

CHAPTER III

EXPERIMENTAL

3.1 Materials

Benzene (AR grade, supported from Thai aromatic Co., LTD) was freshly distilled before being used as a monomer. Aluminium chloride, AlCl_3 (AR grade, Riedel-de-Haen) and Cupric chloride, CuCl_2 (AR grade, Riedel-de Haen) were used as an oxidant and a catalyst for synthesis of PPP. Hydrochloric acid, HCl (AR grade, J.T.Baker) was used as a washing solution of synthesized PPP. Ferric chloride, FeCl_3 (AR grade, Fisher Scientific) and ethanol (99.5%, CARLO ERBA) were used for doping PPP.

ZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3$: 23) purchased from Zeolyst International was used as a minor component of the composites. Sodium chloride, NaCl , (AR grade, Ajex) and Potassium chloride, KCl , (AR grade, Ajex) were used in the cation exchange processes.

Nitrogen gas (99%, TIG), Ammonia gas (99.99%, Poontaweporn Limited Partnership) were used to investigate the electrical conductivity responses of the composites.

3.2 Equipments

A FT-IR Spectrometer, (Nicolet, Nexus 670), with 32 scans and $\pm 4 \text{ cm}^{-1}$ resolution, was used to identify functional groups of synthesized and doped PPP. A Thermal Gravimetric Analyzer (duPont, TGA 2950) was used to study thermal property of PPP under air atmosphere with heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ and temperature scan from $30\text{-}800 \text{ }^\circ\text{C}$. An X-ray Diffraction Microscope, (Phillips, Rigaku) was utilized to observe the crystallinity of materials. The morphology of materials was observed by using a Scanning Electron Microscope, (JEOL, JSM 5200) and their particle size diameter were determined by using a Particle Size Analyzer, (Malvern, Mastersizer X Version 2.15). A Surface Area Analyzer (Quantachrome, Autosorb-1) was used to examine the surface area and total pore volume of zeolite. The true Si/Al

ratio and cation exchange level of zeolite were determined by employing an Atomic Absorption Spectrometer (Varian, SpectrAA 300). The electrical conductivity of PPP and its composites was measured by using a custom-built two-point probe meter, (Keithley, Model 6517A).

3.3 Methodology

3.3.1 Preparation of Poly(*p*-phenylene)

3.3.1.1 *Poly(*p*-phenylene) Synthesis*

The Poly(*p*-phenylene) (PPP) used in this experiment was synthesized by the aromatic monomer-Lewis acid catalyst-oxidant process which was adapted from Peter Kovacic and Alexander Kyriakis (Kovacic *et al.*, 1963) by Peter Kovacic and James Oziomek (Kovacic *et al.*, 1964). The reaction was carried out under nitrogen in a 3-necked flask equipped with a paddle stirrer. A mixture of dry, benzene (2 moles), anhydrous aluminum chloride (0.5 mole) and anhydrous cupric chloride (0.25 mole) was introduced under controlled temperature of 32-37 °C. The reaction was allowed to proceed with efficient stirring for 3 h. from the time of initiation. The mixture was subsequently cooled to 15 °C and was either (1) added to 1.4 L. of ice-cold 18% hydrochloric acid, or (2) filtered, followed by addition of the residue to acid solution. The mixture of crude polymer and aqueous acid was heated at the boil, filtered, and the residue washed with water. After the solid was purified briefly in a blender with water, it was triturated with boiling 18% hydrochloric acid until the filtrate was colorless. Washing with boiling distilled water was continued until the test (silver nitrate; AgNO₃) for chloride ion was negative. After being dried at 110 °C for 3 hr. the product was in the form of a finely divided, light brown solid. Care was taken to avoid contamination.

3.3.1.2 *Poly(*p*-phenylene) Doping*

The doping of PPP with FeCl₃ was carried out by suspending the PPP particles in 100 ml of FeCl₃-ethanol solutions at 60 °C for 10 hr. After filtration of the mixture, the doped PPP was dried under vacuum at ambient

temperature for 12 hr. Finally, the dark brown PPP powders whose color depends on the degree of doping were obtained (Shiga *et al.*, 1993).

3.3.2 Preparation of the Zeolite Materials

The starting ZSM-5 material of an ammonium form (NH₄ZSM-5) with SiO₂/Al₂O₃ ratios of 23 was purchased from Zeolyst International. The cation exchange process was carried out by the conventional method (Kuroda *et al.*, 1999). A mixture of 1 g zeolite per 100 ml of 0.3 M NaCl solution was stirred at 90 °C for 1 h and then filtered, washed with distillation water for several times. After the cation-exchanged zeolite was dried, the zeolite was calcined at 550 °C for 3 h with heating rate of 1 °C/min.

3.3.3 Composite Preparation

Dried PPP powder was sieved with 53 µm sieve prior to being mechanically mixed with cation-exchanged zeolite at %volume of zeolite equal to 10, 20, 30, and 40, respectively. The dry mixed composites was subsequently compressed into a disc form by using a hydraulic press and further their conductivity values were measured by using the two point probe meter.

3.3.4 Characterization

3.3.4.1 *Fourier-Transform Infrared Spectroscopy (FT-IR)*

Each PPP sample was identified the functional groups by using the FT-IR spectrometer in the absorption mode with 32 scans at a resolution of 4 cm⁻¹ in a wavenumber range of 4000-400 cm⁻¹. Samples was grounded prior to being mixed with KBr background and then molded into pellets under the pressure of 7 tons.

3.3.4.2 *Thermogravimetric Analysis (TGA)*

The thermal stability of undoped PPP, doped PPP and poly(*p*-phenylene)/zeolite composite under air atmosphere were investigated by the thermalgravimetric analyzer. Sample powder was put in a platinum pan and simultaneously weighted at 5-15 mg. The instrument was operated from 30 to 800°C with a heating rate of 10°C/min.

3.3.4.3 X-ray Diffractroscopy (XRD)

The X-Ray Difflactrometer was used to examine the crystallinity of PPP and the crystal order of zeolite. Each sample powder was placed into the glass specimen holder. X-ray diffraction patterns were recorded from 2 θ equal to 5-60 degrees for PPP and 3-90 degrees for zeolite.

3.3.4.4 Scanning Electron Microscopy (SEM)

In order to observe the morphology of materials such PPP, zeolite powder and composites, the scanning electron microscope was used. A sample was placed on the stub holder with an adhesive tape and then coated with gold by using a JFC-1100E ion-sputtering device before measurements were taken.

3.3.4.5 Particle size analysis (PSA)

The particle sizes of PPP and zeolite powder were measured by using the particle size analyzer with 45 mm lens. The sample was put into the analyzing water chamber and the water flowed brought the sample across a laser beam at the flow cell. The mean particle size and standard size distribution were reported.

3.3.4.6 Surface Area Analysis (SAA)

The surface area and total pore volume of porous materials such zeolite were investigated by using the surface area analyzer. Dried zeolite was approximately weighed 0.1 g and out gassed at 250 °C overnight before measurement.

3.3.4.7 Atomic Absorption Analysis (AAS)

The atomic absorption analyzer was used to determine the exact amount of silicon-aluminium containing in zeolite and the content of exchangeable cation in the term of cation exchange level. The standard, the blank and sample solutions were prepared for testing each cation; different lamps were used for different cations.

3.3.4.8 Ammonia Temperature Programmed Desorption (NH₃-TPD)

An ammonia temperature programmed desorption was performed in order to study the adsorption property of dPPP and zeolite with various cation types. All of samples were weighted about 0.05 g, pretreated under He gas, and then exposed to 1% NH₃/He under room temperature. After purging with He, the NH₃ desorption was done by heating from 30 °C to 600 °C at ramp rate of 10 °C.

3.3.4.8 Conductivity Measurement: Two-Point Probe Meter

The electrical conductivity (σ) is the inversion of the specific resistivity (ρ) which indicates the ability of material to conduct the electrical charge. In order to measure the electrical conductivity of materials, the two-point probe meter was used. The meter was composed of two probes which made contact with a surface of a sample film. These two probes were connected to a voltage supplier (Keithley, 6517A) which its constant voltage could be changed and the current was reported. The applied voltages were plotted against the measured currents in order to determine the linear Ohmic regime of each sample. Then the applied voltages and measured currents were converted to the electrical conductivity of the sample by using equation (3.1)

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

where σ is specific conductivity (S/cm), ρ is specific resistivity ($\Omega \cdot \text{cm}$), R_s is sheet resistance (Ω/sq), t is thickness of sample pellet (cm), V is applied voltage (voltage drop) (V), I is measured current (A), and K is geometric correction factor of the two-point probe meter.

Sheet resistance was measured by using the two-point probe. The geometric correction factor was required to convert the applied voltage/measured current ratio measured by the two-point probe into sheet resistance. The geometric correction factor was taken into account of geometric effects for the sample size, shape and probe spacing. This factor was determined by using standard materials whose specific sheet resistance values were known. In our experiment, silicon wafer was used as a standard material. Therefore, the relationship between geometric correction factor and the sheet resistance is given by the equation (3.2)

$$R_s = \frac{I}{V} \times K \quad (3.2)$$

Since the geometric correction factor is known, the electrical conductivity of sample was measured by applying constant voltage and measuring

the current in the linear Ohmic regime. Then, the sheet resistance was obtained and converted into the specific conductivity of sample by using the equation (3.3)

$$R_{ss} = \frac{I}{V} \times K = \frac{\rho_s}{t_s} = \frac{1}{\sigma_s \times t_s} \quad (3.3)$$

where σ_s is specific conductivity of sample (S/cm), ρ_s is specific resistivity ($\Omega \cdot \text{cm}$), R_{ss} is sheet resistance of sample (Ω/sq), t_s is thickness of sample pellet (cm), V is applied voltage (voltage drop) (V), I is measured current (A), and K is geometric correction factor of the two-point probe meter.

3.3.5 Gas measurement

Measurements of conductivity responses of dPPP and dPPP/zeolite composites 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 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.

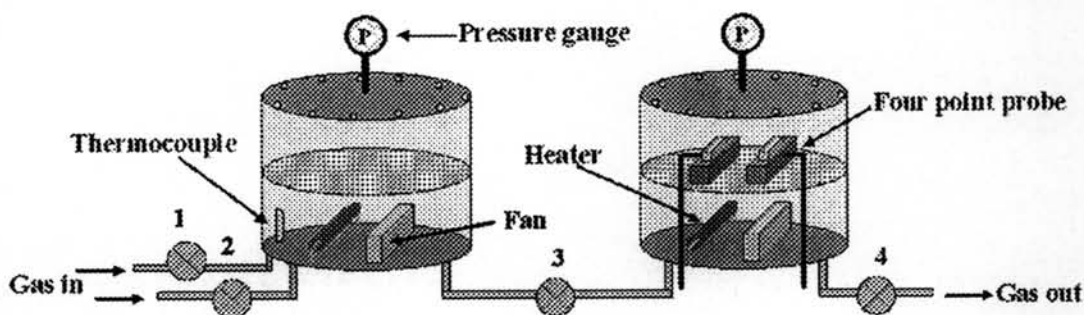


Figure 3.1 Conductivity detectors with gas chamber.

Step 1 A voltage was applied to PPP 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 was closed; valve No. 3 and 4 was opened).

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

Step 4 N₂ gas was fed into the first chamber until the pressure reaches 1 atm as observed from the pressure gauge.

Step 5 Valve No. 3 was opened; the conductivity response of N₂ gas was recorded.

Step 6 Steps 2-6 was repeated until the conductivity response of N₂ was constant (this refers to pre-exposed $\sigma_{N_2, initial}$).

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

Step 8 Ammonia gas will be fed into the first chamber until the pressure reached 0.1 atm as observed from the pressure gauge and N₂ was then fed to mix with previous fed NH₃ until pressure reached 1 atm observed from pressure gauge. The obtained ammonia concentration was 5% by volume.

Step 9 Valve No. 3 was opened; the conductivity response of NH₃-N₂ mixture gas was recorded until it reaches an equilibrium value.

Step 10 Both chambers was closed and evacuated by using a vacuum pump in order to remove gas.

Step 11 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) was closed.

Step 12 N₂ gas was fed into the first chamber until the pressure reaches 1 atm as observed from the pressure gauge.

Step 13 Valve No. 3 was opened then the conductivity response of N₂ gas will be recorded as the final $\sigma_{N_2, final}$.

The differences in the change of electrical conductivity ($\Delta\sigma$) will be calculated by equation (3.4) following;

$$\Delta\sigma = \sigma_{NH_3} - \sigma_{N_2, initial} \quad (3.4)$$

where $\Delta\sigma$ is the difference in specific conductivity (S/cm), σ_{NH_3} is the specific conductivity of NH₃ (S/cm), $\sigma_{N_2, initial}$ is the specific conductivity of N₂ at initial state (S/cm).