dmax 2200/Ultima⁺ diffractometer equipped with a monochromator and Cu K α radiation. The tube voltage and current were set at 40 kV and 30 mA, respectively. The diffraction pattern was recorded in the 2-theta ranges from 5 to 50 degree with scan speed of 5 degree/min for zeolite beta and from 1.2 to 10 degree applied for Al-HMS. The scan step was fixed at 0.02 degree. The scattering slit, divergent slit, and receiving slit for zeolite beta were fixed at 0.5 degree, 0.5 degree, and 0.30 mm, respectively. The analysis was performed at values of 0.5 degree, 0.5 degree, and 0.15 mm were applied for Al-HMS.

Scanning electron microscopy (SEM)

The morphology and particles size of zeolite beta and Al-HMS catalysts were observed using a JSM-5410 LV scanning electron microscope. In SEM analysis, the samples were coated with sputtering gold under vacuum. The samples were analyzed at Faculty of Science, Chulalongkorn university.

Nitrogen adsorption-desorption technique

Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms, BET specific area, external surface area and pore size distribution of catalysts were determined by a BEL Japan BELSORP-mini 28SP adsorptometer. The sample weight was approximately 40 mg and pretreated at 400°C for 3 h. Nitrogen gas was used as an adsorbate at 77 K in measurement step at the department of Chemistry, Faculty of Science, Chulalongkorn university.

Inductively coupled plasma atomic emission spectrometry

Aluminum contents in the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES) at Scientific and Technology Research Equipment Centre, Chulalongkorn University.

^{27}Al MAS nuclear magnetic resonance spectroscopy

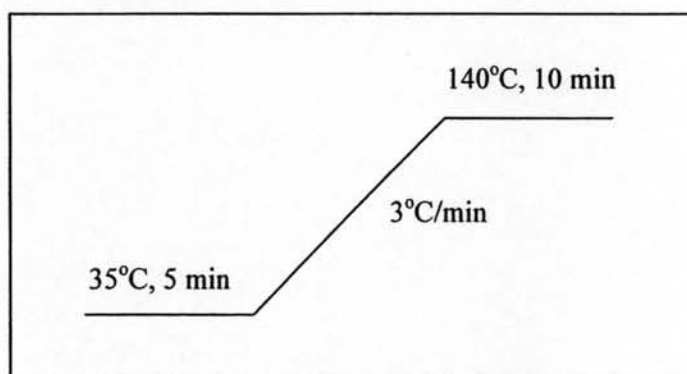
The signal of aluminum tetrahedral in catalysts was conformed by ^{27}Al -magnetic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR, Bruker DPX-300 spectroscopy operating at 78 MHz at National Metal and Materials Technology Center, Pathumthani.

NH_3 -temperature programmed desorption

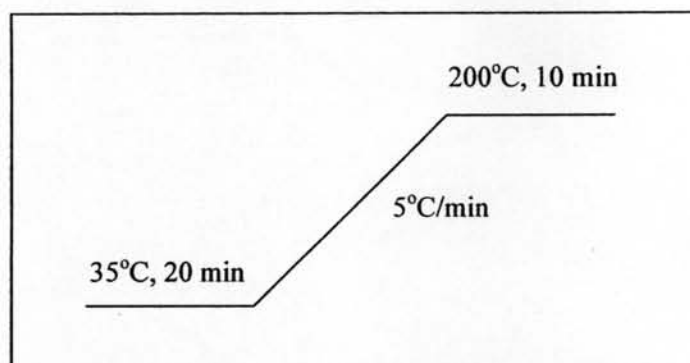
Acidity and acid strength of catalysts were determined using a BEL Japan, BELCAT with the sample weight about 100 mg. The desorbed ammonia was monitored by a thermal conductivity-type detector. The pretreatment was as follows: the catalyst sample was heated up to and kept for 10 min at 610 °C under a flow of helium. After replacing the He flow by a flow of synthetic air and keeping for 20 min at the same temperature, the sample was cooled down to room temperature. The samples were analyzed at the Department of Chemistry, Faculty of Science, Chulalongkorn university.

Gas chromatography

Hydrocarbon gases were analyzed using a Varian CP 3800 gas chromatograph equipped with a 50 m length \times 0.53 mm inner diameter Alumina-PLOT column. Liquid products from cracking were analyzed using the same instrument but equipped with a 30 \times 0.25 mm inner diameter CP-sil 5 column (equivalent to DB-1 column). The detector is flame ionization detector (FID). The sample volumes are 3.0 μl and 1.0 μl for gas and liquid, respectively injections. The column heating programs for gas and liquid analysis are shown in Schemes 3.1 and 3.2, respectively.



Scheme 3.1 The column heating program for gas analysis.

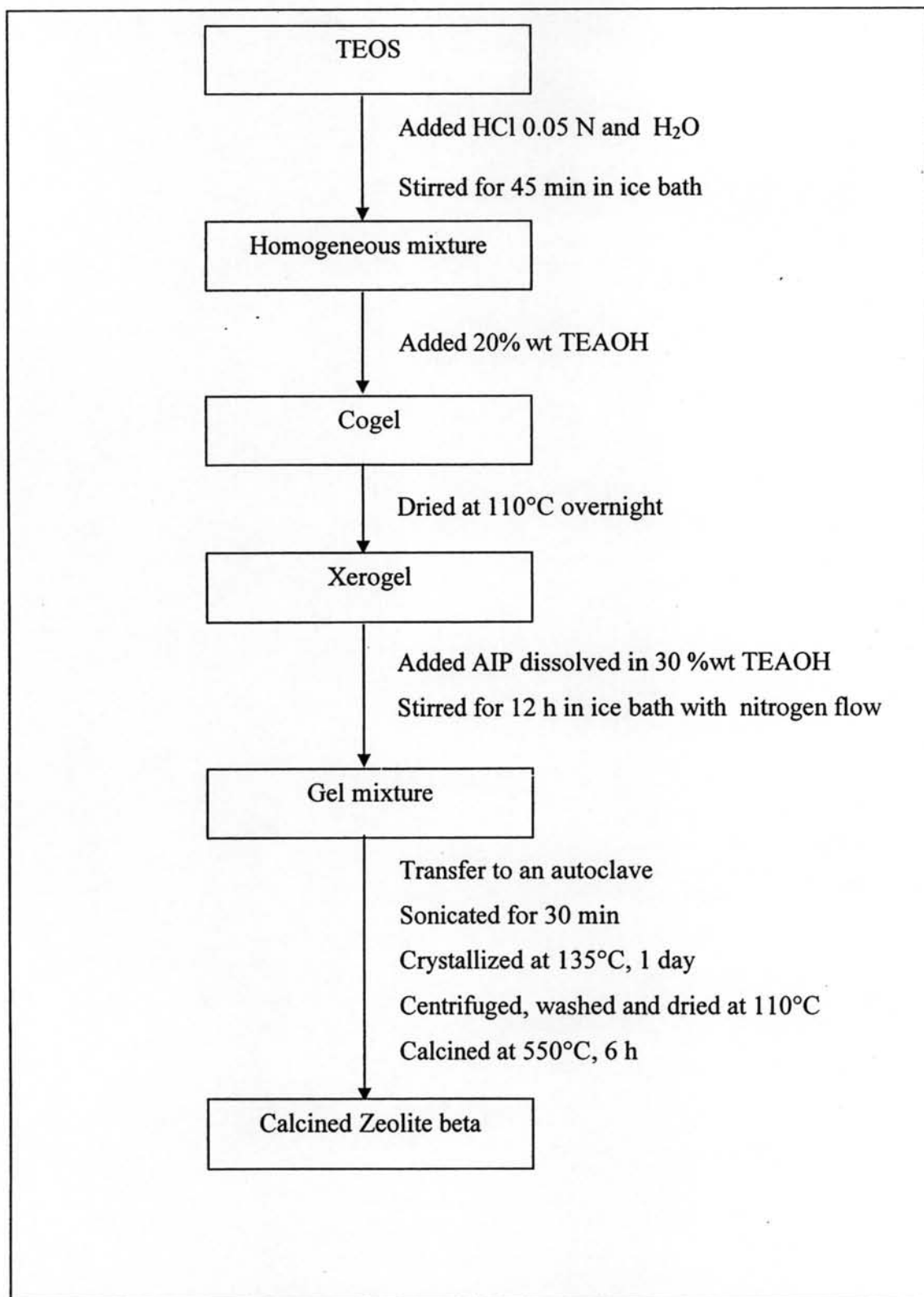


Scheme 3.2 The column heating program for liquid analysis.

3.3 Synthesis of catalysts

3.3.1 Synthesis of Zeolite beta with a mole Si/Al ratio in gel of 60

Zeolite beta catalysts with the Si/Al mole ratio in gel of 60 was prepared using the gel mole composition of $1\text{SiO}_2 : 0.0083 \text{ Al}_2\text{O}_3 : 0.73\text{TEAOH} : 19 \text{ H}_2\text{O}$ (Si/Al = 60) report by J. Aguado *et al.* [12]. Zeolite beta was synthesized from a $\text{SiO}_2\text{-Al}_2\text{O}_3$ xerogel by wetness impregnation with tetraethylammonium hydroxide (TEAOH) followed by hydrothermal autoclave crystallization. The starting amorphous material was prepared by a two-step sol-gel method. In the first step 29.9 g of tetraethyl orthosilicate (TEOS) were hydrolyzed with 10.44 g of 0.05 N aqueous HCl in ice bath for 45 min. Once a homogenous solution was obtained, a 20 wt% TEAOH aqueous solution was dropwise added until the gel point was reached. The cogel obtained was dried overnight at 110°C called xerogel. In the crystallization stage, a 30 wt% aqueous TEAOH solution containing aluminium isopropoxide was added to the obtained xerogel in ice bath with nitrogen flow for 12 hours. The mixture was loaded into autoclave, sonicated for 30 min, and kept at 135°C for 1 day. The crystalline product obtained was separated by centrifugation, washed with deionized water, dried at 110°C overnight and activated by calcination at 550°C for 6 h. The procedure for preparing zeolite beta was summarized in Scheme 3.3.



Scheme 3.3 Zeolite beta synthesis diagram.

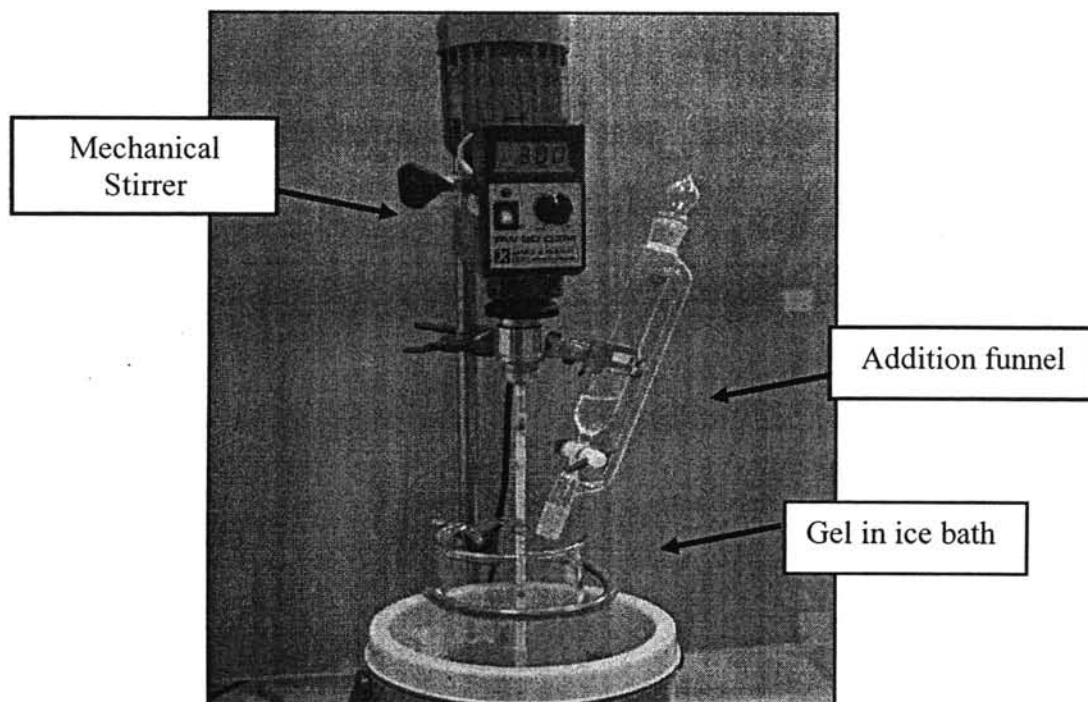


Figure 3.1 Xerogel synthesis apparatus.

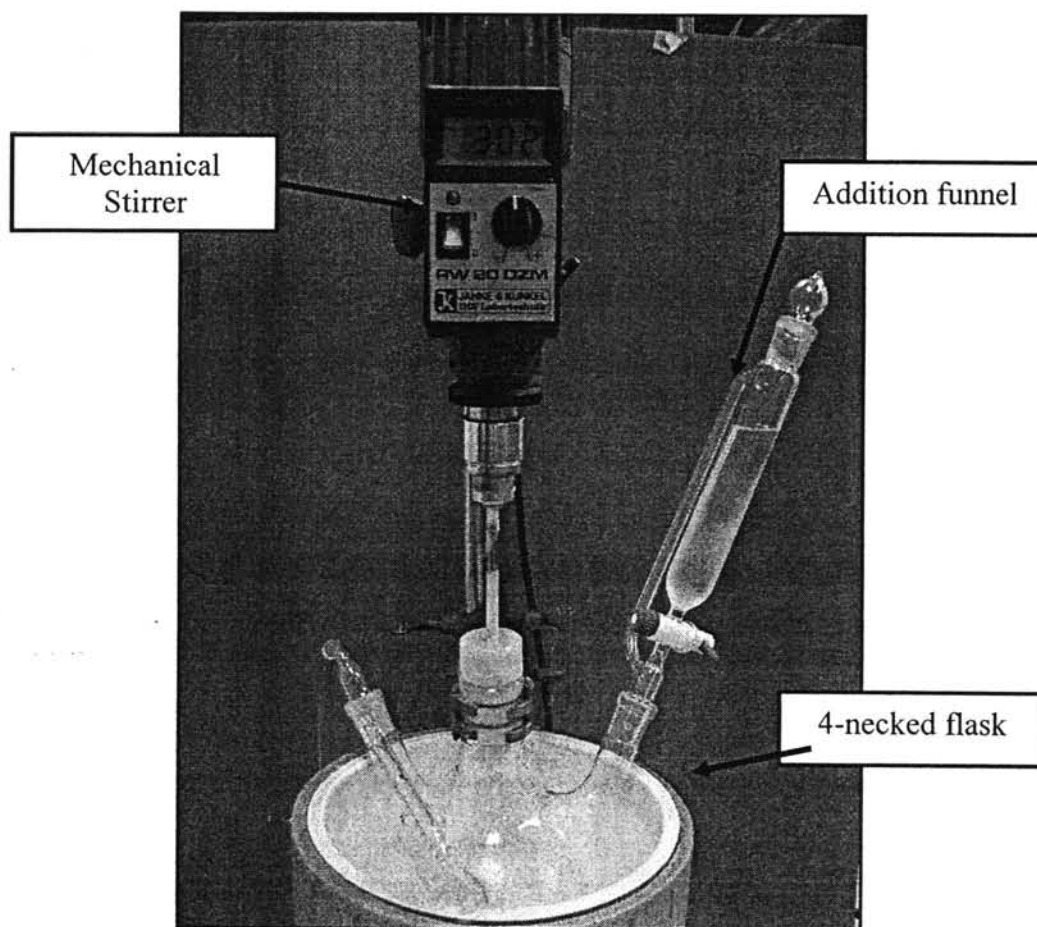


Figure 3.2 Zeolite beta synthesis apparatus.

3.3.2 Synthesis of Al-HMS with the Si/Al mole ratio in gel of 40

Al-HMS synthesis was performed by modifying the procedures reported by Tuel *et al* [43], and Rao *et al*. The gel mole composition of 1SiO_2 : $0.0125\text{Al}_2\text{O}_3$: 0.25HDA : 8.3EtOH : $100\text{H}_2\text{O}$ was prepared by dissolving 12.07 g of hexadecylamine (HDA) in the mixed solvent of ethanol and water (76.476 g of ethanol and 198.4 g of water) in a 1000-cm³ beaker. The mixture was stirred for 20 min until homogeneous solution was obtained. Then 1.02 g of aluminum isopropoxide (AIP) was added to the mixture under vigorous stirring for 30 min. A portion of 41.66 g of tetraethyl orthosilicate (TEOS) and a portion of 162.0 g of water were then added dropwise in sequence into the mixture with stirring for 2 h. After aging with the resulting gel for 20 h, the white solid product was filtered and washed several times until pH equal to 7.0. The solid was air dried for 1 day. As-synthesized Al-HMS yielded approximately 22 g. The hexadecylamine template was removed by calcination of the sample at the temperature of 550°C for 10 h. The synthesis procedure of Al-HMS was shown in Scheme 3.4.

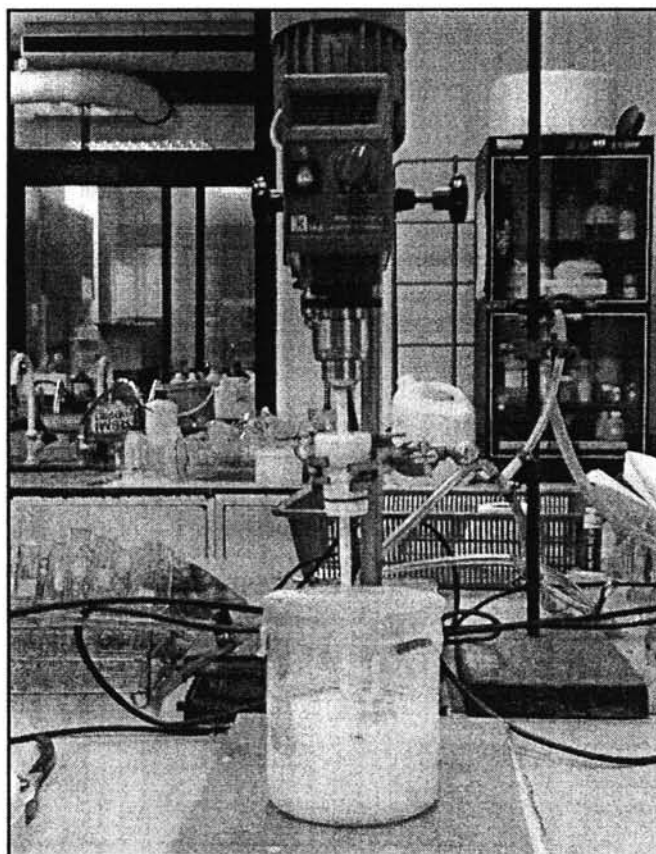
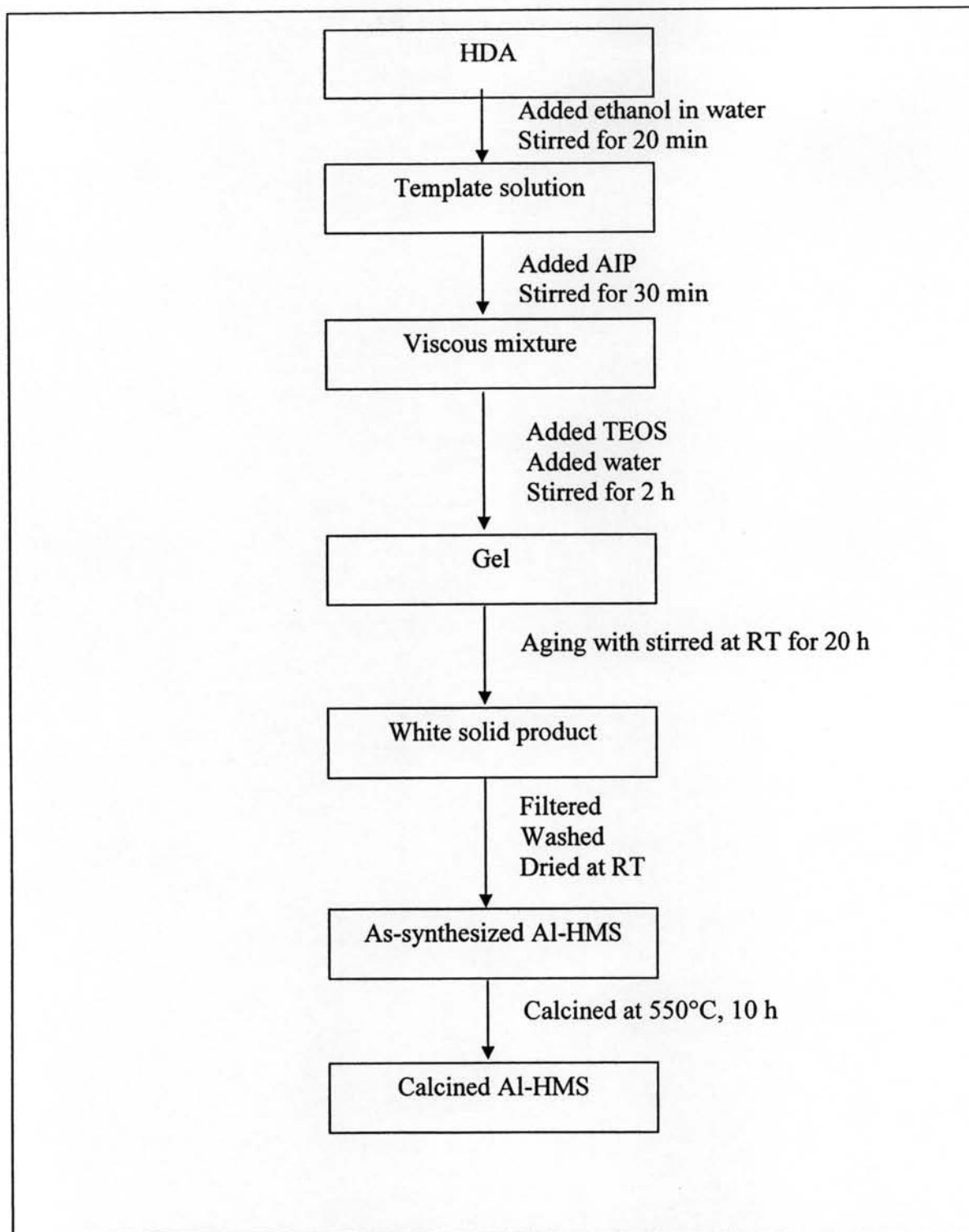


Figure 3.3 Al-HMS synthesis apparatus.



Scheme 3.4 Diagram of Al-HMS synthesis.

3.3.2.1 Synthesis of Al-HMS with various Si/Al ratios

The Al-HMS samples with various Si/Al mole ratios in gel of 40, 60, and 200 were prepared using the similar method described in section 3.3.2. Different quantity of aluminium required for each sample were shown in Table 3.1.

Table 3.1 Required amount of AIP in the preparation of Al-HMS samples with various Si/Al ratios in gel.

Sample	Si/Al mole ratio in gel	Quantity of AIP (g)
Al-HMS 40	40	1.0210
Al-HMS 60	60	0.6807
Al-HMS 200	200	0.2042

3.3.3 NH₄Cl treatment on Al-HMS

One gram of calcined Al-HMS with Si/Al mole ratio in gel of 40 was refluxed in a NH₄Cl solution at the boiling temperature for 3 h. The solid product was filtered, washed, dried, and calcined at 550°C for 10 h. Different concentrations of NH₄Cl were studied as shown in Table 3.2.

Table 3.2 Different concentration of NH₄Cl for treat Al-HMS samples.

Sample	Concentration of NH ₄ Cl (mol/l)
T1MAI-HMS 40	1
T2MAI-HMS 40	2
T3MAI-HMS 40	3

3.3.4 Sample preparation for ICP analysis

A 0.0400 g of a calcined catalyst was soaking with 10 cm³ of conc. HCl in a 100-cm³ Teflon beaker. Then 10 cm³ of 48% hydrofluoric acid was added dropwise to get rid off silica in the form of volatile SiF₄. The sample was heated but not boiled until dryness on a hot plate and the fluoride treatment was repeated two times. 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 dryness again. An amount of 10 cm³ deionized water was added to and warmed about 5 min to complete dissolution. The solution was

transferred to a 50-cm³ polypropylene volumetric flask and the volume was made with deionized water. The flask was capped and shaken thoroughly. The solution was transferred into a plastic bottle with a treaded cap lined under with a polyethylene seal.

3.4 Activity of catalysts in PP and HDPE cracking

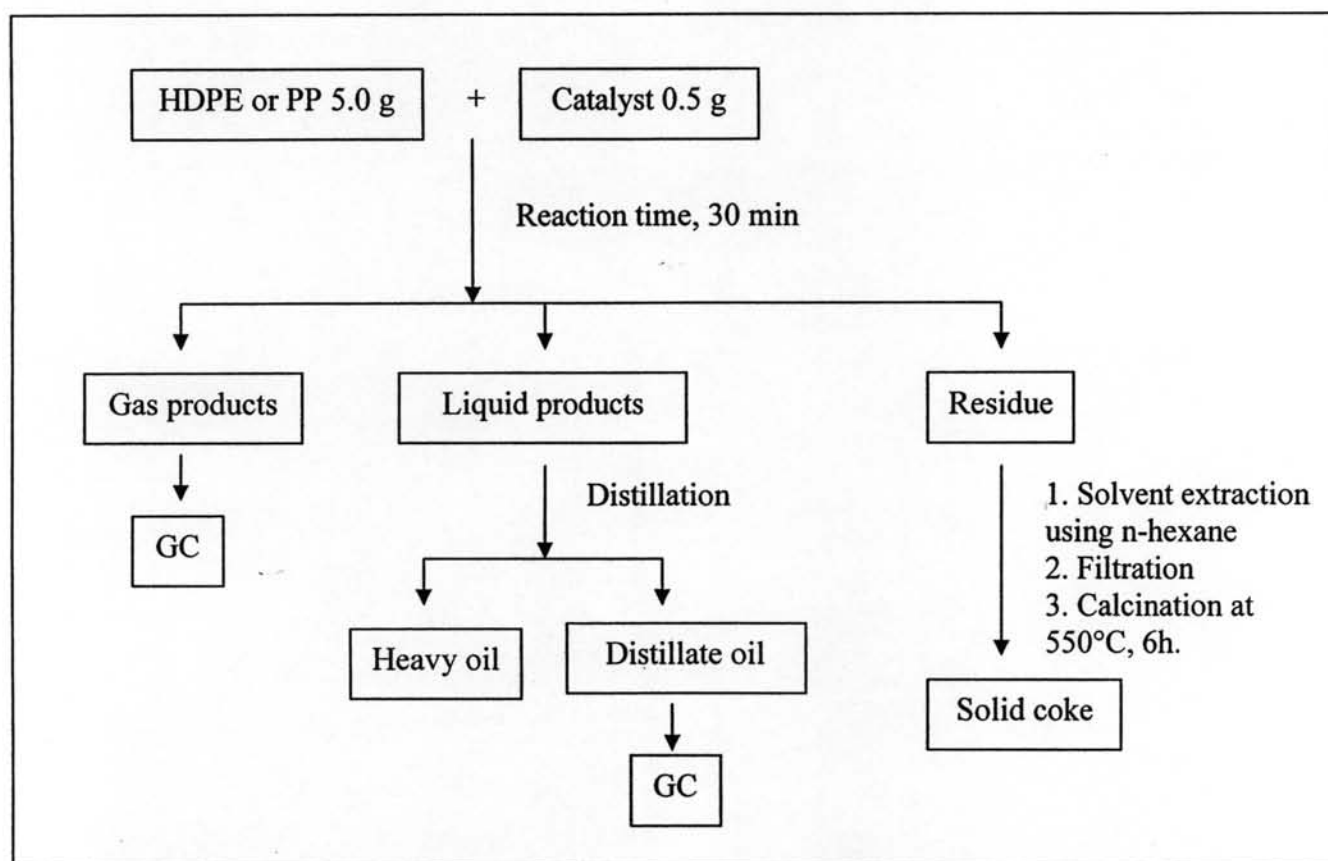
The cracking of PP and HDPE were carried out using zeolite beta/Al-HMS mixed catalysts. Cracking of plastic polymer was carried out in a glass reactor (4.4 cm. i.d. and 37 cm. in length) under atmospheric pressure by batch operation as shown in Figure 3.4 and Scheme 3.5. A total of 5 g of PP pellet and 0.5 g of catalyst were loaded into the reactor. For thermal cracking, only PP or HDPE were loaded into the reactor. In a typical run, the reactor was set up, and purged with N₂ at flow rate of 20 ml/min to remove the air. The reactor was heated to a reaction temperature (350°C) with heating rate 20°C/min using a split-tube furnace equipped with a programmable temperature controller and a K-type thermocouple. The temperature was maintained 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-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:

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

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

$$\begin{aligned} \text{mass of gas fraction} &= \text{mass of the reactor with plastic and catalyst before reaction} - \\ &\quad \text{mass of the reactor with residue and used catalyst after} \\ &\quad \text{reaction} - \text{mass of liquid fraction} \end{aligned}$$

The cracking 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 frozen under liquid nitrogen in order to reduce pressure before distillation at 200°C as shown in Figure 3.5. The distillate oil was analyzed by a GC. The values of retention time of components in the distillate 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 3.5.



Scheme 3.5 Catalytic cracking of PP and HDPE using zeolite beta/Al-HMS as catalyst.

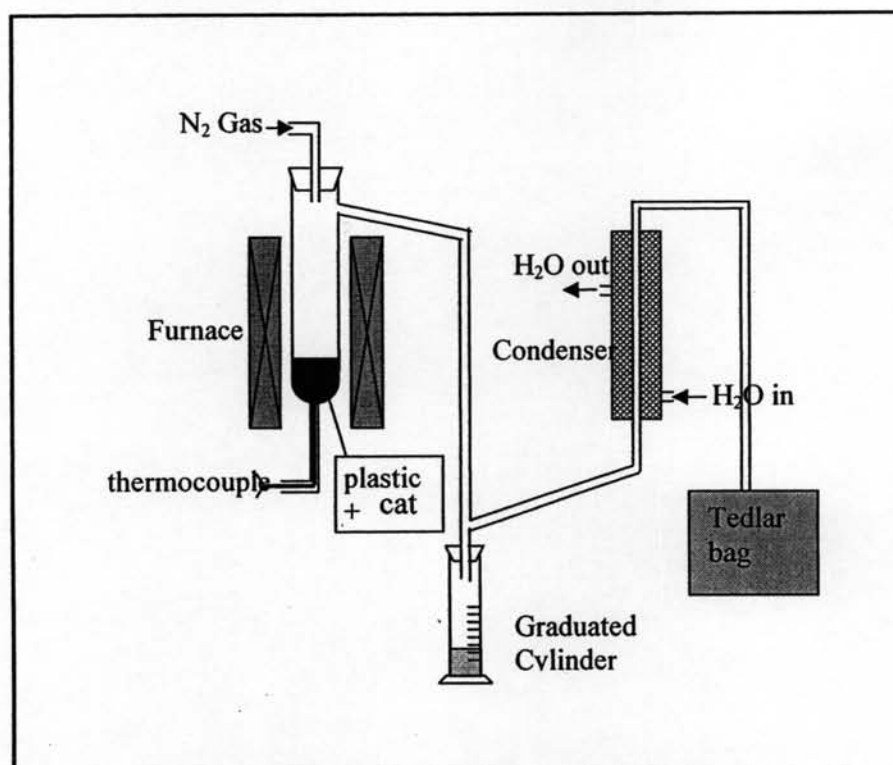


Figure 3.4 Catalytic cracking apparatus.

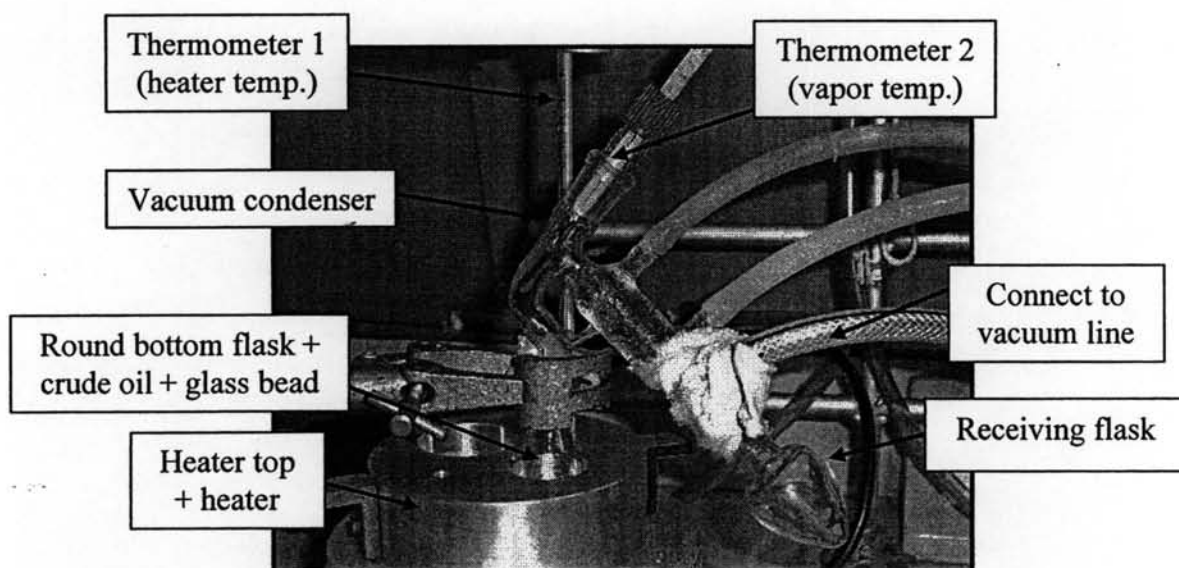


Figure 3.5 Vacuum distillation apparatus.

3.4.1 Activity of various zeolite beta/Al-HMS mixed catalysts in PP cracking

3.4.1.1 Effect of NH₄Cl treatment on Al-HMS in PP cracking

The cracking of PP pellets was performed at 350°C in the similar way to what described in Section 3.4. The NH₄Cl treated Al-HMS catalysts with a Si/Al mole ratio of 40 were studied comparing with the calcined catalyst.

3.4.1.2 Effect of Si/Al ratio in Al-HMS catalysts

The cracking of PP pellet was carried out using Al-HMS with various Si/Al ratios (40, 60, and 200) as catalysts. The reaction was performed in the similar way to what described in Section 3.4 and the experiments were set up at the reaction temperature of 350°C.

3.4.1.3 Effect of Al-HMS ratios in mixed zeolite beta/Al-HMS Catalyst

The cracking of PP pellet was carried out using using zeolite beta/Al-HMS mixed catalysts with various ratios of Al-HMS. The experiments were set up at the 350°C. Different quantites of Al-HMS for each sample were used as shown in Table 3.3

Table 3.3 Different ratios of Al-HMS in mixed catalysts.

Sample	Ratio of Al-HMS in mixed catalysts (%wt)
0%Al-HMS	Pure zeolite beta
20%Al-HMS	20
40%Al-HMS	40
60%Al-HMS	60
80%Al-HMS	80
90%Al-HMS	90
95%Al-HMS	95
100%Al-HMS	Pure treated Al-HMS

3.4.1.4 Effect of plastic to catalyst ratio

The cracking of PP pellet was carried out using zeolite beta/Al-HMS mixed catalysts with various plastic to catalyst ratios (2.5%, 5% and 10%). The reaction was performed in the similar way to what described in Section 3.4 and the experiments were set up at the reaction temperature of 350°C.

3.4.1.5 Effect of temperature

The cracking of PP pellet was carried out using using zeolite beta/Al-HMS mixed catalysts at the reaction temperature of 350°C, 380°C and 410°C.

3.4.2 Activity of various zeolite beta/Al-HMS mixed catalysts in HDPE cracking

3.4.2.1 Effect of Al-HMS ratios in mixed Catalyst

The cracking of HDPE pellet was carried out using treated Al-HMS catalysts with the Si/Al ratio of 40 at reaction temperature of 380°C. The different weight percent of Al-HMS in the mixed catalysts were investigated as follows 0%Al-HMS, 5%Al-HMS, 10%Al-HMS, 20%Al-HMS, 40%Al-HMS, 60%Al-HMS, 80%Al-HMS and 100%Al-HMS.

3.4.2.2 Effect of plastic to catalyst ratio

The cracking of HDPE pellet was carried out using zeolite beta/Al-HMS mixed catalysts with various catalyst to plastic ratio (2.5%, 5% and 10%). The reaction was performed in the similar way to what described in Section 3.4 and the experiments were set up at the reaction temperature of 380°C.

3.4.2.3 Effect of temperature

The cracking of HDPE pellet was carried out using using zeolite beta/Al-HMS mixed catalysts with various temperature reactions. The reaction was performed in the similar way to what described in Section 3.4 and the experiments were set up at the reaction temperature of 350°C, 380°C and 410°C.

3.5 Catalyst regeneration

The reuses of catalysts were investigated. A used catalyst was regenerated by calcining in air at 550°C for 6 h. The regenerated catalysts were characterized by

nitrogen adsorption-desorption technique, NH_3 -TPD. The activity of regenerated catalyst was performed for cracking of PP at reaction temperature 380°C and HDPE at 410°C . The reaction was performed in the similar way to what described in Section 3.4.