

CHAPTER III

EXPERIMENTS

3.1 Equipment

Ovens and Furnaces

During the synthesis course of catalysts, the starting mixture was heated using 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 elevated temperature was achieved in a Carbolite RHF 1600 muffle furnace with programmable heating rate.

XRD

The structure of synthesized mesoporous materials were identified using a Rigaku D/MAX-22000 X-ray diffractometer (XRD) at Petroleum and Petrochemical College, Chulalongkorn University with nickel filtered Cu K α radiation (30 kV, 30mA) at an angle of 2θ range from 1.5 to 10°. The scan speed was 2°/min and the scan step was 0.02°. The three slits (scattering, divergent and receiving slits) are fixed at 0.5°, 0.5° and 0.15 mm, respectively.

XRF spectrometer

Silicon and aluminum contents in the catalysts were determined using SISON ARL 8410 X-ray fluorescence spectrometer at the Department of Scientific Service, Ministry of Science and Technology.

ICP-AES spectrometer

Aluminum contents in the catalysts were analyzed using the Perkin Elmer Plasma-1000 inductively coupled plasma-atomic emission spectrometer (ICP-AES) at

the Scientific and Technological Research Equipment Center of Chulalongkorn University.

NMR spectrometer

Solid state ^{27}Al -MAS-NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR spectrometer at the National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency.

Nitrogen Adsorptometer

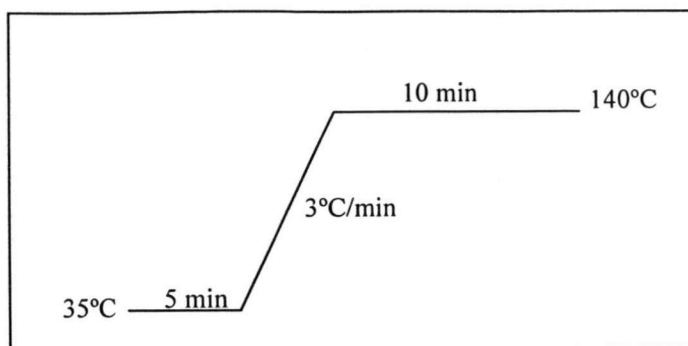
Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms, BET specific surface area, and pore size distribution of the catalysts was carried out using a BEL Japan BELSORP 28SA adsorptometer at Professor T. Tatsumi's Laboratory, Yokohama National University, Japan.

NH₃-TPD Machine

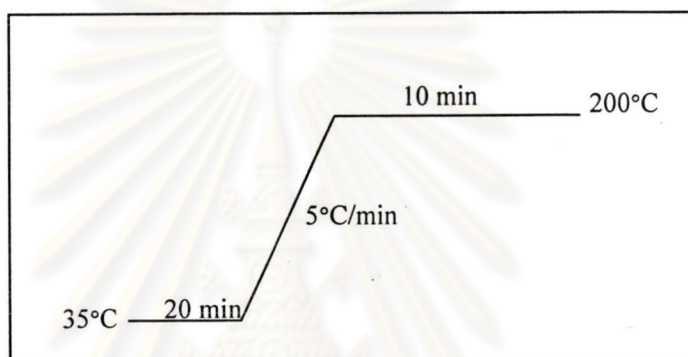
Acid strength of catalysts were determined using the BEL Japan REX-P2000 instrument equipped with the AVELVA M-QA100F quadrupole mass spectrometer at Yokohama National University, Japan.

Gas Chromatograph

Hydrocarbon gases were analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm inner diameter Alumina-PLOT column (J & W Scientific INC). Liquid samples were analyzed using a Shimadzu GC-14B gas chromatograph equipped with a 30-m long and 0.25-mm inner diameter DB-1 (0.25 μm film thickness) column (J & W Scientific INC). All GC detectors are flame ionization detectors (FID). The GC heating programs for 3- μl gas and 0.20- μl 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

To remove a trace amount of moisture nitrogen, highly pure grade purchased from Thai Industrial Gases (TIG) was passed through a 40 cm x 2.5 cm tube of the molecular sieve 4A. Sodium silicate solution was kindly provided by Thai Silicate Company. Tetraethyl orthosilicate (98% TEOS), cetyltrimethylammonium chloride (CTMACl) and bromide (CTAB) were commercially available from Fluka. Sodium aluminate was supplied from Riedel-de Haën. Aluminum isopropoxide was from TCI, Japan. Standard gas mixture and liquid mixture for GC analysis were kindly obtained from Thai Olefins. Other chemicals were from Merck or Fluka, otherwise specifically identified.

3.3 Investigation for Synthesis Methods of Al-MCM-41

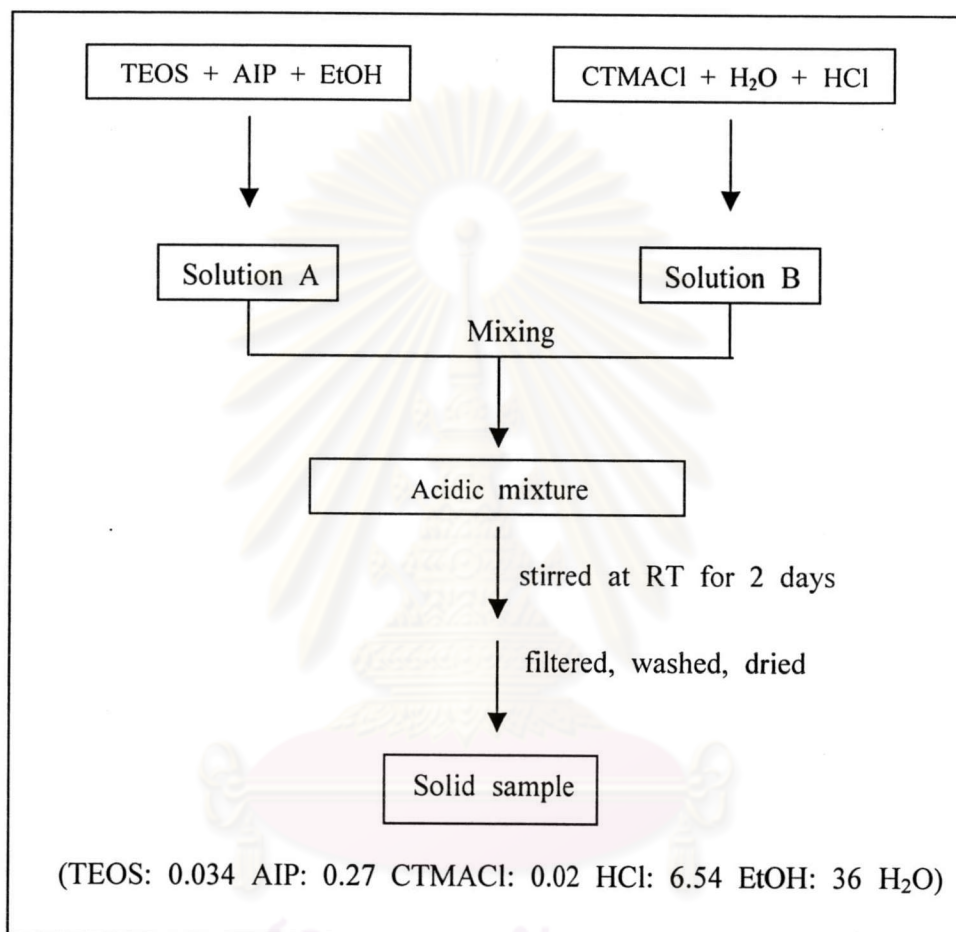
3.3.1 Synthesis of Al-MCM-41 under Acidic Condition

This synthesis method was attempted according to the method reported by Aguado *et al.*⁶²⁻⁶³. Solution A was prepared by dissolving 21.26 g tetraethyl orthosilicate (TEOS) and 0.69 g aluminum isopropoxide (AIP) in ethanol and Solution B was obtained by mixing 9.09 g cetyltrimethylammonium chloride (CTMACl) and 0.20 cm³ HCl in 64.74 g distilled water. After adding Solution A to Solution B the gel was formed at the molar ratio of TEOS : 0.034 AIP : 0.27 CTMACl : 0.02 HCl : 6.5 EtOH : 36 H₂O. The resulting gel was slowly stirred at room temperature for 2 days and the milky suspension was obtained. The solid sample was filtered off, washed and dried at room temperature. The schematic diagram of this whole procedure is shown in Scheme 3.3. Apparatus for preparation of the gel mixture is shown in Figure 3.1. The white solid product was obtained at a yield of 0.40 g. It was identified by XRD.

3.3.2 One-Temperature Synthesis of Al-MCM-41 under Basic Condition

Into a 500-cm³ 4-necked round bottom flask containing 97.74 g of a 14.7% solution of cetyltrimethylammonium bromide (CTAB) in water, an amount of 15.45 g water glass solution containing 9.68% Na₂O, 30.23% SiO₂, and 59.85% H₂O was added dropwise with stirring using a mechanical stirrer. The mixture was stirred vigorously at room temperature for 30 min to obtain a homogeneous milky suspension. To the suspension a solution of 0.36 g of sodium aluminate in 9.00 g distilled water was added dropwise. The mixture with the molar ratio of SiO₂ : 0.33 Na₂O : 0.028 Al₂O₃ : 0.51 CTAB : 73 H₂O, was then aged by stirring at room temperature for 5 h. The milky suspension became a viscous white slurry. The slurry was transformed to a Teflon bottle and capped tightly. The bottle was put in the oven at the temperature of 100°C for 8 days without pH adjustment. The schematic diagram of this whole procedure is shown in Scheme 3.4. The white solid product

was filtered off, washed, dried over the suction filtration apparatus. An as-synthesized product was obtained at a yield of 3.84 g. It was characterized by XRD.



Scheme 3.3 Diagram of the procedure in preparation of Al-MCM-41 under acidic condition.

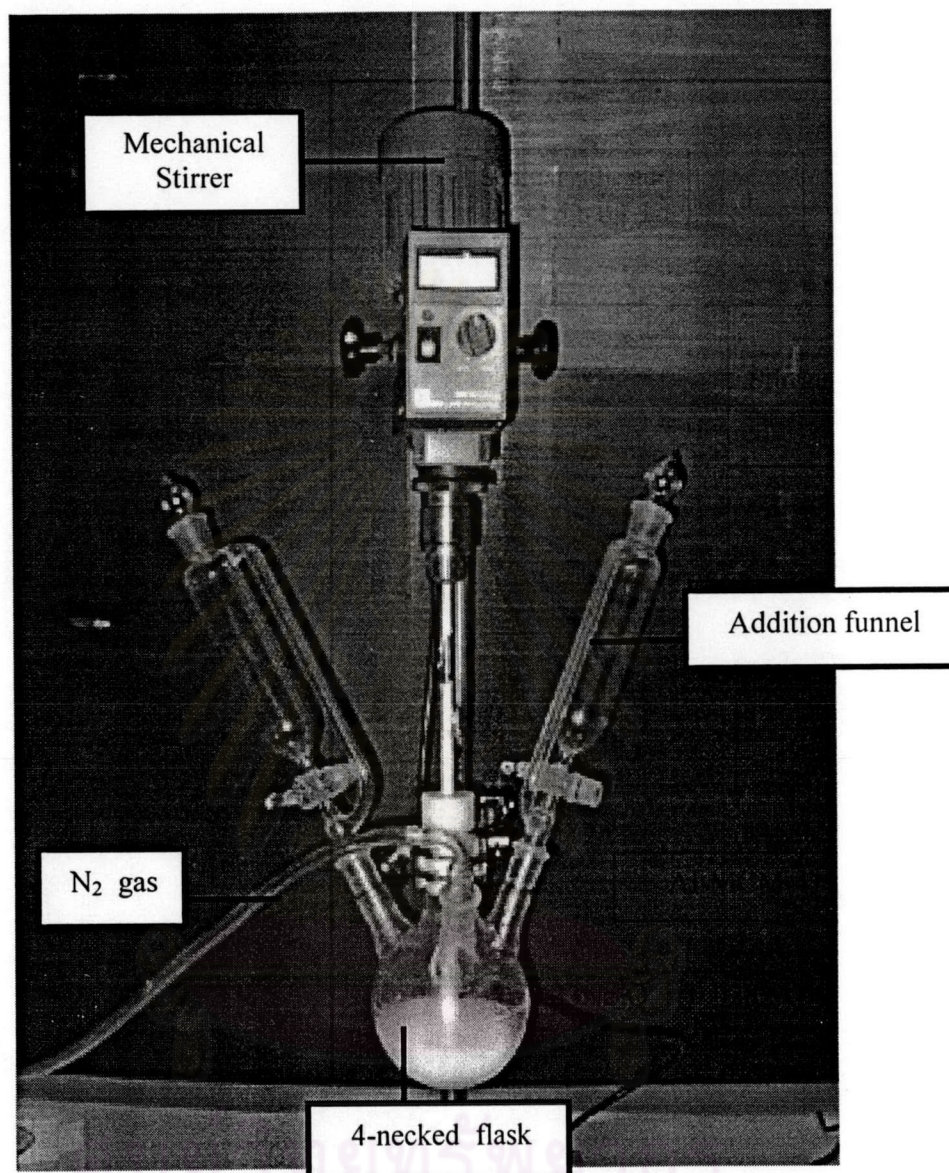
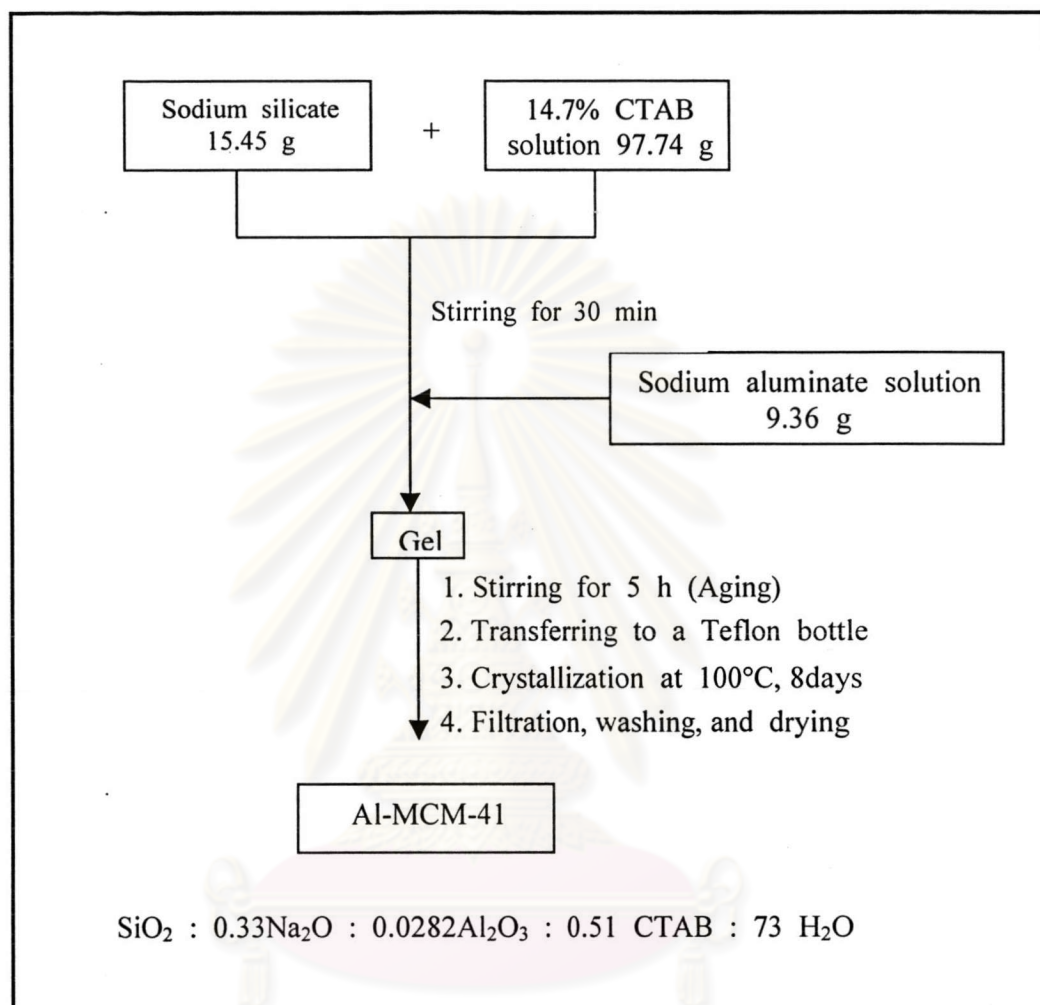


Figure 3.1 Apparatus for synthesis of Al-MCM-41.



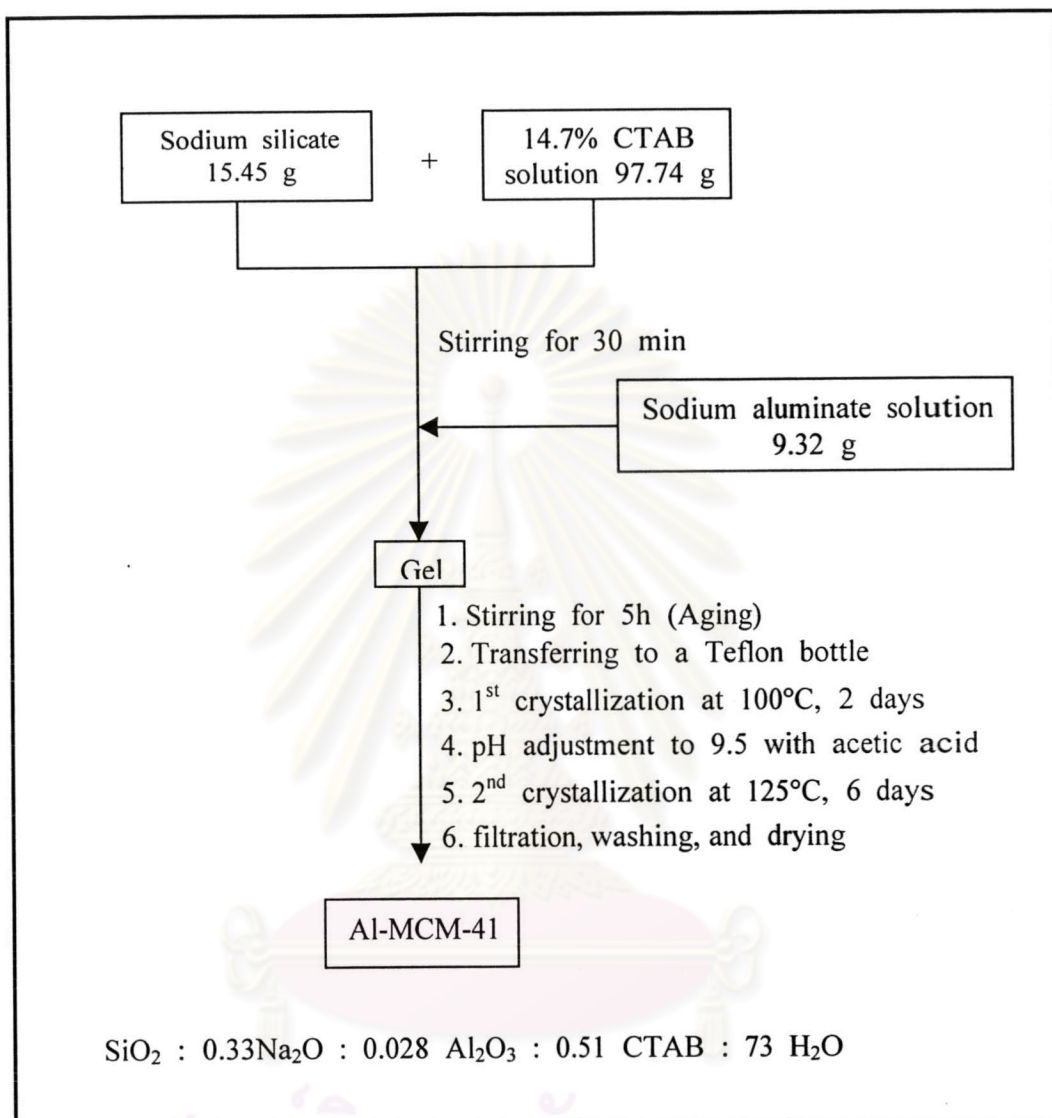
Scheme 3.4 Diagram of the procedure of one-temperature synthesis of Al-MCM-41 under basic condition.

3.3.3 Two-Temperature Synthesis of Al-MCM-41 under Basic Condition

Into a 500-cm³ 4-necked round bottom flask containing 97.74 g of a 14.7% solution of cetyltrimethylammonium bromide in water, an amount of 15.45 g water glass solution containing 9.68% Na₂O, 30.23% SiO₂, and 59.85% H₂O was added dropwise with stirring using a mechanical stirrer. The mixture was stirred vigorously at room temperature for 30 min to obtain a homogeneous milky suspension. To the suspension a solution of 0.36 g of sodium aluminate in 9.00 g distilled water was added dropwise. The mixture with the molar ratio of SiO₂ : 0.33 Na₂O : 0.028 Al₂O₃ : 0.51 CTAB : 73 H₂O, was then aged by stirring at room temperature for 5 h. The milky suspension became a viscous white slurry. The slurry was transformed to a Teflon bottle and capped tightly. The bottle was put in the oven at the temperature of 100°C for 2 days with pH adjustment to the value of 9.5 and subsequently at 125°C for 6 days. The schematic diagram of this whole procedure is shown in Scheme 3.5. The white solid sample was filtered off, washed, dried over the suction filtration apparatus. The as-synthesized product was obtained at a yield of 7.43 g. The white solid product was characterized using XRD, XRF and ICP-AES instruments.

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

The Al-MCM-41 samples with various Si/Al ratios in gel of 17, 20, 40, 60, and 80 were prepared under basic condition via the two-temperature synthesis using the similar method to that described in Section 3.3.3. Different amounts of aluminum required for each sample were used as shown in Table 3.1. The Al-MCM-41 samples were characterized using XRD, XRF, ICP-AES, solid-state ²⁷Al-NMR, NH₃-TPD, and nitrogen adsorption instruments.



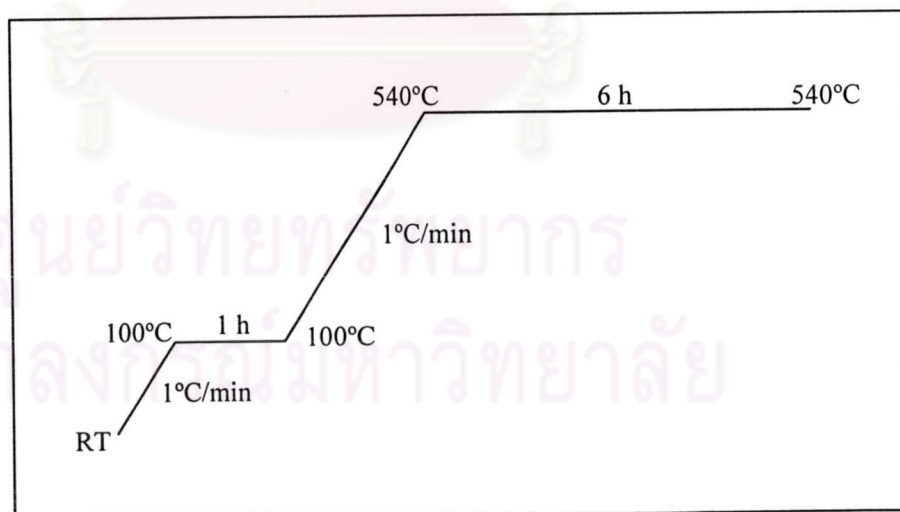
Scheme 3.5 Diagram of the procedure of two-temperature synthesis of Al-MCM-41 under basic condition.

Table 3.1 Required amounts of sodium aluminate in the preparation of Al-MCM-41 with various Si/Al ratios in gel of 17, 20, 40, 60 and 80

Si/Al molar ratio in gel	NaAlO ₂ dissolved in 9.00 g H ₂ O (g)
17	0.36
20	0.32
40	0.16
60	0.11
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 3.6. The calcined sample was kept in a desiccator prior to use.



Scheme 3.6 A heating program for removal of organic template from the pores of Al-MCM-41.

3.6 Sample Preparation for ICP-AES Analysis

In a 100-cm³ Teflon beaker 0.0400 g of a calcined catalyst was soaking with 10 cm³ of 6 M HCl and subsequently 10 cm³ of 48% hydrofluoric acid (Merck) 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 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 5 cm³ of 6 M HCl was added to the beaker and the solution was warmed up for 5 min to dissolve the remains. An amount of 10 cm³ deionized water was added to and warmed for 5 min to complete dissolution. The solution was transferred to a 50-cm³ polypropylene volumetric flask and made to the volume 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. The standard solution of 1000-ppm aluminum in HNO₃ (from BDH) was diluted to 1, 5, 10 and 20 ppm to establish a calibration curve.

3.7 Catalytic Test for Degradation of Polypropylene over Al-MCM-41

3.7.1 Effect of Temperature on the Activity of Al-MCM-41

Degradation of polypropylene was carried out in a cylindrical borosilicate reactor with a side arm and a thermowell for thermocouple insertion. The reactor is 30 mm wide and 220 mm high. Apparatus for degradation of polypropylene is shown in Figure 3.2. A In a typical experiment, 1.0 g (W₁) of propylene cut into small pieces was mixed thoroughly with 0.40 g (W₂) of a catalyst in the reactor. To remove air from the whole catalytic system, nitrogen gas was passed through the system for 10 min. Under nitrogen flow at 10 cm³/min from the top of reactor, the well mixed polypropylene and the catalyst was heated from room temperature to a required temperature (350, 450, or 550°C) in 15 min using a split-tube furnace equipped with a programmable temperature controller and a K-type thermocouple. The reaction

temperature was kept constant for 30 min. The gaseous products leaving the reactor with the nitrogen stream were passed through a condenser cooled by a cold water at 5°C. The gaseous products were collected into a Tedlar bag since the start of heating while the liquid products were condensed backed to reactor. After completion of the reaction, the reactor was cooled down to room temperature and weighed. The weight loss (W_3) corresponds to the weight of gaseous products formed. To separate the liquid products from the system, the reactor was connected to a vacuum pump with a cold trap in between. The reactor was weighed again and the weight loss (W_4) after evacuation is in charge for the volatile liquid products. The remaining liquid products were extracted from the catalyst using diethyl ether as solvent. The difference in weight of the reactor (W_5) before and after extraction is the non-volatile liquid products. Thus, the total liquid products were determined by addition of W_4 and W_5 . Compositions in gaseous and volatile liquid products were analyzed using GC. The %coke formed was determined by the weight loss (W_6) upon calcination of the used catalyst after extraction of all products. The heating program for calcination of the used catalyst is shown in Scheme 3.6.

$$\text{Yield of gaseous products (\%)} = (W_3/W_1) \times 100$$

$$\text{Yield of liquid products (\%)} = (W_4 + W_5)/W_1 \times 100$$

$$\text{Coke (\% wt of catalyst)} = (W_6/W_2) \times 100$$

$$\text{Conversion of propylene (\%)} = (W_3 + W_4 + W_5 + W_6)/W_1 \times 100$$

3.7.2 Effect of Si/Al Ratio on the Activity of Al-MCM-41

The degradation of polypropylene was carried out using Al-MCM-41 catalysts with various Si/Al ratios (20, 40, 60, and 80) as catalysts. The reaction was performed in the similar way to what described in Section 3.7.1 except that the experiments were set up at the only reaction temperature of 550°C.

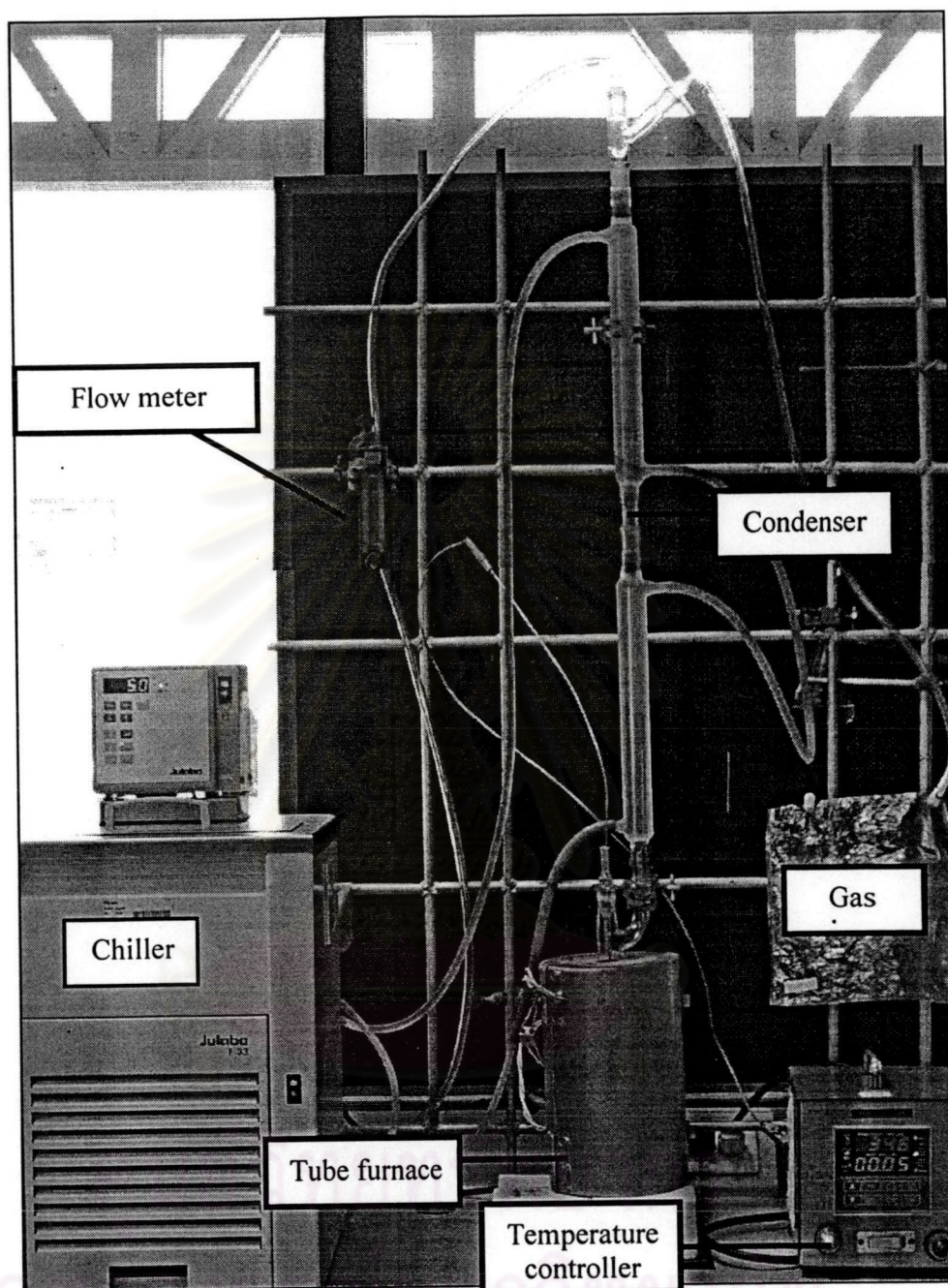


Figure 3.2 Apparatus for degradation of polypropylene.

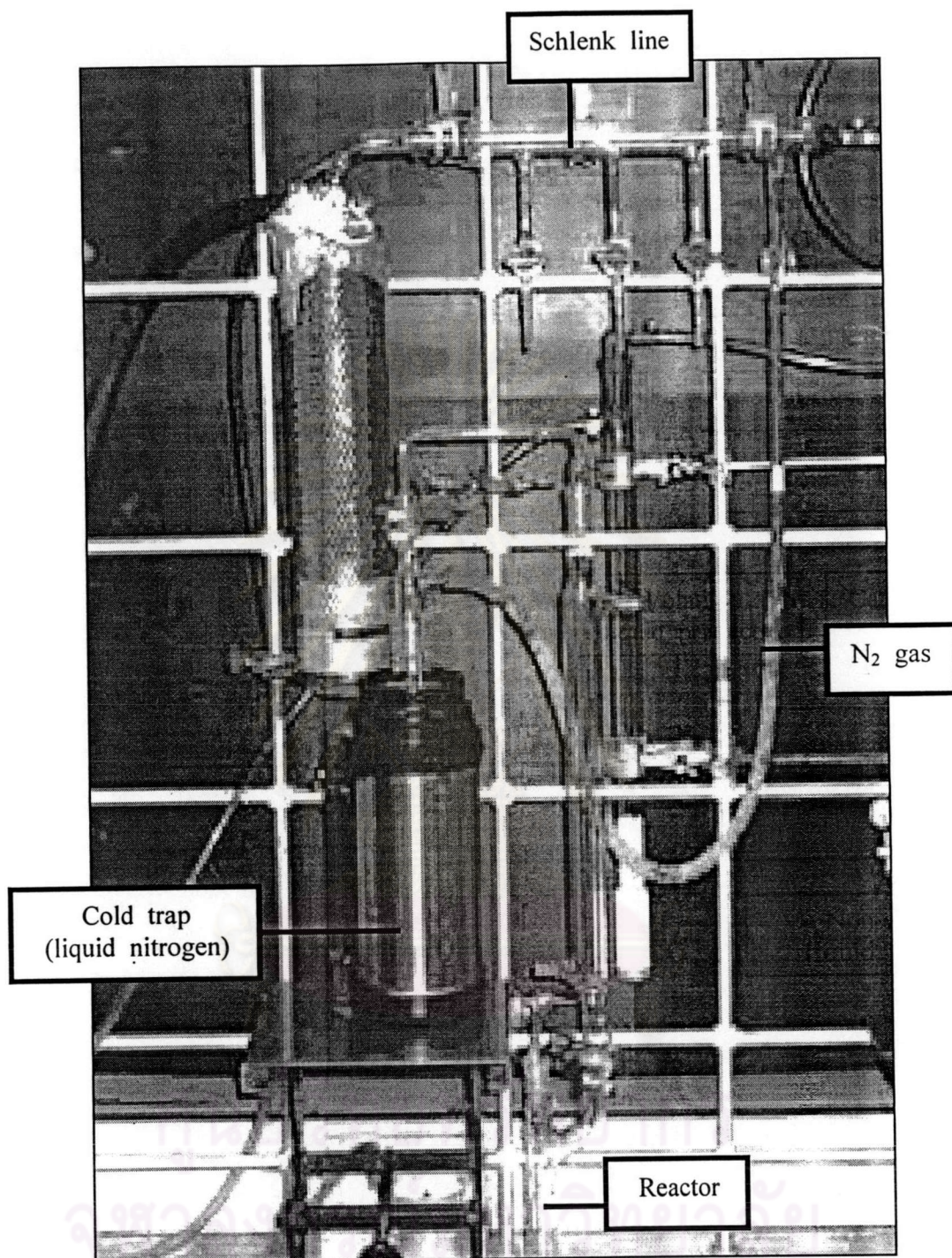
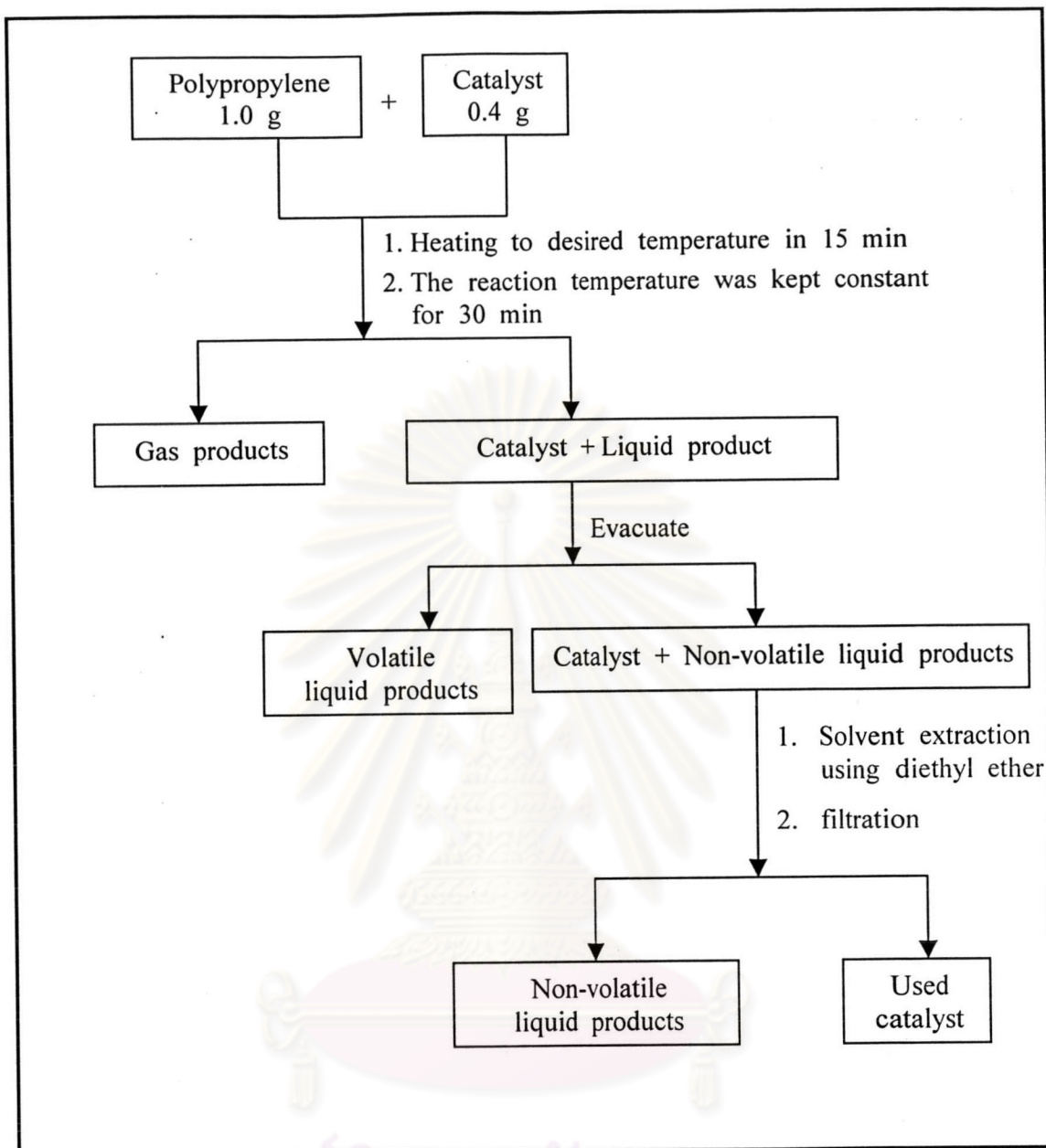


Figure 3.3 Evacuated line.



Scheme 3.7 Catalytic degradation of polypropylene using Al-MCM-41 as catalyst.

3.8 Catalyst Regeneration

The spent catalysts of single use (Si/Al = 20 and 80) were subjected to regenerated and reused. They were regenerated by calcination in air at 540°C for 6 h. The regenerated catalysts were characterized by XRD.



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