CHAPTER III
EXPERIMENTAL

3.1 Materials

α,α'- Dichloro-p-xylene (Aldrich) and Tetrahydrothiophene (Aldrich) was used to synthesize monomer. Analytical grade methanol (Merck) was used as solvent. Sodium hydroxide (Merck) and Hydrochloric acid (Merck) were used as a basic and acid reagent, respectively. Sulfuric acid (Merck) was used as an oxidant. Sodium chloride (Merck) and Cupper(II) chloride (Merck) were used as ion-exchange agent. Zeolite : Na-13X (Aldrich), NH_4-ZSM5 (Si/Al =23,80) (Zeolyst), NH_4-ferrierite(Zeolyst) were used as adsorbent. Carbon monoxide (CO, TIG) stock of was used as the target gas. Nitrogen (N_2, TIG) was used as the surface cleaning gas.

3.2 Methodology

3.2.1 Poly(*p*-phenylene vinylene) (PPV) Synthesis and Doping Process

3.2.1.1 Preparation of Monomer

α,α'-dichloro-p-xylene, tetrahydrothiophene and methanol are purchased from the Aldrich Company. All chemicals are used without further purification. Synthesis of the p-xylene-bis(tetrahydrothiophenium chloride)monomer is achieved by reacting α,α'-dichloro-p-xylene at a concentration of 0.75 M with excess tetrahydrothiophene at 50 °C in methanol: water (80:20) solution for 24 h. This monomer is purified concentrating the reaction solution and precipitating the product in cold acetone (0 °C), filtration and vacuum drying.

3.2.1.2 Preparation ofPprecursor Sulfonium Polyelectrolyte

Synthesis of Poly(p-xylene-bis(tetrahydrothiophenium chloride))

The precursor sulfonium polyelectrolyte is prepared in aqueous solution by the base induced polymerization of an appropriate *bis*-sulfonium monomer, The reaction is usually carried out at low temperatures in fairly dilute monomer solutions and in equimolar base to monomer ratios in order to suppress the premature formation of unsaturated polymer segments by thermal or base induced elimination of solubilizing

side chains. The polymerization reaction is terminated by the addition of dilute aqueous hydrochloric acid to the reaction mixture which is then dialysed against water in order to separate the high molecular weight fraction from the monomeric and oligomeric residues as well as the sodium and chloride ions.

3.2.1.3 Preparation of Poly(p-phenylene vinylene)

Poly(*p*-phenylene vinylene) can be ogtained by heating Poly(p-xylene-bis(tetrahydrothiophenium chloride)) films under vacuum at 180 °C for 6h.

3.2.1.4 Doping Process

The 9 M. Sulfuric acid is used as dopant solution at mole ratio of PPV repeating unit per sulfuric acid equal to 1:10 . The doping process would occur after adding a dopant solution to a polymeric powder and it is monitored by observing the colour changes of powder from bright yellow to black.

3.2.2 Preparation of Zeolite

Each of zeolite powder: ZSM5 (Si/Al = 23,80), Ferrierite were immersed in 0.3 M NaCl aqueous solution to obtain Na^+ in framework with the ratio of zeolite for 1 g to 100 ml at room temperature for 12 h. Then the precipitate sample was filtered and washed doubly with hot water. Na^+ zeolite was collected and dried at 80 °C in drying oven overnight.

3.2.3 PPV /Zeolite Composites

The zeolite will be grinned and dried. The homogenous mixing of doped PPV and zeolite are accomplished by using a mesh screen. Then samples are pressed into disc by a hydraulic press machine with a volume ratio of zeolite to PPV equal to 10:1. Their conductivity values were measured by using the two point probe technique.

Preparation of monomer

To a round bottom flask adds
- α,α'-dichloro-p-xylene (10 g)
- tetrahydrothiophene (15 ml)
- methanol (150 ml)

↓ stirr 24h at 50 °C

p-xylene-bis(tetrahydrothiophenium chloride) monomer

↓

purification by
- concentrating the reaction solution
- precipitating by cold acetone

↓

filtration and vacuum drying

Preparation of Poly(p-xylene-bis(tetrahydrothiophenium chloride))

To a round bottom flask
- p-xylene-bis(tetrahydrothiophenium chloride) monomer
- 0.4 M NaOH

↓

stirr under N_2 flow at 0 C , 120 min

↓

stop the reaction with 0.4 M HCL

↓

dialysis in CH_3OH/H_2O (1:1 by volume) for 3 days

Preparation of Poly(*p*-phenylene vinylene) ;PPV

Poly(p-xylene-bis(tetrahydrothiophenium chloride))

↓ heat under vacuum at 180 °C,6h

Poly(*p*-phenylene vinylene)

3.3 Characterization

3.3.1 Fourier-Transform Infrared Spectrometer (FT-IR)

PPV 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.

3.3.2 Thermogravimeteric Analyzer (TGA)

The moisture content and degradation process of undoped poly(p-phenylene vinylene), doped poly(p-phenylene vinylene), 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 900 °C with a heating rate of 10oC/min.

3.3.3 X-ray Diffractrometer (XRD)

The crystallinity of poly(p-phenylene vinylene) and the crystal order of zeolite were determined by an X-ray diffraftometer (Phillips PW 1830/00 No. DY1241 Diffractometer, model Rigaku). A pellet form of poly(p-phenylene vinylene) sample was placed on quartz specimen. X-ray diffraction patterns were started from 2θ equal to 5 to 90 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 Zeolite was observed at 2θ equal to 5 to 90 degrees

3.3.4 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 poly(p-phenylene vinylene) in powder 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 poly(p-phenylene

vinylene) were obtained by using an acceleration voltage of 25 kV with a magnification of 1000-3500 times.

3.3.5 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 cupper (II) oxide in zeolite 13X, ZSM5 (Si/Al = 23), Ferrierite and ZSM5 (Si/Al = 80) were determined. The amount of cation (Cu^{2+} and Na^{+}) in side 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.

3.3.6 Particle Size Analyzer

The particle sizes of poly(p-phenylene vinylene) 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.

3.3.7 BET

BET (Sorptomatic) 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.

3.3.8 Electron spin resonance (ESR)

ESR was used to determine an oxidation state of copper ion. The ESR spectra of copper ion were run at room temperature on a Varian E-109 spectrometer equipped with a dual cavity always employing the same instrumental parameters.

3.3.9 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 (3.3.9.1) as follow:

$$\sigma = \frac{1}{\rho} = \frac{1}{Rs \times t} = \frac{I}{K \times V \times t} \qquad (3.3.9.1)$$

where σ = specific conductivity (S/cm)

ρ = specific resistivity (Ω.cm)

Rs = 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 (3.3.9.2) as follows:

$$K = \frac{\rho ref}{Rs \times t} \qquad (3.3.9.2)$$

where ρref = known resistivity calibrated from the 4-point probe device (Ω.cm)

t = film thickness (cm)

Measurements of conductivity responses of doped poly(p-phenylene vinylene) and poly(p-phenylene vinylene)/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 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.

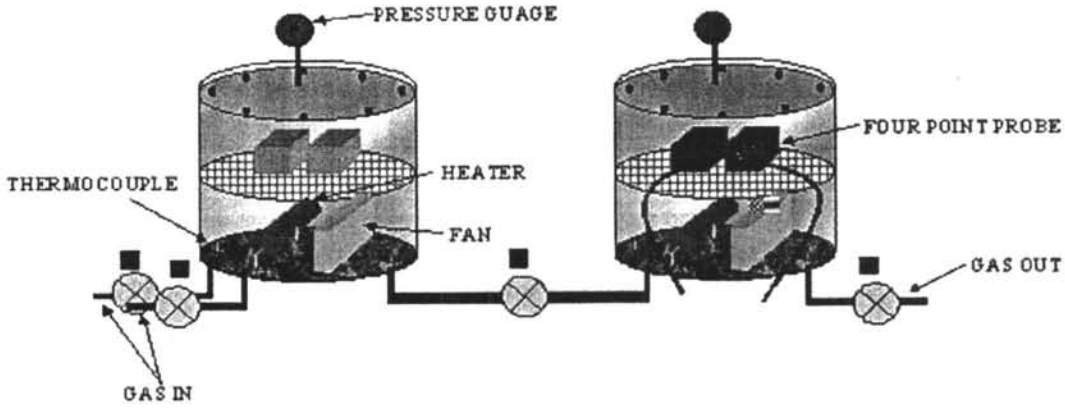

Figure 3. 1 Conductivity detectors with gas chamber.

Step 1 A voltage was applied to poly(*p*-phenylene vinylene) 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 N2 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 N2 gas was recorded.

Step 6 Step 2-6 were repeated until the conductivity response of N2 was constant (this refers to σN_2,final).

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 1 atm as observed from the pressure gauge.

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

Step 10 Valve No. 1,2 were closed; second chamber was evacuated by using a vacuum pump.

Step 11 Valve between the two chambers (No. 3) and valve between the second chamber and the vacuum pump (No.4) were closed. Then N2 gas was fed to first chamber until the pressure reached 2 atm.

Step 12 Valve No. 3 was opened; the conductivity response of N2 gas was recorded (σN_2,after expose).

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

The differences in the change of electrical conductivity ($\Delta\sigma$) at various doping ratios were calculated by Equation (3.3.9.3) following;

$$\Delta\sigma = \sigma_{CO} - \sigma_{N2,initial} \qquad (3.3.9.3)$$

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

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

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