

CHAPTER III EXPERIMENTAL



3.1 Materials

Aniline monomer (Merck) was used as a monomer. Ammonium peroxydisulphate (Merck) was used as an oxidant without further purification. Ammonia solution (25%, ACS reagent grade) used as a basic reagent. Analytical grade methanol (Labscan) was used to wash emeraldine base in the polyaniline synthesis process. Analytical grade hydrochloric acid (37% HCl, Aldrich), maleic acid (98% MA, Fluka) and camphor-10-sulfonic acid (99% CSA, Fluka) were used as protonic acid in the doping process.

Aqueous solution of HTAB (25 wt%, Aldrich), a concentrated ammonia solution (25%, ACS reagent grade), sodium chloride (99%, CALRO ERBA) and sodium silicate solution with the Na/Si ratio of 0.5 (2.4 wt % Na₂O, 9.2 wt % SiO₂, and 88.4 wt % H₂O) were used to synthesize the mesoporous molecular sieve MCM 41. CuCl₂·2H₂O (99%, Merck) was used as the ion exchange solution.

Nitrogen gas (N₂ 99% purity, TIG) was used as the carrier gas. Carbon monoxide (CO, TIG) stock was a mixture with nitrogen at 1000 ppm.

3.2 Methodology

3.2.1 Preparation of Polyaniline

3.2.1.1 *Polyaniline Synthesis*

The polyaniline used in this experiment was synthesized by the oxidative polymerization process of MacDiarmid and co-workers (MacDiarmid, 1986). The aniline monomer was purified under vacuum at 58 °C prior to used. 14.67 grams of (NH₄)₂S₂O₈ in 98.44 ml 1 M HCl was dropwise added to 7.67 grams of aniline monomer in 1 M HCl 89.06 ml ml of in 3-neck round bottom reaction flask. After vigorously stirring at 5-0 °C for 3 hours, the green emeraldine hydrochloride precipitate was collected and washed repeatedly with 80:20 water:methanol solutions

until the wash solution were colorless. This powder was subsequently converted into the emeraldine base form by immersing it in 0.1 M NH_4OH 312.5 ml for 3 hours and further washed with 80:20 water:methanol solutions until wash solutions were neutral. Polyaniline powder was finally obtained after filtrate was dried in a vacuum oven at 50 °C for 48 hours.

3.2.1.2 Doping Process

In order to obtain hydrochloric acid doped polyaniline, 0.1 M aqueous solution of HCl was prepared by adding 20.87 ml of 37% hydrochloric acid into 79.13 ml of distilled deionized water in a 250 ml volumetric flask. 1.448 grams of emeraldine base powder was immersed in 1 M HCl with particular volumes 4 ml and 40 ml (Chuapradit *et al*, 2002). The mixtures were then stirred at room temperature for a week to ensure that the reaction reached equilibrium. After filtered and dried at 60 °C in vacuum oven for 2 days to eliminate moisture (Li and Wan, 1999), PANI doped with HCl with ratio 1 and 10 were finally obtained.

Maleic acid doped PANI was prepared similarly to HCl doped PANI. 29.02 grams of maleic acid was used to prepare 1 M stock solution of MA by adding it with distilled deionized water in a 250 ml volumetric flask. Thereafter, 1.448 grams of emeraldine base powder was immersed in 1 M MA with particular volumes of 4 ml and 40 ml. The mixtures were then stirred at room temperature for a period of oneweek. After drying mixture at 60 °C in oven for 2 days, PANI doped with MA with ratio 1 and 10 were finally obtained.

Camphore sulphuric acid doped PANI was prepared by immersing emeraldine base powder 1.448 grams into 1 M CSA aqueous solution. The 1M aqueous solution of CSA was prepared by adding 58.66 of CSA with distilled deionized water in a 250 ml volumetric flask. Then, 1.448 grams of emeraldine base powder was immersed in 1 M CSA with particular volumes of 4 ml and 40 ml. Finally powder was filtered and dried to get 1 and 10 CSA dope PANI at 60 °C in oven for 2 days.

Dried sample were stored in desiccators at room temperature for later use.

3.2.2 Preparation of Zeolite

3.2.2.1 *Synthesis of Mesoporous Molecular Sieve MCM-41*

The procedure to synthesize mesoporous molecular sieve MCM-41 was by Kim, J.M. and co workers (Ryoo *et al.*, 1997). Sodium silicate solution, a concentrated ammonium, and 25% HTAB were added into a polypropylene bottle with a molar composition 4SiO_2 : 1HTAB : $1\text{Na}_2\text{O}$: $0.15(\text{NH}_4)_2\text{O}$: $200\text{H}_2\text{O}$ at room temperature. After that, HTAB-silicate gel was stirred for 1 hour, the PP bottle was heated to 370 K in an oven for 1 day. The cap was loosened repeatedly to reduce the ammonia pressure while temperature was increasing. pH of the mixture was reduced to 10.2 by dropwise adding 30% acetic acid to the mixture at room temperature under a vigorous stirring. The PP bottle was heated again to 370 K for 1 day and then cooled to room temperature. 3 mol of NaCl was added into the bottle in order to increase hydrothermal stability of the framework, subsequently we added a sodium aluminate solution (Si/Al ratio 30) to the reaction mixture. The reaction mixture was stirred 30 min more after finishing the addition and heated again to 370 K for 1 day. The pH was adjusted to 10.2, by adding 30% acetic acid and heating for 1 day at 370 K in oven. The precipitate was filtered and washed with distilled water and dried in an oven at 370 K 12 hours. Sample powder was calcined under O_2 flow while temperature was increasing to 813 K over 10 hours and then maintained at that temperature for 10 hours.

3.2.2.2 *Ion Exchange in Zeolite*

Each of zeolite powder, y, 13X and MCM-41, were immersed in CuCl_2 aqueous solution to obtain Cu^{2+} in framework. 1M stock solution of CuCl_2 was prepared by adding 17.2202 grams $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with distilled deionized water 100 ml volumetric flask. CuCl_2 stock solution was pipetted for 1.039 ml and diluted with distilled water in a 500ml volume metric flask to prepare $2.1 \times 10^{-4}\text{M}$ CuCl_2 . Zeolite powder was immersed in $2.1 \times 10^{-4}\text{M}$ CuCl_2 with the ratio of zeolite for 1 gram to the solution of 200 ml at room temperature for 12 hours. Then the precipitate sample was filtered and washed doubly with hot water. Cu^{2+}

contained in zeolite was collected after precipitate was dried at 80°C in a drying oven for 3 hours.

Zeolite Y and 13X were calcined at 200 °C under nitrogen flow for 2 hours to eliminate the volatile organics from their structures. The calcined sample was further grounded and sieved with a mesh (53µm) before further use.

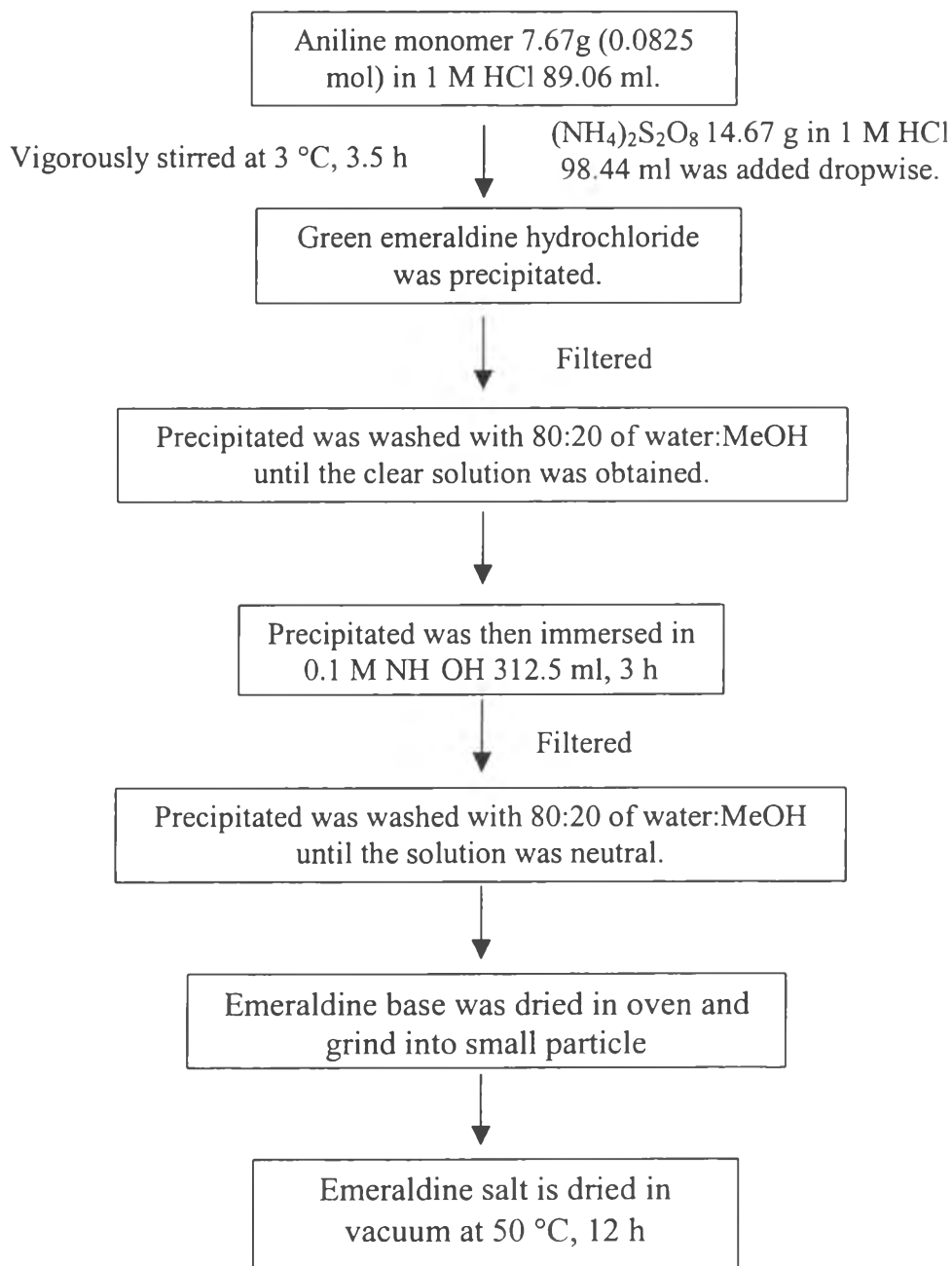


Figure 3.1 Synthesis path of polyaniline.

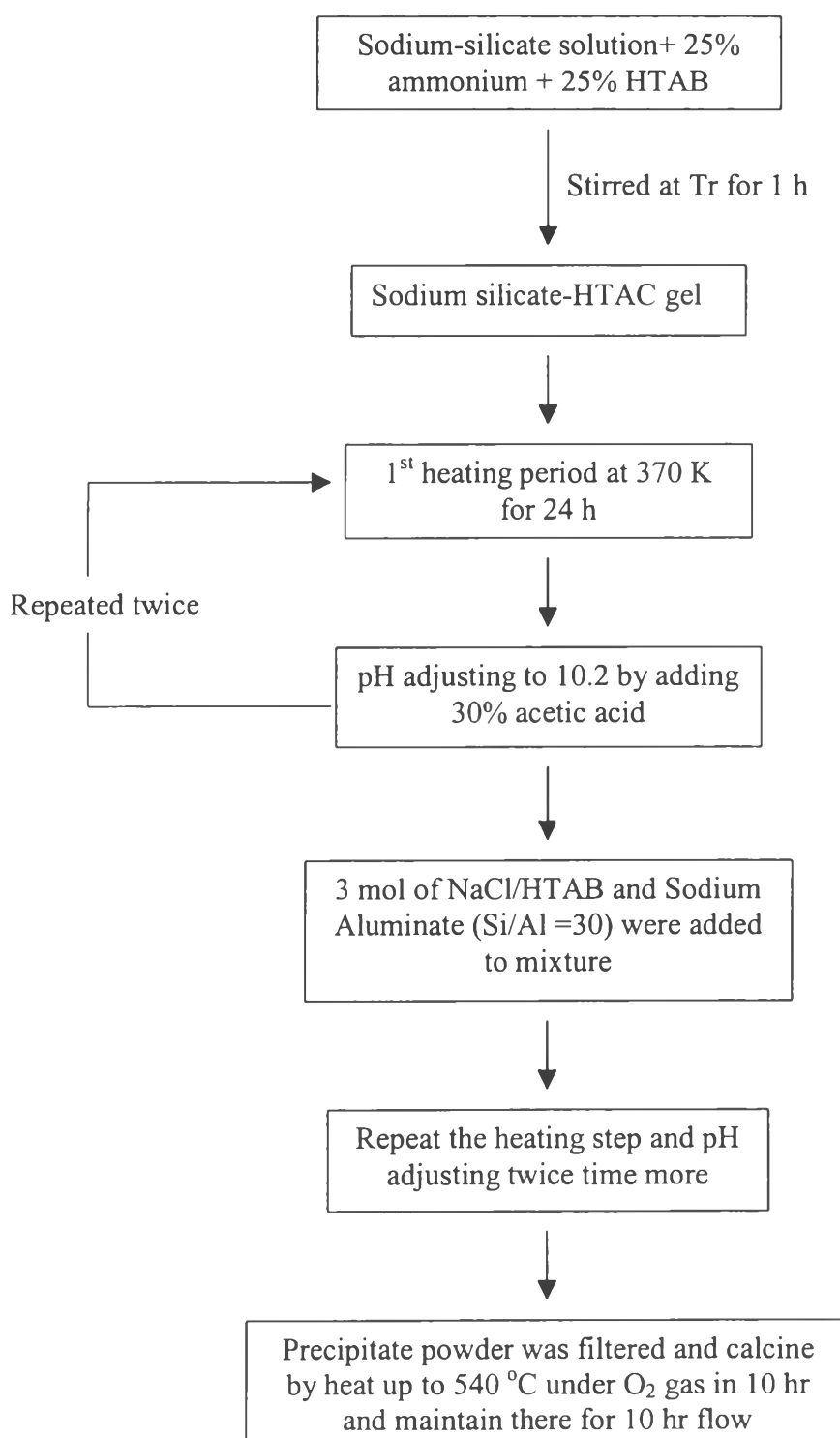


Figure 3.2 The preparation of AlMCM41.

3.2.3 Composite Preparation

Three types of zeolite powder was dried at 120 °C for 24 hours and sieved with a mesh particle size of 53 µm prior to their uses. Polyaniline/zeolite composites were prepared by dry mixing of the zeolites to polyaniline at weight ratios equal to 5, 10, 20, 30 and 40 respectively. The composites were compressed into a disc form by using a hydraulic press and further their conductivity values were measured by using the four point probe technique.

3.2.4 Characterization

3.2.4.1 *Fourier-Transform Infrared Spectrometer (FT-IR)*

Each PANI sample was identified for functional groups by FT-IR spectrometer (Bruker, FRA 106/S) in the absorption mode with 32 scans at a resolution of 4 cm⁻¹. Samples were grounded with a mortar, mixed with KBr and molded into pellets under the pressure of 8 tons. The observed spectra were in the range of 400-4000 nm.

3.2.4.2 *Thermogravimetric Analyzer (TGA)*

The moisture content and degradation process of undoped polyaniline, doped polyaniline, zeolite and polyaniline/zeolite composite were determined by a thermalgravimetric analyzer (Dupont, TGA 2950). Sample powder was weighted at 10-15 mg and put in a titanium pan. The instrument was operated from 30 to 800°C with a heating rate of 10°C/min.

3.2.4.3 *Elemental Analyzer (EA)*

The doping level of doped polyaniline was calculated from the amounts of carbon (C), Hydrogen (H) and nitrogen (N) atoms. The elemental analyzer, Perkin-Elmer, 2400 Series II CHS/O Analyzer, was used in this case.

The samples were weighed at 1.5-2.5 mg and sealed in the tin capsules and put in the sample cell. The sample was dropped in the combustion zone at a temperature between 975-1100 °C with helium as the carrier gas. The amounts

of carbon (C), hydrogen (H) and nitrogen (N) were determined. The doping level of CSA and HNO₃ doped polyaniline was determined.

3.2.4.4 X-ray Diffractometer (XRD)

The crystallinity of polyaniline and the crystal order of zeolite were determined by an X-ray diffractometer (Phillips PW 1830/00 No. DY1241 Diffractometer, model Rigaku). A pellet form of polyaniline sample was placed on aluminium specimen. X-ray diffraction patterns were started from $2\theta = 5$ to 60 degrees.

The crystal structure of the zeolites was also determined by grinding sample with a mortar and placing it on a glass specimen. X-ray pattern of MCM-41 was observed at 2θ equal to 1.5 to 10 degrees. Zeolite Y and 13X patterns were measured and recorded between 2θ equal to 3 to 90 degrees.

3.2.4.5 Scanning Electron Microscope (SEM)

Scanning electron micrographs were taken with a JEOL, model JSM-5200 scanning electron microscope to determine the morphology and surface appearance of PANI in powder and pellet forms, and to identify morphology of zeolite powder. A piece of sample was placed on the holder with an adhesive tape and coated with a layer of gold by using a JFC-1100E ion-sputtering device before measurements taken. The scanning electron micrographs of polyaniline were obtained by using an acceleration voltage of 25 kV with a magnification of 1000-3500 times.

3.2.4.5 X-ray Fluorescence (XRF)

X-ray fluorescence (BUKER;SRS 3400) was used to determine amounts of inorganics in each zeolite sample. The amounts of oxide of metal, silica oxide, alumina oxide, sodium oxide and copper (II) oxide in zeolite Y, 13X and MCM-41 were determined. The amount of cation (Cu²⁺) inside framework can be calculated from these amounts.

Zeolite powder and boric acid were weighted at 0.5 grams and 4.5 grams respectively, grounded and mixed together with mechanical mixing for 2-3 min. Powder mixture was then placed in a sample holder and pressed by a hydraulic press (150 lb/2 min) to make samples into a pellet form.

3.2.4.6 Particle Size Analyzer

The particle sizes of polyaniline and zeolite samples were determined by using a particle size analyzer, (Malvern Instruments Ltd. Masterizer X Version 2.15). The lenses used in this experiment were 45 and 300 mm. The sample was placed in a sample cell across a laser beam. This instrument measured the average particle size and the standard size distribution. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

3.2.4.7 BET

BET (Autosorb-1) was used to measure the pore size and surface area of each zeolite. Zeolite powder was weighted 3040 mg and outgassed at 300 °C before each measurement.

3.2.5 Conductivity Measurement: Four-Point Probe Meter

Electrical conductivity is the inversion of specific resistivity (ρ) which indicates the ability of material to transport electrical charge. The meter consists of four probes, making contact on a surface of film sample. Two inner probes were connected to a voltmeter for recording a change in voltage, while the outer two probes were connected to a constant current source. The voltage change was converted to the electrical conductivity of polymer using equation (3.1) as follow:

$$\sigma = \frac{1}{\rho} = \frac{l}{R_s \times t} = \frac{I}{K \times V \times t} \quad (3.1)$$

where σ = specific conductivity (S/cm)
 ρ = specific resistivity (Ω .cm)

- R_s = sheet resistivity (Ω)
- I = applied current (A)
- K = geometric correction factor
- V = voltage drop (V)
- t = pellet thickness (cm)

The geometrical correction factor was taken into account of geometric effects, depending on the configuration and probe tip spacing and was determined by using standard materials where specific resistivity values were known. In our case, the sheet resistivity was measured by using the four-point probe and then the geometric correction factor was computed by equation (3.2) as follows:

$$K = \frac{\rho_{ref}}{R_s \times t} \quad (3.2)$$

where ρ_{ref} = known resistivity calibrated from the 4-point probe device ($\Omega \cdot \text{cm}$)
 t = film thickness (cm)

Measurements of conductivity responses of doped polyaniline and polyaniline/polyimide blend were recorded by using a specially constructed gas cell. It consisted of two chambers connected in series. The chambers were made from stainless steel No.304. The second chamber contained two four point probe meters for conductivity measurement. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chambers.

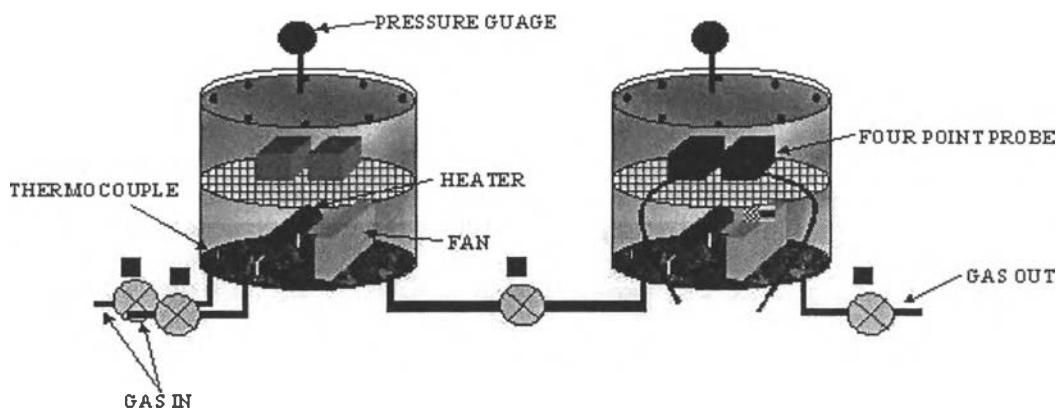


Figure 3.3 Conductivity detectors with gas chamber.

Step 1 A current was applied to polyaniline pellets in order to measure conductivity before exposing to gas.

Step 2 Both chambers were closed and evacuated by using a vacuum pump in order to remove gases (valve No. 1 and 2 were closed, valve No. 3 and 4 were opened).

Step 3 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 4 N_2 gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 5 Valve No. 3 was opened; the conductivity response of N_2 gas was recorded.

Step 6 Step 2-6 were repeated until the conductivity response of N_2 was constant (this refers to preexposed $\sigma_{N_2,preex.}$).

Step 7 Both chambers were closed and evacuated by using a vacuum pump in order to remove gases.

Step 8 Carbon monoxide gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 9 Valve No. 3 was opened; the conductivity response of CO gas at 1000 ppm was recorded until it reached an equilibrium value.

Step 10 Valve No. 3 was closed; second chamber was evacuated by using a vacuum pump. Then N₂ gas was fed to first chamber until the pressure reached 2 atm.

Step 11 Valve No. 3 was opened; the conductivity response of CO gas at 500 ppm was recorded until it reached an equilibrium value.

Step 12 Step 10 and 11 were repeated so that the conductivity responses of CO at 250, 125, 62.5, 31.25, 15.62, 7.81 and 3.90 ppm were recorded.

Step 13 Both chambers were closed and evacuated by using a vacuum pump in order to remove gas.

Step 14 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed.

Step 15 N₂ gas was fed into the first chamber until the pressure reached 2 atm as observed from the pressure gauge.

Step 16 Valve No. 3 was opened then the conductivity response of N₂ gas was recorded as the final $\sigma_{N_2,final}$.

The differences in the change of electrical conductivity ($\Delta\sigma$) at various doping ratios were calculated by Equation (3.3) following;

$$\Delta\sigma = \sigma_{CO} - \sigma_{N_2,final} \quad (3.3)$$

where $\Delta\sigma$ = the difference in specific conductivity (S/cm)

$\sigma_{N_2,final}$ = the specific conductivity of N₂ at final (S/cm)

σ_{CO} = the specific conductivity of CO (S/cm)