CHAPTER III

EXPERIMENTAL

3.1 Chemicals and gases

Silica source, tetraethyl orthosillicate (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 form Fluka. Sodium hydroxide (NaOH) was supplied from Merck. Polypropylene pellets (density = 0.91 g/cm^3 melting point = 163°C injection molding grade) were kindly obtained from SCG Plastics Co., Ltd. Lubricant oil 4T JASO MA 40 was commercially available from HONDA. Grease (genuine parts) was commercially available from ISUZU motor, LTD. Other chemicals were provided from Merck or Fluka, otherwise specially identified.

3.2 Instruments, apparatus and analytical techniques

Centrifuge

The separation and collection of zeolite beta and zeolite beta/Al-HMS composite solid after crystallization were processed by a Sanyo Centaur 2 centrifuge at speed of 6,000 rpm.

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 calcination, 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" [60].

Powder X-ray diffraction (XRD)

The XRD pattern and d-spacing of zeolite beta, Al-HMS, and zeolite beta/Al-HMS composite catalysts were determined by a Rigaku, Dmax 2200/Ultima$^+$ diffractometer equipped with a monochromator and Cu Kα radiation. The tube voltage and current were set at 40 kV and 30 mA, respectively. The diffraction pattern was recorded in the 2-theta range from 5 to 50 degree with a scan speed of 5 degree/min for zeolite beta and from 1.2 to 10 degree applied for Al-HMS. A 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 for Al-HMS.

Scanning electron microscopy (SEM)

The morphology and particles size of zeolite beta, Al-HMS and zeolite beta/Al-HMS catalysts were observed using a JSM-5410 LV scanning electron microscope. In SEM analysis, the samples were coated with spluttering 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

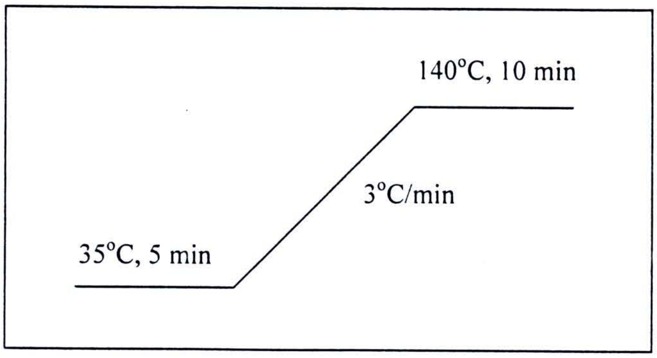
Aluminum contents in the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES) at Scientific and Technology Research Equipment Centre, Chulalongkorn University.

^{27}Al MAS nuclear magnetic resonance spectroscopy

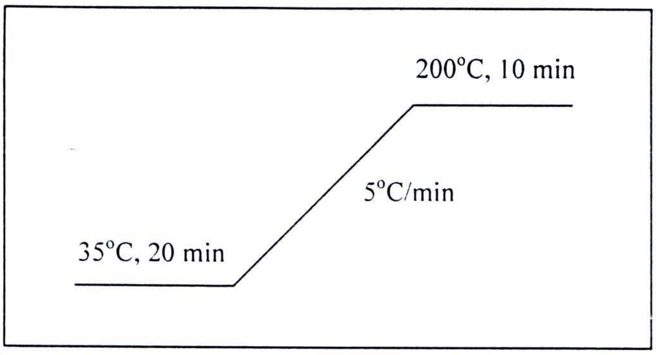
The signal of aluminum tetrahedral in catalysts was conformed by ^{27}Al-magnetic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR, Bruker DPX-300 spectroscopy operating at 78 MHz at National Metal and Materials Technology Center, Pathumthani.

Gas chromatography

Hydrocarbon gases were analyzed using a Varian CP 3800 gas chromatograph equipped with a 50 m length × 0.53-mm inner diameter Alumina-PLOT column. Liquid products from cracking were analyzed using the same instrument but equipped with a 30 × 0.25 mm inner diameter CP-sil 5 column (equivalent to DB-1 column). The detector is a 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.

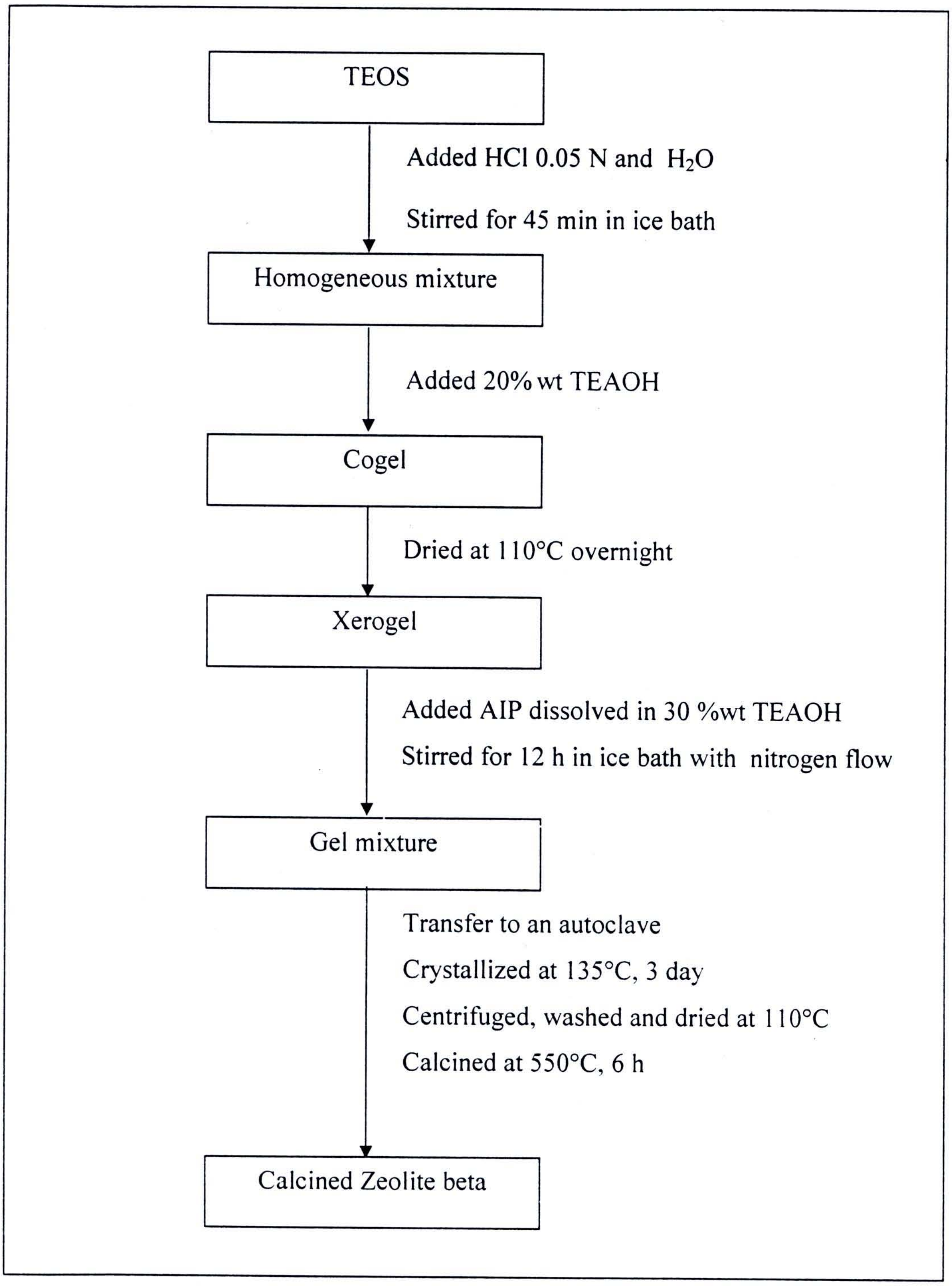


Scheme 3.2 The column heating program for liquid analysis.

3.3 Synthesis of catalysts

3.3.1 Synthesis of zeolite beta with a Si/Al mole 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 $1SiO_2$: 0.0083 Al_2O_3: 0.73 TEAOH : 19 H_2O (Si/Al = 60) report by J. Aguado *et al.* [61]. Zeolite beta was synthesized from a SiO_2-Al_2O_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 an 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 and named "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 under stirring. The mixture was loaded into autoclave, and kept at 135°C for 3 day. The crystalline product obtained was separated by centrifugation, washed with deionized water, dried at 110°C overnight. As-synthesized zeolite beta yielded approximately 20g, and 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.

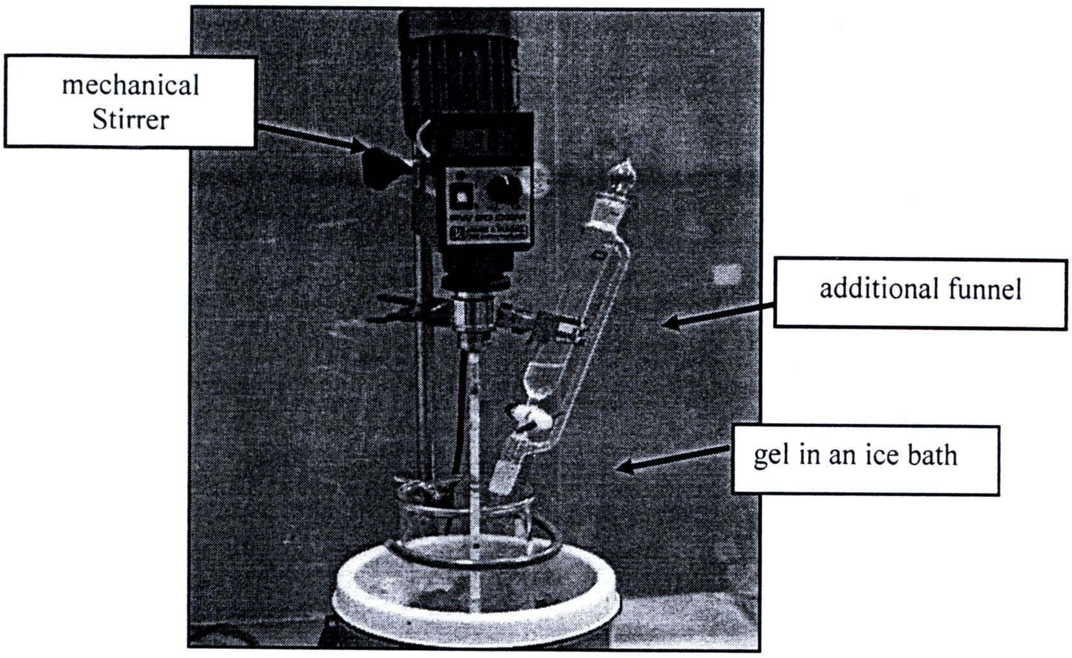


Figure 3.1 Xerogel synthesis apparatus.

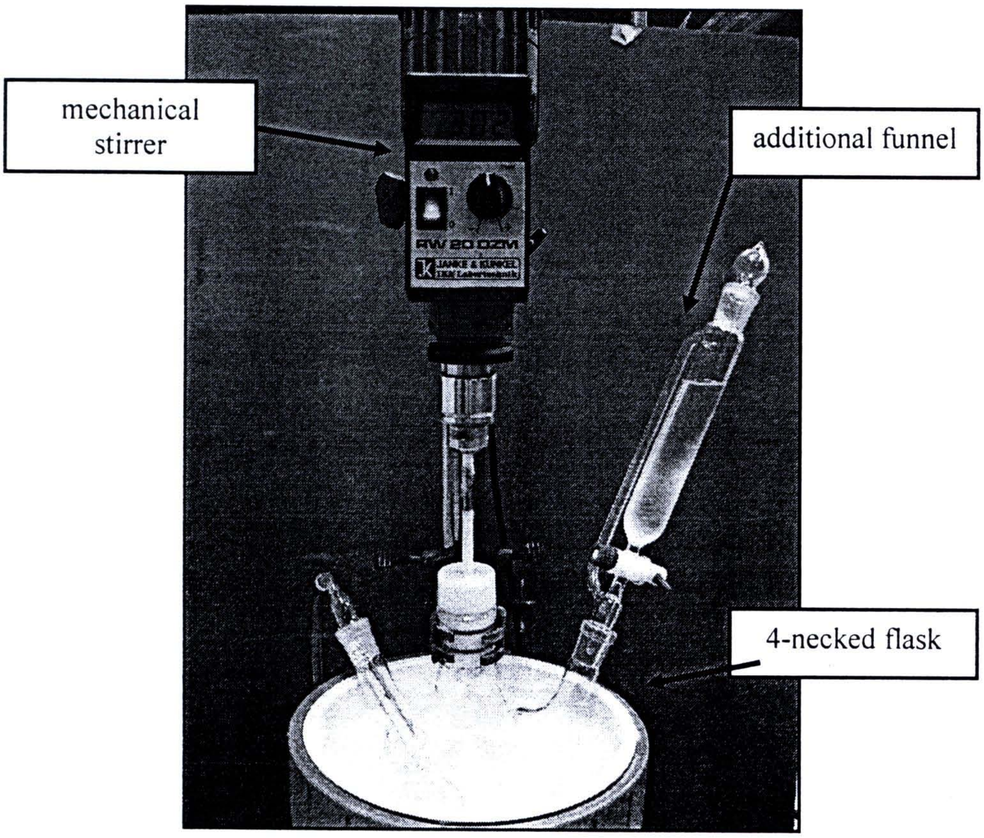


Figure 3.2 Zeolite beta synthesis apparatus.

3.3.2 Synthesis of Al-HMS with the Si/Al mole ratio in gel of 60

Al-HMS synthesis was performed by modifying the procedures reported by Tuel *et al* [46] and Rao et al[41]. The gel mole composition of 1SiO$_2$: 0.0083 Al $_2$O$_3$: 0.25 HDA: 8.3 EtOH: 100 H$_2$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-cm^3 beaker. The mixture was stirred for 20 min until homogeneous solution was obtained. Then 0.6807 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 of filtrare equals to 7.0. The solid was air died 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.

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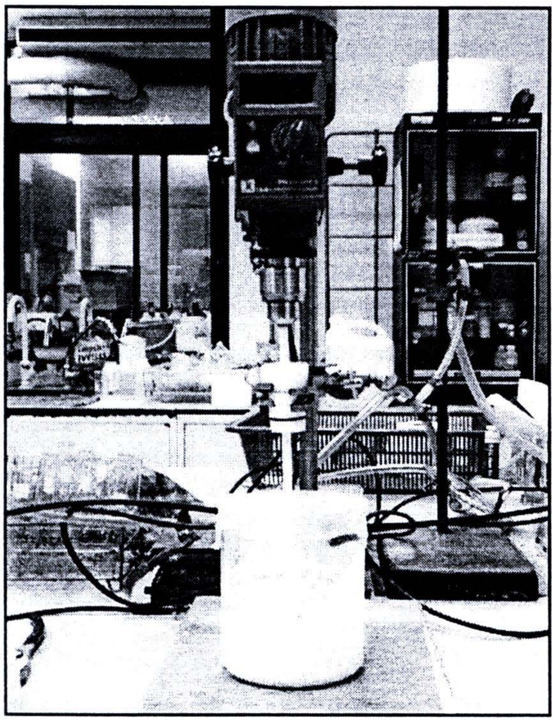
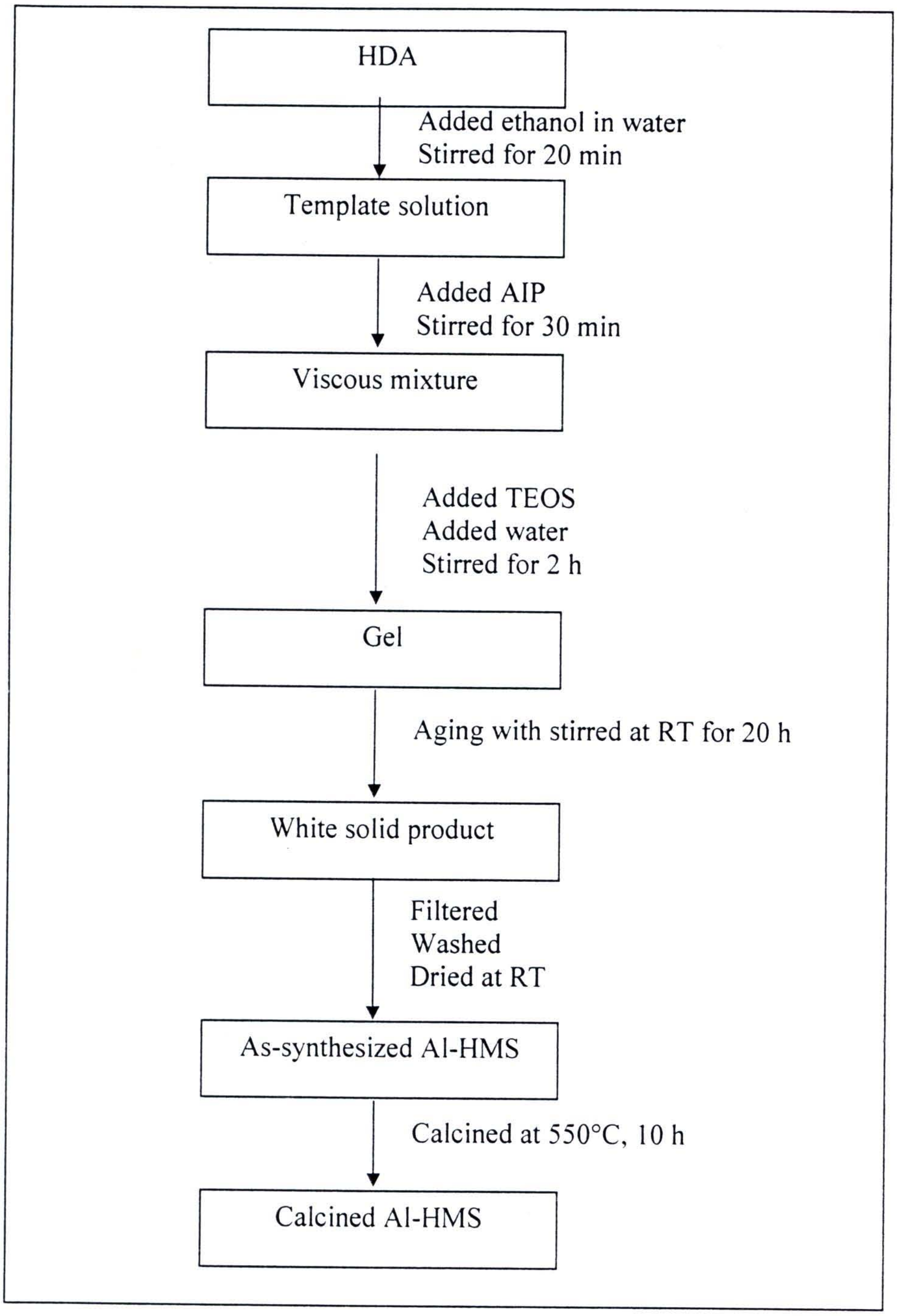


Figure 3.3 Al-HMS synthesis apparatus.



Scheme 3.4 Diagram of Al-HMS synthesis.

3.3.3 Synthesis of zeolite beta/Al-HMS composite

The zeolite beta /Al-HMS composite was synthesized as follows: hexadecylamine (HDA, 0.25 mole) was dissolved in a mixed solvent of ethanol (8.3 mole) and water (100 mole). The mixture was then stirred until a homogeneous solution was obtained. Tetraethyl orthosilicate (TEOS, 1 mole) and water were added dropwise in sequence into the mixture with continuous stirring for 2 h. Then, 2 g of zeolite beta which was dissolved in 1 M NaOH, was added. Zeolite beta with the gel molar composition of 1 SiO_2: 0.0083 Al_2O_3: 0.73 TEAOH : 19 H_2O was synthesized and crystallized at 135°C for 3 days as the method reported by Aguado [61]. After that, the pH value of mixture solution was adjusted to 8.5 with 2 M HCl. The resulting gel was then recrystallized at room temperature for 36 h. The white solid product was obtained, filtered, and washed with deionized water until the pH value of filtrate was equal to 7.0. The organic template was removed by calcination of the sample at the temperature of 500°C for 5 h.

3.3.3.1 Synthesis of zeolite beta/Al-HMS composite with various crystallization time

The zeolite beta/Al-HMS composite with various crystallization time from 12 to 36 h were synthesized using the same method described in Section 3.3.3.

3.3.3.2 Synthesis of zeolite beta/Al-HMS composite with various concentration of NaOH concentration and time on dissolving zeolite beta

The effect of NaOH concentration on dissolution of zeolite beta before adding the HMS template solution was studied. The concentrations of NaOH were varied from 0.5 to 1 M and the dissolution time was observed at 15 and 30 minutes.

3.3.3.3 Synthesis of zeolite beta/Al-HMS composite with various crystallization time of zeolite beta

The composite samples were synthesized in the similar way as described in section 3.3.3, however, the crystallization time on zeolite beta synthesis was studied at 16, 18 and 76h. All zeolite beta/Al-HMS composite were characterized by XRD. The optimal crystallization of zeolite beta was selected for synthetic condition.

3.3.3.4 Preparation of zeolite beta/Al-HMS composite with various Si/Al ratios

The zeolite beta/Al-HMS composite samples with various Si/Al ratios in gel of 40, 60 and 120 were synthesized using the same method as that described in Section 3.3.3. Different amounts of aluminum required for each sample were used as indicated in Table 3.1. All zeolite beta/Al-HMS composite catalysts were characterized by XRD.

Table 3.1 Required amounts of aluminum isopropoxide in the preparation of zeolite beta/Al-HMS composite with various Si/Al ratios in gel of 40, 60 and 120

Sample	**Si/Al molar ratio in gel**	**Amounts of aluminum isopropoxide (g)**
zeolite beta/Al-HMS composite (40)	40	11.7285
zeolite beta/Al-HMS composite (60)	60	7.8191
zeolite beta/Al-HMS composite (120)	120	3.9096

3.3.4 Sample preparation for ICP analysis

A 0.0400 g of calcined catalyst was soaking with 10 cm^3 of conc. HCl in a 100-cm^3 Teflon beaker. Then 10 cm^3 of 48% hydrofluoric acid was added dropwise to get rid off silica in the form of volatile SiF_4. 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 cm^3 of a mixture of 6 M HCl: 6 M HNO_3 at a ratio of 1:3 was added slowly and warmed until dryness again. An amount of 10 cm^3 deionized water was added to and warmed about 5 min to complete dissolution. The solution was transferred to a 50-cm^3 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 Conversion of lubricant oil, grease or polypropylene

The cracking reactions of lubricant oil, grease or polypropylene were carried out using zeolite beta/Al-HMS composite catalysts. Cracking of lubricant oil, grease or polypropylene were 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 lubricant oil, grease or polypropylene and 0.5 g of catalyst were loaded into the reactor. For thermal cracking, only lubricant oil, grease and polypropylene were loaded into the reactor. In a typical run, the reactor was set up, and purged with N_2 at a flow rate of 20 ml/min as carrier gas. The reactor was heated to a reaction temperature with heating rate 20°C/min using a split-tube furnace equipped with a programmable temperature controller and a K-type thermocouple. The gas fraction which flowed from the reactor with the nitrogen stream was passed through a condenser with controlled temperature 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-cm^3 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:

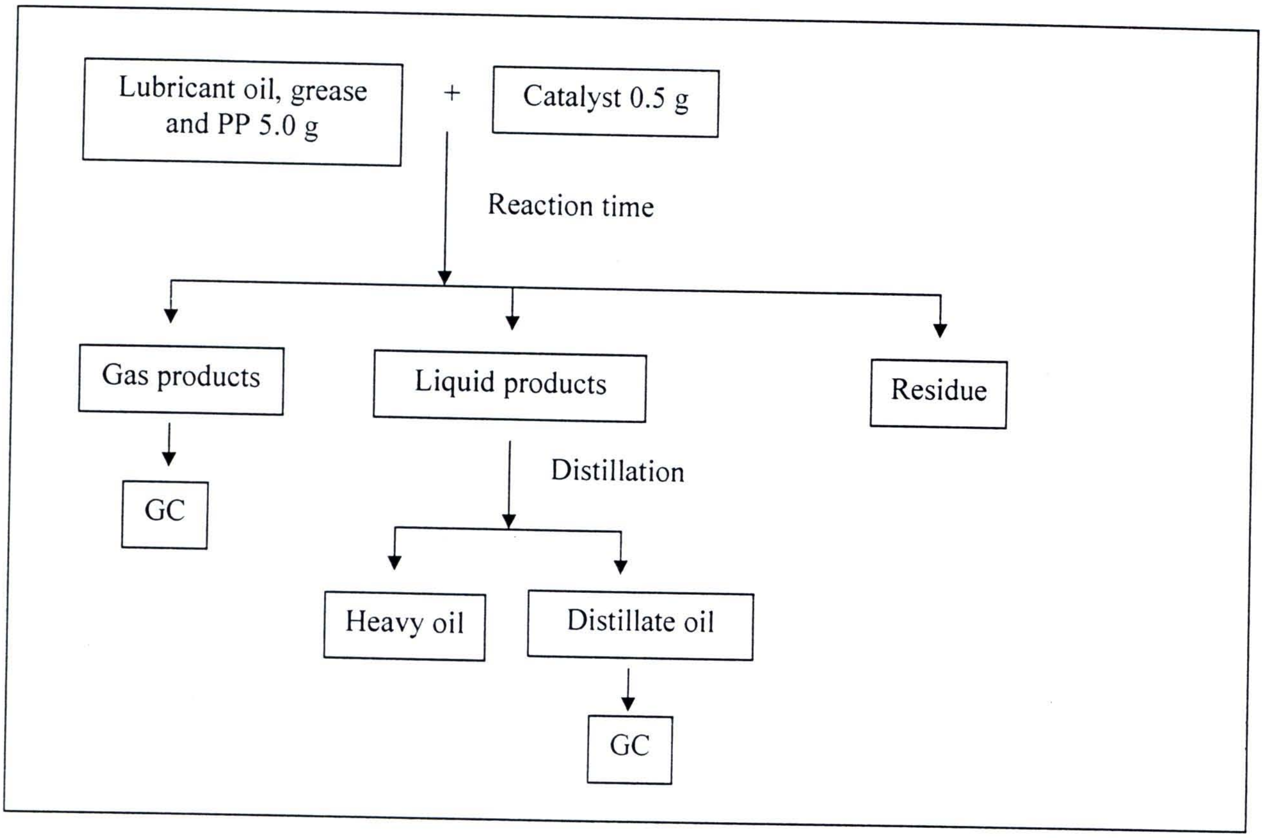
$$\text{Conversion (wt\%)} = \frac{\text{mass of liquid fraction} + \text{mass of gas fraction}}{\text{mass of plastic}} \times 100$$

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

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 - mass of liquid fraction

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 heating program for regeneration of the used catalyst is shown in Scheme 3.5



Scheme 3.5 Catalytic cracking of lubricant oil, grease and PP using zeolite beta/Al-HMS composite as catalyst.

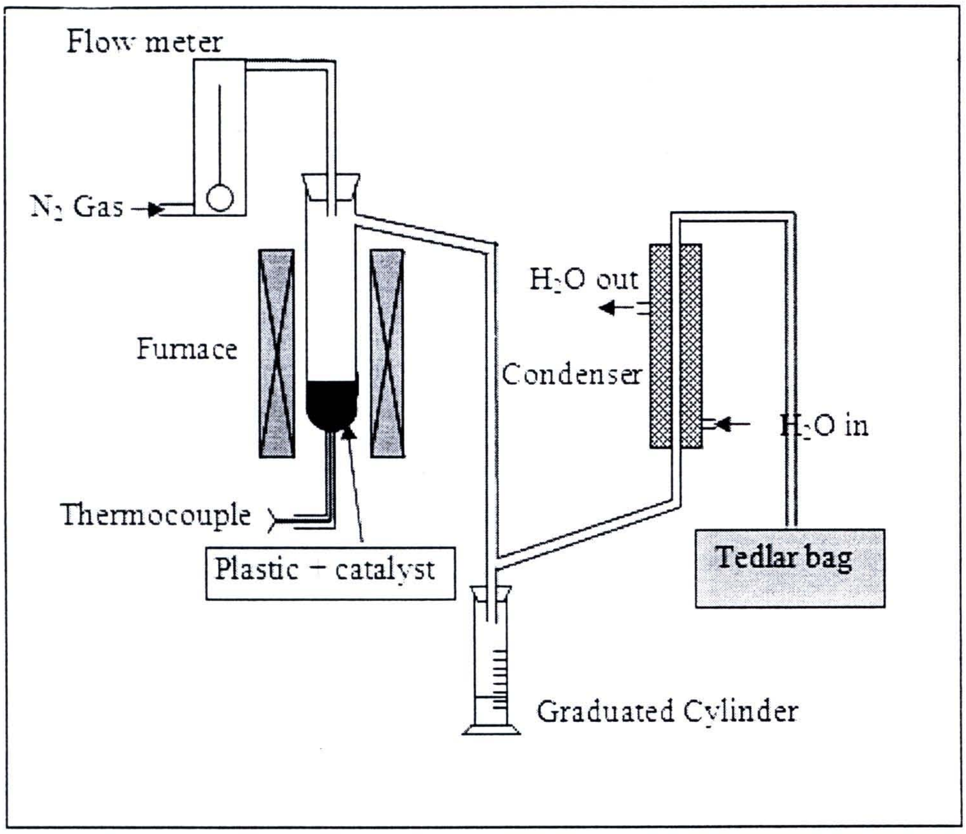


Figure 3.4 Catalytic cracking apparatus.

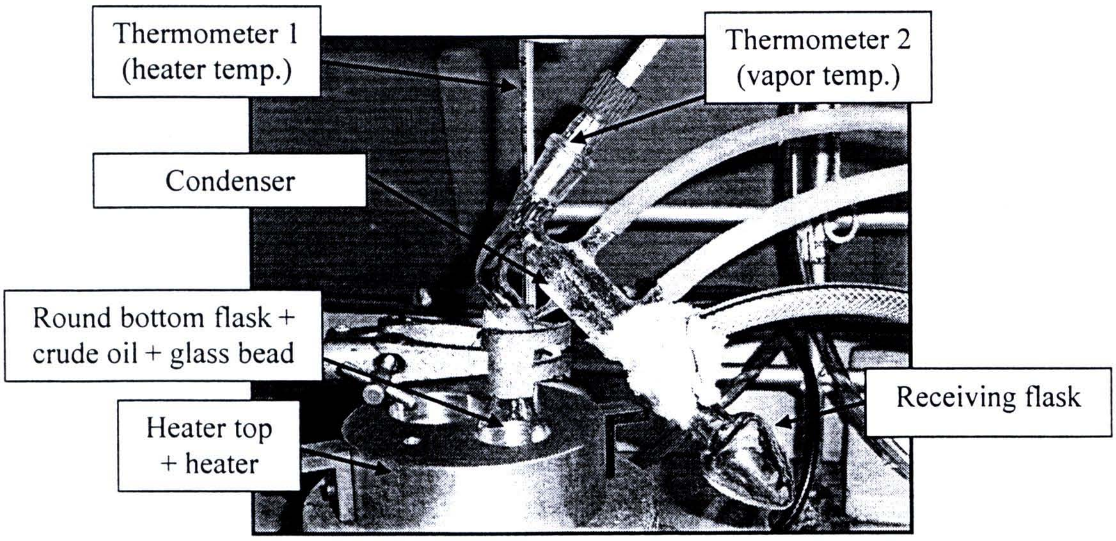


Figure 3.5 Vacuum distillation apparatus.

3.4.1 Activity of zeolite beta/Al-HMS catalysts in cracking of lubricant oil

3.4.1.1 Effect of reaction time

The cracking of lubricant oil was carried out using zeolite beta/Al-HMS composite catalysts with Si/Al ration of 60 in gel of zeolite beta for 120 min. 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 400°C.

3.4.1.2 Effect of temperature

The cracking of lubricant oil was carried out using Al-HMS, zeolite beta and zeolite beta/Al-HMS composite catalysts at the reaction temperature of 350°C, 380°C and 400°C. The reaction time this was based on the condition in section 3.4.1.1.

3.4.1.3 Effect of various catalyst

The cracking of lubricant oil was performed using Al-HMS, zeolite beta and zeolite beta/Al-HMS composite catalyst. The reaction was performed in the same way as what described in Section 3.4. The experiments were set up at reaction temperature which based on the condition in section 3.4.1.2.

3.4.2 Activity of zeolite beta/Al-HMS composite catalysts in cracking of grease

3.4.2.1 Effect of temperature

The cracking of grease was carried out using Al-HMS, zeolite beta and zeolite beta/Al-HMS composite catalysts at the reaction temperature of 350°C, 380°C and 400°C. The reaction time of 90 min was based on the condition of lubricant oil.

3.4.2.2 Effect of reaction time

The zeolite beta/Al-HMS composite catalysts was used for studying the effect of reaction time for 120 min. 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 400°C.

3.4.2.3 Effect of various catalysts

The cracking of grease was performed using Al-HMS, zeolite beta and zeolite beta/Al-HMS composite catalyst. The reaction was performed in the same way as what described in Section 3.4. The experiments were set up at reaction temperature which based on the condition in section 3.4.2.2.

3.4.3 Activity of various zeolite beta/Al-HMS composite catalysts in PP cracking

3.4.3.1 Effect of the reaction time

The cracking of PP was carried out using zeolite beta/Al-HMS (Si/Al=60) composite catalysts for 120 min ,chose two point, which find appropriated reaction time for cracking. 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.

3.4.3.2 Effect of the reaction temperature

The catalytic cracking of PP was carried out using Al-HMS, zeolite beta and zeolite beta/Al-HMS composite catalyst with different temperature reactions. The reaction was performed using the same method that described in Section 3.4. The experiments were set up at reaction temperatures of 350, 380 and 400°C.

3.4.3.3 Effect of Si/Al ratios in catalyst

The temperature 380°C was used in the degradation of PP using zeolite beta/Al-HMS composite with Si/Al ratios 40, 60 and 120 respectively. The reaction was performed using the same method that described in Section 3.4.

3.5 Catalyst regeneration

The reuses of catalysts were investigated. A used catalyst was regenerated by calcining in air at 500°C for 5 h. The regenerated catalysts were characterized by XRD and nitrogen adsorption-desorption technique. The activity of regenerated catalyst was performed for cracking of PP at reaction temperature 380°C for 60 min. The reaction was performed in the similar way to what described in Section 3.4.