

CHAPTER III

EXPERIMENTAL

3.1 Instrument and apparatus

Ovens and furnaces

Crystallization of SBA-15 during the synthesis was performed at 100°C using a UM-500 oven as heater. Calcination of the solid catalysts at elevated temperature was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

X-ray powder diffractometer

The structure of synthesized mesoporous materials were identified using a Rigaku D/MAX-2200 Ultima+ X-ray diffractometer (XRD) equipped with CU K α radiation (40 kV 30 mA) and a monochromator at 2 theta angle between 0.5 to 3 degrees. 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 contents in the catalysts were analyzed using a Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

²⁷Al-NMR spectrometer

²⁷Al-MAS-NMR spectra were performed using a Bruker Advance DPX 300 MHz NMR spectrometer.

Surface area analyzer

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 BEL Japan, BELSORP-mini instrument. The sample weight was near 40 mg and weighed exactly after pretreatment at 400°C for 3 h before each measurement.

NH₃-TPD instrument

Acid strength of catalysts was determined using the BEL Japan, BELCAT with the sample weight about 200 mg and highly pure ammonia gas.

Scanning electron microscope

SEM image was done to determine the morphology using a JEOL JSM-5410 LV scanning electron microscope. All samples were coated with sputtering gold under vacuum.

Gas chromatograph

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

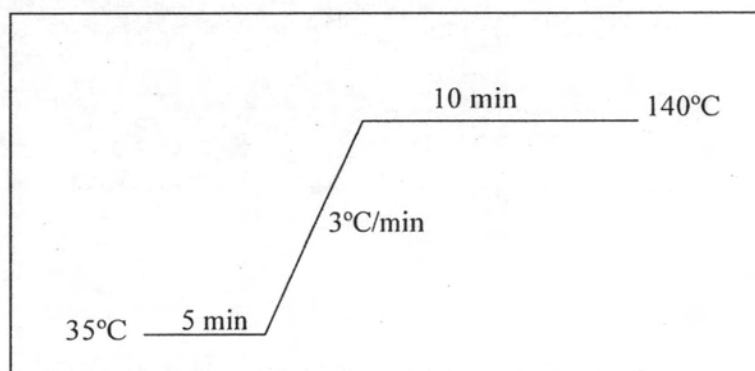


Figure 3.1 The GC column heating program for gas analysis.

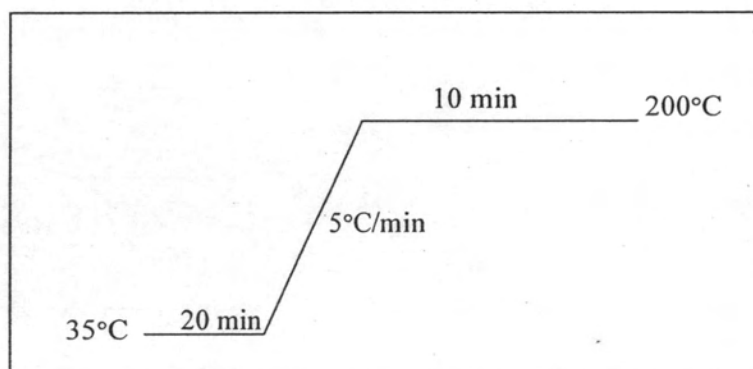


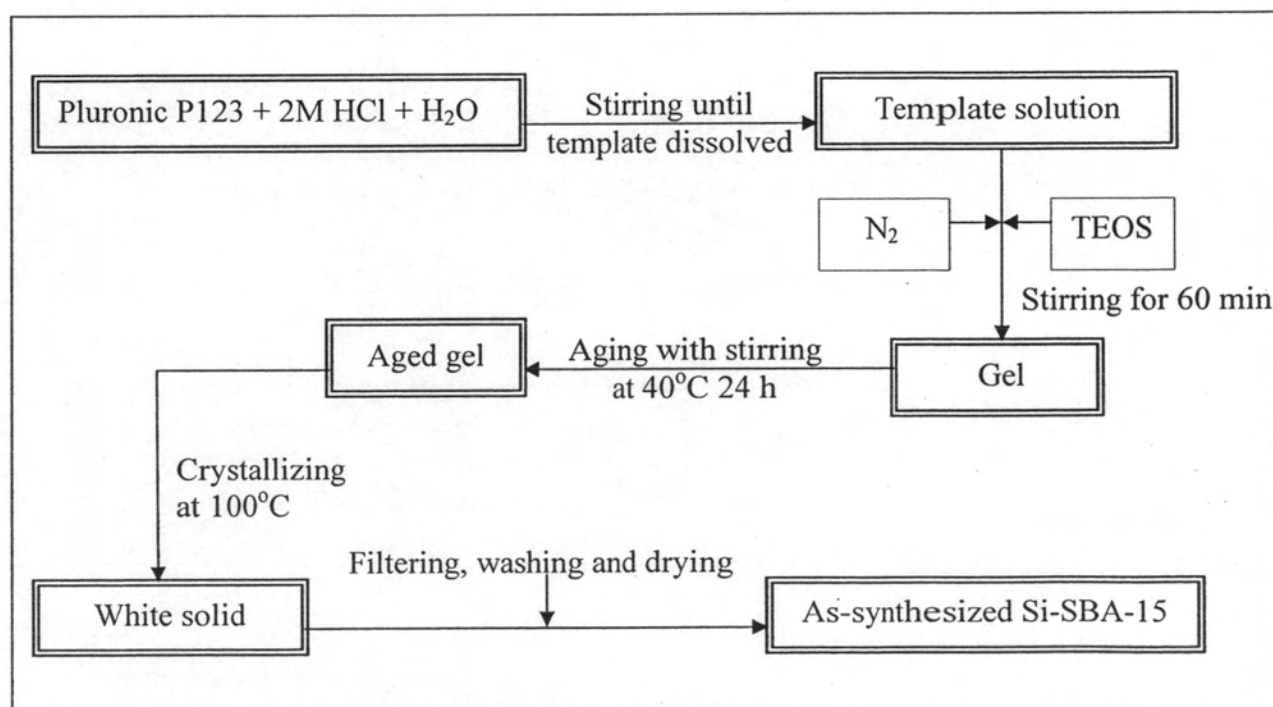
Figure 3.2 The GC column heating program for liquid analysis.

3.2 Chemicals and gases

Tetraethyl orthosilicate (98% TEOS) was commercially available from Fluka. Sodium aluminate was supplied from Riedel-de Haën. Triblock copolymer Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, average molecular weight = 5800) was available from Aldrich. Standard gas mixture for GC analysis was kindly provided from PTTCHEM. Polypropylene beads were kindly obtained from Polypropylene Co., Ltd. Other chemicals were provided from Merck or Fluka, otherwise specifically identified.

3.3 Synthesis procedure of Si-SBA-15

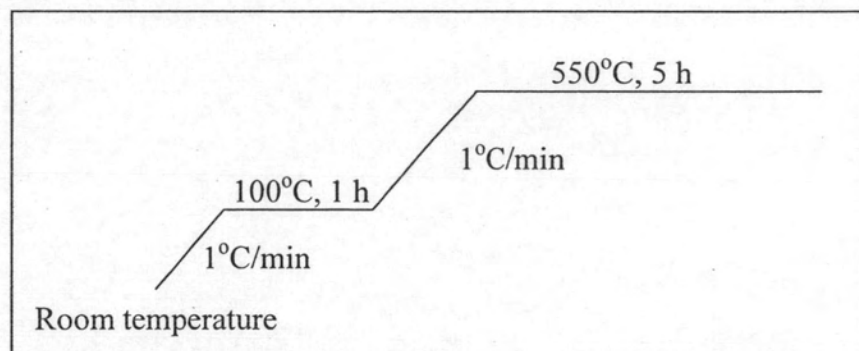
Pure silica SBA-15, a mesoporous material was synthesized using a method reported by Zhao *et al.* [10] using triblock copolymer Pluronic P123 as a template. A 4.0 g of template was dissolved in 30 g of water and 120 g of 2M HCl solution. Subsequently, 8.50 g of tetraethyl orthosilicate (TEOS) was added, stirred for 1 h and then kept at 40°C for 24 h with stirring. The resulting gel was transferred into a Teflon bottle and heated at 100°C for 48 h without stirring. As-synthesized SBA-15 was recovered by filtration, washed with deionized water for several times, and dried in the air. The white powder material was obtained. The procedure for preparing the Si-SBA-15 is shown in Scheme 3.1.



Scheme 3.1 Preparation diagram for Si-SBA-15.

3.4 Organic template removal

To remove the template, PEO₂₀-PPO₇₀-PEO₂₀, the solid sample was calcined in a muffle furnace from room temperature to 550°C for 5 h as shown in Scheme 3.2.



Scheme 3.2 Calcination temperature program for Si-SBA-15.

3.5 Synthesis of Al-SBA-15

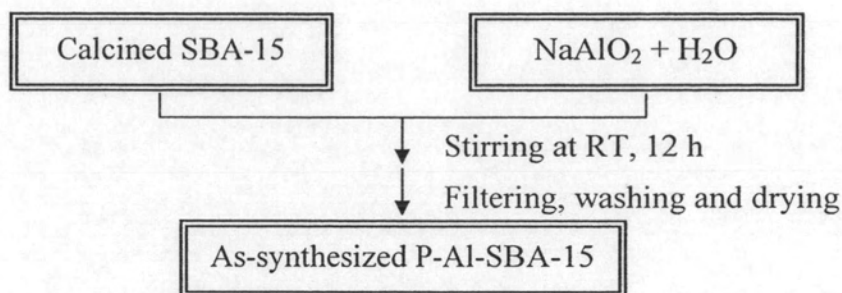
In this work, mesoporous silica SBA-15 was incorporated with aluminum via two different synthesis procedures that are direct synthesis and post synthesis procedures.

3.5.1 Direct synthesis of Al-SBA-15 [37]

By this mean, aluminum-containing SBA-15 was synthesized using the same method as mentioned above but an appropriate amount of aluminum precursor, aluminum tri-sec-butylate, was added into a gel prior to the crystallization at elevated temperature.

3.5.2 Post-synthesis of Al-SBA-15 [19]

Alumination of SBA-15 was conducted of stirring 0.5 g of calcined SBA-15 in 50 ml of water containing various amounts of sodium aluminate at room temperature for 12 h [Scheme 3.3]. The solid material was then filtered, washed with deionized water, and dried at room temperature. The stoichiometric amounts of sodium aluminate used are shown in Table 3.1.



Scheme 3.3 Alumination of SBA-15 [19].

Table 3.1 Required amounts of sodium aluminate in the preparation of Al-SBA-15 with the Si/Al molar ratios in reactant mixture of 10, 25, 50, 100 and 200

Si/Al molar ratio in gel	NaAlO ₂ dissolved in 50.0 g H ₂ O (g)
10	0.1290
25	0.0515
50	0.0258
100	0.0129
200	0.0064

Note : Al-SBA-15 is denoted that P-Al-SBA-15(X) and D-Al-SBA-15(X), where P represents for the Al-SBA-15 from post synthesis method, D for Al-SBA-15 from the direct synthesis method, and X for the Si/Al molar ratio in gel.

3.6 Ion exchange of Al-SBA-15

The sodium ions in Al-SBA-15 sample prepared by post synthesis method were removed by reacting Al-SBA-15 with the following procedures listed in Table 3.2. The Al-SBA-15 was divided into two intermediate types, which are wet (after filtration) and dried samples.

Table 3.2 Ion exchange conditions for Al-SBA-15

Condition		Reaction time (h)
1	non treated	-
2	Dried sample, treated with 1 M NH ₄ Cl, RT	0.5
3	Dried sample, treated with 0.01 M NH ₄ Cl under reflux	24
4	Dried sample, treated with 0.01M HNO ₃ under reflux	24
5	Dried sample, treated with 1 M NH ₄ Cl under reflux	12
6	Dried sample, treated with 2 M NH ₄ Cl under reflux	24
7	Wet sample, treated with 0.01 M NH ₄ Cl under reflux	24
8	Wet sample, treated with 0.01 M HNO ₃ under reflux	24
9	Wet sample, treated with 1 M NH ₄ Cl under reflux	12
10	Wet sample, treated with 1 M NH ₄ Cl under reflux	24
11	Wet sample, treated with 2 M HNO ₃ under reflux	24

3.7 Sample preparation for ICP-AES analysis

A 0.0400 g of calcined sample was soaking with 10 cm³ of conc. HCl and subsequently 10 cm³ of 48% hydrofluoric acid (Merck) was added dropwise to get rid of silica in the form of volatile SiF₄. 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 dryness again. Then an amount of 10 cm³ de-ionized water was added and warmed for 5 min to complete dissolution. The solution was transferred to a 50-cm³ polypropylene volumetric. The solution in the flask was brought to the mark with de-ionized 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.

3.8 Catalytic cracking of polypropylene over Al-SBA-15

3.8.1 General procedure in catalytic cracking of PP

The catalytic cracking of polypropylene (PP) was performed at 380°C in a batch reactor with continuous N₂ flow 20 ml/min. Figure 3.3 shows a schematic diagram of the experimental setup used in this study.

In each experiment, 5 g of plastic was loaded into the reactor and mixed with the appropriate amount of calcined catalyst powder. The reactor was heated to the desired reaction temperature in 15 min, which was kept constant for a period of 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:

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

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 are gas fraction, liquid fraction, and residue. Liquid product obtained from the reaction was separated into two fractions, light oil and heavy oil, by vacuum distillation using small distillation kit at the heater temperature of 200°C. The gas fraction and light oil fraction were analyzed by GC. The term residue consists of both coke and wax remaining in the catalytic line. The %coke formed 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 is shown in Scheme 3.2.

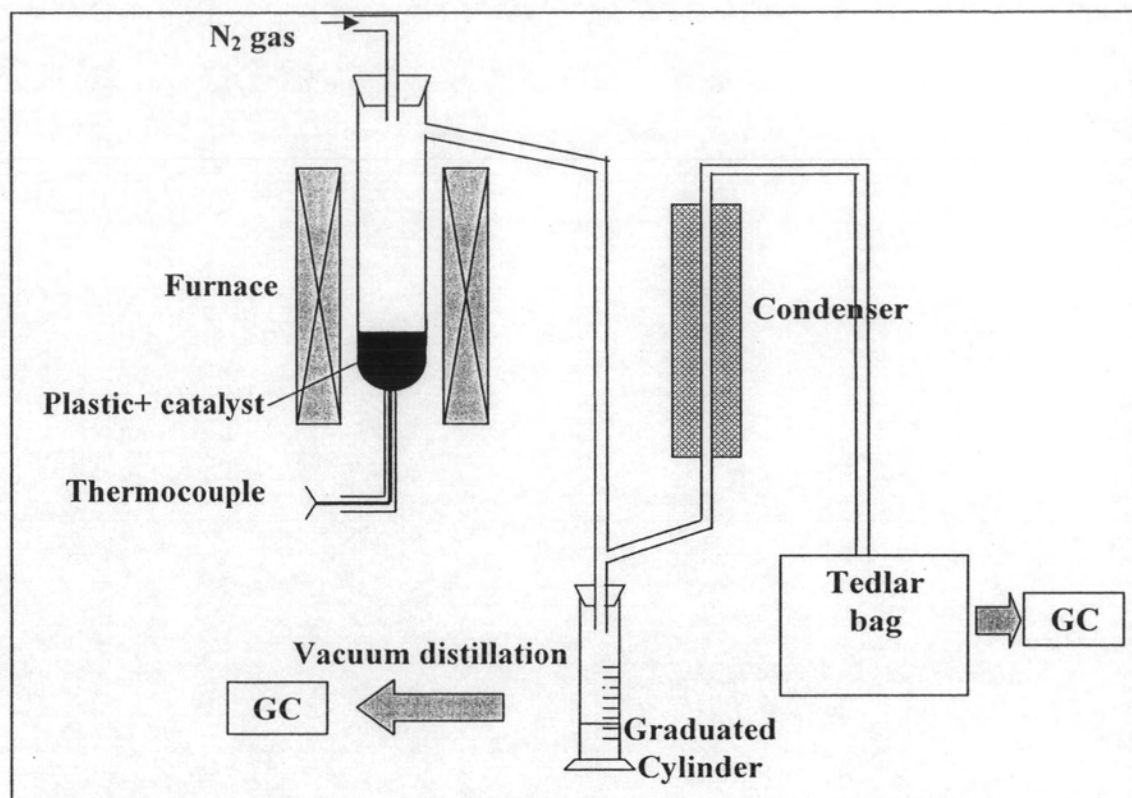


Figure 3.3 Apparatus for plastic cracking.

3.8.2 Thermal cracking and catalytic cracking over non acidic SBA-15

The reaction temperature plays an important role in cracking process; hence, in this study the thermal cracking of PP without catalyst was investigated and compared with cracking over non acidic silica SBA-15 at the reaction temperature of 380°C.

3.8.3 Effect of sodium ion in catalyst

The effect of sodium ion in catalyst was investigated using the general procedure as described in Section 3.8.1 but the cations of catalyst were varied by using non-ion-exchanged catalyst (mixed Na/H form) and ion exchanged catalyst (proton form) prepared from two different ion exchange routes that are 0.01 M HNO_3 and 0.01 M NH_4Cl .

3.8.4 Effect of reaction temperature

The effect of temperature on cracking of PP was studied in the same way as general procedure, but the reaction temperature was varied to 360, 380, and 400°C.

3.8.5 Effect of polymer to catalyst ratio

The catalytic cracking reaction was carried out according to the procedure above in 3.8.1, but the amount of catalyst (H-Al-SBA-15) was changed to 5 wt%, 10 wt%, and 15 wt% catalyst of PP.

3.8.6 Effect of aluminum content in catalyst

The degradation of polypropylene was carried out using H-Al-SBA-15 with the Si/Al molar ratios in gel of 10, 25, 50, 100, and 200 as catalysts. The reaction was performed in the same way as Section 3.8.1.

3.9 Recycle of catalyst

The spent catalyst of single use (Si/Al = 10) was subjected to be reused with and without regeneration. The spent catalyst was washed several times with n-hexane after the first run, and dried in oven for reuse without regeneration. In addition, the spent catalyst was regenerated by calcination in air at 550°C for 5 h and characterized by XRD and surface area analysis before testing for its activity.

3.10 Catalytic activity test for polypropylene waste cracking

The optimum condition selected from the results of Section 3.8.1 to Section 3.8.5 was applied to cracking of polypropylene waste which came from drinking water glasses.