

CHAPTER IV
DEVELOPMENT OF POLYTHIOPHENE/ZEOLITE COMPOSITES
AS H₂ SENSOR

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Abstract

Poly(3-thiopheneacetic acid), P3TAA, was chemically synthesized via an oxidation polymerization and doped with perchloric acid to improve its conductivity. Using PTAA as the matrix, composites were fabricated with zeolites by dry mixing to be used as an H₂ sensor. Zeolite L (L), Mordenite (MOR) and Beta (BEA) were chosen in our study. The electrical conductivity sensitivity toward H₂ was investigated for the effects of zeolite contents, zeolite type, cation type, and cation concentration. The negative electrical conductivity response and sensitivity appeared when exposed with H₂. The weaker interaction exists between H₂ and the polaron or the bipolaron species than the interaction between N₂ and active site of Pth₂₀₀:1. For the effect of zeolite contents, 20 %v/v of MOR has the highest sensitivity values. The reduction of sensitivity values from 20 to 50 %v/v arises from the diminishing active sites available for the interaction between H₂ and the polaron or the bipolaron species. At 20 %v/v of L, MOR and BEA, the electrical conductivity sensitivity increased with decreasing Al content due to the reduced interaction with H₂ and the greater interaction between H₂ and the active sites on the polymer chain. The higher electronegativity and smaller ionic radius of Li⁺ loaded in MOR caused the lower electrical conductivity sensitivity than Na⁺ and K⁺. Na⁺ was loaded in zeolite L at 0,

15, 20, 30 and 50 mole%, the electrical conductivity sensitivity increased with increasing Na⁺ content.

Keywords: Polythiophene/Gas sensor/Conductive Polymer/ZeoliteL, Zeolite Modenite, Zeolite Beta

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Introduction

Hydrogen is a promising alternative fuel since it can be used completely pollution-free and can readily be produced from renewable energy resources. It is efficient energy because of containing more chemical energy per weight than hydrocarbon fuels. Uses of hydrogen can be found in many applications such as a fuel in fuel cell, in gas run diesel engines, and in microturbines. Moreover, hydrogen is an important raw material for the aerospace, chemical, semiconductor and other sectors [1]. Although hydrogen is very useful but it is lighter than air so it can easily build up explosive proportions with air. In order to warn of gas leaks and to indicate the efficiency of combustion, H₂ sensor is a necessary safety device.

The demands for accurate and dedicated sensors to provide precise process control and automation in manufacturing process, and also to monitor and control environmental pollution, have accelerated the development of new sensing materials and sensor technology over last decade [2].

Recently, there have been interests in using conductive polymers in gas sensing materials, as alternatives to metal or metal oxide sensing films. Conductive polymers can offer a variety of advantages for sensor applications over the metallic or ceramics counterparts: conductive polymers are relatively low cost materials and lighter; their fabrication techniques are relatively simple and straightforward since there are no needs for clean room and high temperature processes; they can be deposited on various types of substrates and can be operated at lower applied voltage in many conditions, these materials exhibit moderately fast reversible electrical

conductivity changes when exposed to gases or vapors at room temperature; they have flexibility in molecular architectures such as side chain attachments, and modifications by charged or neutral particles either in the bulk or on the surface [3].

Many conductive polymers have been used as gas sensing materials (Prissanaroon *et al.*, 2000). Polypyrrole (PPy) is the one of the most interesting amongst many conductive polymers known due to its relatively high environmental stability and the ease in synthesizing and doping with various dopants [4]. Polyaniline (PANI) has several interesting features such as inexpensiveness ease to process, high yield, and excellent chemical stability [5]. Another conductive polymer, polythiophene, is also a candidate gas sensor material. It has good mechanical properties, high electrical conductivity, and environmental stability in both doped and pristine form [6].

Not only conductive polymers can be used for gas sensor but also zeolite is another candidate. Zeolite, a class of microporous aluminosilicate crystals, contains molecular-sized void spaces within their crystal structures. Because of their unique structure, zeolites and related microporous materials possess molecular-sieving property, which has widely been utilized as catalysts, ion-exchanges and adsorbents. As a sensing layer, zeolites are very favorable due to its additional high thermal stability and chemical resistance. These properties are desirable in fabricating robust sensors for NO and SO₂. Moreover, the characteristic molecular sieving has been applied in the gas sensors to detect H₂O and large organic molecules which can discriminate each other [7].

Combining the advantages of the two materials, we propose to mix a conductive polymer that is poly(3-thiophene acetic acid) with a variety of zeolites to be used as selective gas sensors. The effects of zeolite type, zeolite concentration, cation type, and cation concentration on electrical conductivity response of composite were investigated in this work. We will use zeolites L, Mordenite, and Beta since they have nearly the same pore sizes but have different structures and Si/Al ratios.

Experimental

Materials

Using 3-thiopheneacetic acid, 3TAA (AR grade, Fluka) as the monomer and anhydrous ferric chloride, FeCl_3 (AR grade, Riedel-delHean) as the oxidant that were used as received. Chloroform, CHCl_3 (AR grade, Lab-Scan), methanol, CH_3OH (AR grade, Lab-Scan) and dimethyl sulfoxide (DMSO) were dried over CaH_2 for 24 hours under the nitrogen atmosphere and then distilled and used as solvents. Hydrochloric acid, HCl (AR grade, Lab-Scan) was used to neutralize and to precipitate the polymer synthesized. Sulfuric acid, H_2SO_4 , was used to protect the oxidative decomposition of monomer. Diethyl ether and deionized water were used to extract and wash materials. Sodium hydroxide, NaOH , was used as the hydrolyzing agent. Perchloric acid dopant, HClO_4 (AR grade, Panreac Quimica) was used as received.

Zeolite L, Modenite and Beta, having K, Na and H as the cations respectively, were purchased from Tosoh Corp. They were used to mix with PTAA for altering gas adsorption properties.

Gases were supplied by TIG. Nitrogen gas was used as the carrier gas. Hydrogen gas (99.999%) was used as the target gases.

Instruments

A Fourier transform infrared spectrometer (Thermo Nicolet, Nexus 670), with the number of scans of 32, was used for identifying functional groups of side chain of polythiophene. A UV-Visible absorption spectrometer (Perkin Elmer, Lambda 10) was used to investigate the doping level of polythiophene. A thermalgravimetric analyzer (DuPont, model TGA 2950), with the temperature scan from 30 to 800 °C with a heating rate of 10°C/min under air flow was used to study thermal property of undoped and doped polythiophenes. A scanning electron microscope (JOEL, model JSM-5200-2AE) was used to determine the morphological structure of polythiophene and composites. A custom-built two-point probe electrometer (Keithley, Model 6517A) was used to measure electrical conductivity of the polythiophene and polythiophene/zeolite composites. BET (Sorptomatic 1990, Thermo Finnigan) was used to determine the surface area and the pore volume of

zeolites. Crystallinity was investigated by XRD (Phillips, Rigaku). Contents of ions were identified by the atomic absorption (AAS, Varian, spectr AA. 300).

Synthesis of Poly(3-Thiopheneacetic acid) (P3TAA)

Poly(3-thiopheneacetic acid) was synthesized by the oxidative coupling polymerization according to the method of Kim *et al*, 1999. 10.0 g of 3-thiopheneacetic acid (3TAA) was refluxed for 24 h in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄, to protect the oxidative reaction of the monomer at the carboxylic acid group during polymerization. Then, the methanol was evaporated and the residue was extracted with diethyl ether. The extract was washed with deionized water, dried with anhydrous MgSO₄, and filtered. The 3-thiophene methyl acetate (3TMA) was recovered after evaporation of diethyl ether by a rotating evaporator.

The prepared monomer, 3TMA, of 10 mmol was dissolved in 20 ml chloroform and then added dropwise to a solution of 40 mmol ferric chloride in 30 ml chloroform under nitrogen atmosphere. The reaction was carefully maintained at 0°C (± 0.5 °C) for 24 h. The mixture was precipitated by pouring into an excess amount of methanol. Then the precipitate was washed with methanol and deionized water to remove the residual oxidant and the oligomers after filtering. Finally P3TMA was obtained.

P3TMA was hydrolyzed by heating 0.5 g precipitate in 50 ml of 2.0 M NaOH solution for 24 h at 100°C. Poly(3-thiopheneacetic acid) (PTAA) was obtained by neutralization and precipitation with a dilute HCl solution. The P3TAA was repeatedly washed with deionized water before vacuum drying at room temperature for 2 days.

Characterization Method

Undoped and doped poly(3-thiopheneacetic acid) powder was identified for their functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670) operated in the absorption mode with 32 scans and a resolution of ± 4 cm⁻¹, covering a wavenumber range of 4000-400 cm⁻¹. Optical grade KBr (Carlo Erba Reagent) was

used as the background material. The synthesized P3TAA was mixed with dried KBr at a ratio of P3TAA:KBr = 1:20 and molded into pellets under the pressure of 6 tons. In order to investigate the spectrum of Pth_200:1 and zeolite L, Mordenite and Beta, before exposure, under exposure and after exposure with H₂ gas, a gas cell with ZnSe window was used.

UV-Vis absorption spectrophotometer (Shimadzu, UV-2550) was used to identify the successfully doped of polythiophene. Measurements were taken in the absorbance mode in the wavelength range of 200-800 nm. Synthesized P3TAA and doped P3TAA were grinded into a fine powder and dissolved in DMSO at the concentration of 2.8134×10^{-6} M.

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to investigate thermal property of undoped and doped poly(3-thiophene acetic acid) (P3TAA). Polymer powder was loaded into an aluminium pan and heated at temperature scan from 30 to 800°C with a heating rate of 10°C/min under air condition..

Scanning electron micrographs were taken with a scanning electron microscope (JEOL, JSM-5200) to determine the morphology of poly(3-thiophene acetic acid), zeolites and polythiophene/zeolite composites in powder forms. Sample powder was placed and adhered on a stub with a carbon tape. Before measuring, sample surface was coated with gold by using JFC-1100E ion-sputtering device for 4 seconds.

The average particle size and the standard size distribution of poly(3-thiophene acetic acid) and zeolite were determined by using a particle size analyzer (Malvern, Masterizer X), using 45 mm lenses in order to measure the particle size in microns level. Consequently, the specific surface area was calculated from the particle diameter with the assumption of being a spherical particle.

Crystallinity and structure of poly(3-thiopheneacetic acid) and zeolite powders were identified by an x-ray diffractometer (Phillips, Rigaku). Sample powder was packed onto a glass plate and measured with $2\theta = 2-90^\circ$, $2-50^\circ$ for polythiophene and the zeolites, respectively. Undoped and doped poly(3-thiophene acetic acid), with ion exchanged zeolite were also examined.

Electron Dispersive Spectroscopy (EDS) (Oxford, PentafetLink) was used to investigate doping level of poly(3-thiophene acetic acid). An amount of each element, such as C, S and Cl, was calculated. Sample preparation is the same as that of SEM.

Proton Nuclear Magnetic Resonance was used to identify the successfully synthesized of poly(3-thiopheneacetic acid). Undoped and doped of poly(3-thiophene acetic acid) were dissolved in chloroform and DMSO respectively before testing.

Atomic Absorption Spectrophotometer (Varian, spectr AA.300) was used to determine the amount of cations which were ion exchanged into zeolite. Standard, blank and sample solutions were prepared before testing the cation type in the zeolites. Specific lamp was used to identify of each cation type in the zeolites.

The surface area and the pore size of each zeolite were identified by BET (Sorptomatic1990, Thermo Finnigan). Zeolite powder was out gassed at 300 °C over night before adsorption and desorption with He and N₂ gases. During operation zeolite powder was cooling by liquid N₂.

The H₂ adsorption properties of Pth_200:1, Pth_200:1/MOR, L, MOR and BEA were investigated by TPD. H₂ was adsorbed at 50 °C.

The electrical conductivity of undoped poly(3-thiopheneacetic acid) was studied by using a custom-built two-point probe coupled with an electrometer (Keithley, Model 6517A). The specific conductivity σ (S/cm) values of the pellets were obtained by measuring the bulk pellet resistance R (Ω). The relation $\sigma = (1/Rt)(1/K) = (I/Vt)(1/K)$ was used to calculate specific conductivity, where t is the pellet thickness (cm), I is current change (A), V is apply voltage (voltage drop) (V) and K is the geometric correction factor which is equal to the ratio w/l , where w and l are the probe width and the length, respectively. The geometrical correction factor (K) was determined by calibrating the two-point probe with semi-conducting silicon sheets of known resistivity values. These two probes were connected to a voltmeter (Keithley, Model 6517A) for apply constant voltage source and recording a change in current. Electrical conductivity values of several samples were first measured at various applied voltage to identify their linear Ohmic regimes.

Preparation of Doped poly(3-thiopheneacetic acid)

Polythiophene was doped by perchloric acid (HClO_4) as dopant following the method of Kim *et al.*, 2000. Grinded polythiophene was stirred in 2.0 M HClO_4 at room temperature for 3 days. The ratio of $\text{HClO}_4/3\text{TAA}$ for doping was 200:1. Doped polythiophene was obtained after been filtered and vacuum-dried. After the doping process, their electrical conductivity was measured by using a custom-built two-point probe electrometer (Keithley, Model 6517A).

Preparation of the Ion Exchange Zeolites

Zeolite L and Mordenite were exchanged with different cations in order to investigate the effect of zeolite concentration and cation types. Zeolite L was stirred in 1 M of an NaCl at 80 °C for 2 hours, using 70 ml per gram zeolite and zeolite Mordenite was stirred in 1M of an LiCl and KCl in similar procedure. This process was repeated many times until zeolite contained the required amount of cation. After filtering and washing with distillation water for several times, the ion exchanged zeolite was dried and calcined at 500 °C for 5 hours.

Preparation of the P3TAA/Zeolite Composite

Polythiophene/zeolite composites were prepared by mechanical mixing of polythiophene and zeolite powder. Before mixing, polythiophene was grinded and sieved with a mesh size of 38 μm . Composites were pressed into a pellet form by a hydraulic press machine. Polythiophene was used as the matrix and the dispersed phase was zeolite. Sample with different volume ratios of zeolite to polymer were prepared to investigate the effect of zeolite content on electrical conductivity when exposed with H_2 gas.

Electrical Conductivity Measurement

Electrical conductivity of doped poly(3-thiopheneacetic acid) and composites of this polymer with zeolites was carried out by using a special constructed gas cell. It consisted of two chambers connected in series. The chambers were made from stainless steel. The first chamber and the second chamber were

called mixing and measurement chamber, respectively. The temperature controllers, connecting to both chambers, were used to monitor and control the temperature within the gas chambers. The second chamber contained two four point probe meters for conductivity measurement. The procedure for measuring the electrical conductivity in the presence of H₂ gas was follows. First, both chambers were evacuated of air and moisture by using a vacuum pump and the constant voltage was applied to the sample that was connected with the four point probe in the second chamber, nitrogen gas was passed through the first chamber until pressure reached 1 atm. Then valve between both chambers was opened until both chamber had equal pressure. When sample had a steady conductivity, this value was recorded ($\sigma_{\text{initial N}_2}$). The nitrogen valve was turned off and the chamber was then vacuumed. The H₂ gas was let in and the conductivity was recorded after reaching equilibrium. The H₂ gas was then turned off and the chamber was then vacuumed and nitrogen gas was introduced to obtain a steady conductivity value ($\sigma_{\text{Final N}_2}$). The electrical conductivity response ($\Delta\sigma = \sigma_{\text{H}_2} - \sigma_{\text{initial N}_2}$) and sensitivity ($\Delta\sigma/\sigma_{\text{initial N}_2}$) of P3TAA and P3TAA/Zeolite sample with H₂ were calculated.

Results and Discussion

Characterization of Poly(3-thiopheneacetic acid) and Zeolites

The FT-IR spectrum of the synthesized P3TAA was recorded in order to identify characteristic absorption peaks [8]. The characteristic peaks of P3TAA were found at 3200-3000 cm⁻¹, 3000-2800 cm⁻¹, 1700 cm⁻¹, 1300-1200 cm⁻¹ and 830 cm⁻¹. These peaks can be assigned to the C-H bond stretching on the thiophene ring; the aliphatic C-H bond stretching; the carboxylic acid C=O stretching; the thiophene ring stretching; the carboxylic acid C-O stretching and the out-of-plane thiophene C-H stretching, respectively [8]. The most characteristic feature in this spectrum is the extremely broad O-H absorption occurring in the region from 3400-2400 cm⁻¹; it can be attributed to the strong hydrogen bonding of the dimer. This absorption band often obscures the C-H stretching vibration peak occurring in the same region. It is

obvious from the absorption peak at around 1700 cm^{-1} that the ester groups were not deteriorated during the oxidative polymerization.

The UV-visible absorption spectra of undoped and doped P3TAA solution in DMSO shows two dominant absorption peaks at 267, 417 nm and 270, 470 nm corresponding to the π - π^* transition of the bithiophene unit and the polymer backbone, respectively [8,9,10]. However doped P3TAA has lower absorbance than undoped P3TAA and it has new peak appearing at 701 corresponding to the localized of polaron state [10].

The TGA thermogram of synthesized P3TAA shows two degradation steps at 186°C and 356°C corresponding to the side chain degradation and the backbone degradation, respectively [11]. The doped P3TAA with perchloric acid has lower thermal stability due to have two degradation steps at 104 and 300°C .

The mean particle diameter of undoped and doped P3TAA was determined to be approximately $19.58\pm 0.41\ \mu\text{m}$ and $20.83\pm 0.28\ \mu\text{m}$, respectively. The particle size of P3TAA has bigger due to aggregate of P3TAA powders. These were obtained by grounding and sieving through mesh size $38\ \mu\text{m}$. The mean particle diameter of zeolite L, Mordenite and Beta were determined to be 7.71 ± 0.24 , 16.76 ± 0.17 , $2.41\pm 0.03\ \mu\text{m}$, respectively.

The morphology of undoped and doped P3TAA, zeolite L, Mordenite, Beta and P3TAA/zeolite composites was observed and investigated using scanning electron microscopy (SEM). Both undoped and doped P3TAA particles were quite irregular in shape. The shape of each zeolite was different; but it is quite uniform in both size and shape. Figure 1 shows SEM monograph of Pth_200:1/L_20, Pth_200:1/MOR_20 and Pth_200:1/BEA_20 composites at zeolite volume fraction of 20% where we can observe a nonuniform distribution of zeolite particles within the matrix.

The X-ray diffraction pattern of synthesized undoped P3TAA represented some sharp peaks and one broad peak at 2θ equal to 22.92 that corresponds to the interlayer d-spacing of $3.88\ \text{Å}$. This could be attributed to the stacking distance of successive thiophene ring between two polymers [12]. The broad diffraction at this wide angle can be attributed to both amorphously packed polythiophene main chains

and scattering from disordered side chain [13]. The degree of crystallinity was determined from the ratio of the sharp peak area divided by the total area. The crystallinity of P3TAA was approximately 3.16%. For doped P3TAA, only one broad peak appeared at 2θ equal to 23.12 that corresponds to the interlayer d-spacing of 3.84 Å. This indicates that it was totally amorphous.

The specific surface area of zeolite L, Mordenite and Beta are 283, 336 and 555 m²/g which correspond to the pore volumes of 0.27, 0.23 and 0.37, respectively. Zeolite Beta has the highest specific surface area and the pore volume. The three zeolites have similar pore width. Pore widths of zeolite L, Mordenite and Beta are about 5.86, 6.18 and 6.29 Å, respectively.

The amounts of ion-exchange were obtained by the atomic adsorption spectrophotometer. The amount of Na⁺ in zeolite L are 14.83, 20.11, 31.09 and 49.80 mole% for the first, the second, the fifth and the ninetcenth exchanges, respectively. For MOR ion-exchanged with Li⁺ and K⁺, the corresponding mole percentages are 89.48 and 92.36 for the fifth exchanges, respectively. Table 1 summarizes the mole % of ion-exchanged.

The TPD profiles of adsorbed H₂ of L, MOR and BEA are shown in Figure. 2. Figure 2 shows the main peak at around 880 °C desorption of H₂ of L. H₂ desorption of MOR and BEA have slightly higher temperatures at dominant peaks about 900 °C. This indicates the stronger site for H₂ adsorption in MOR and BEA than L.

Electrical Conductivity in Air and N₂

The specific conductivity of undoped P3TAA (Pth_U) was measured by a custom-built two point probe (Keithley, Model 6517A). The specific electrical conductivity values of Pth_u and Pth_200:1 were $2.70 \times 10^{-4} \pm 2.43 \times 10^{-6}$ S/cm and $4.85 \times 10^{-2} \pm 3.23 \times 10^{-4}$ S/cm, respectively. Extended chains P3TAA were obtained by the repulsion force between the positive charges of the counter anions (ClO₄⁻) along back bone. So the specific conductivity of Pth_200:1 has higher than Pth_u because electrons can move more easily along the polymer chain. Table 2 list the average

electrical conductivity values of Pth_200:1 and others composites with zeolite L, MOR and BEA. The average electrical conductivity value in air, taken from two samples each, of Pth_200:1 is $(4.62 \pm 1.58) \times 10^{-1}$ S/cm. This value is higher than others composites due to the addition of insulating of zeolite and the decrease in the number of active sites, the polaron or bipolaron species. The electrical conductivity of Zeolite L, MOR and BEA are $(1.45 \pm 0.421) \times 10^{-3}$, $(5.18 \pm 0.54) \times 10^{-3}$ and $(9.46 \pm 0.235) \times 10^{-4}$, respectively. The reductions in electrical conductivity in N₂ relative to those in air were also found for all samples. The electrical conductivity in N₂ of Pth_200:1 decreases to $(1.00 \pm 0.59) \times 10^{-5}$ S/cm. The greater electrical conductivity values in air can be attributed to the interaction of moisture and O₂ with the active sites, the polaron and the bipolaron species [14].

Electrical Conductivity in H₂ of Pth_200:1 and Composites: Effect of Zeolite Types

The electrical conductivity response ($\Delta\sigma = \sigma_{\text{gas}} - \sigma_{\text{initial N}_2}$) is defined as the difference in the steady state electrical conductivity values when exposed to target gas and the steady state conductivity when exposed to N₂ at 1.3 atm and at 29 ± 1°C. Due to the differences in initial electrical conductivity of various composites, the sensitivity ($\Delta\sigma / \sigma_{\text{initial N}_2}$), is defined as the ratio between the electrical conductivity response and the electrical conductivity when exposed to N₂.

The electrical conductivity response and sensitivity of all samples are listed in Table 2. The pattern of electrical conductivity when samples were exposed and evacuating by H₂ are also shown in Figure 3 and 4. The electrical conductivity response and sensitivity of Pth_200:1 are $(-2.38 \pm 1.91) \times 10^{-6}$ and $(-2.19 \pm 0.62) \times 10^{-1}$, respectively. The negative electrical conductivity response and sensitivity can be identified by the interaction between H₂ and Pth_200:1. The representative H₂ can interact at the positive charge on the thiophene ring, or the polaron and the bipolaron species, via the induction bonding electron density of H₂. The absorbate molecules are polarized (H^{δ+} - H^{δ-}). This proposed mechanism is similar to N₂ but it has a stronger interaction. So when the exposed to N₂, electrons on a polymer chain can move faster and has higher electrical conductivity than those of a polymer chain

exposed with H₂. This causes the negative response towards H₂ relative to N₂. Figure 5 shows the proposed mechanism of the H₂-Pth_200:1 interaction.

The interaction between Zeolite with H₂ molecules can be identified as the physical adsorption between H₂ and Zeolite framework and the physical adsorption between H₂ and cation in the zeolite framework. An H₂ molecule interacts with an active site via the bonding electron density accumulated between the two H atoms [15]. Adding 20% v/v of zeolites L, MOR and BEA into Pth_200:1, the electrical conductivity responses are $(-1.62 \pm 0.49) \times 10^{-8}$, $(-2.66 \pm 0.14) \times 10^{-6}$ and $(-3.82 \pm 3.72) \times 10^{-4}$ S/cm corresponding to the sensitivity values of $(-7.66 \pm 1.33) \times 10^{-2}$, $(-4.37 \pm 0.59) \times 10^{-1}$ and $(-7.32 \pm 0.47) \times 10^{-1}$, respectively. Table 2 shows the sensitivity values of the composites containing zeolites L, MOR and BEA. The difference in the electrical conductivity sensitivity values of these composites can be attributed to different SiO₂/Al₂O₃ ratios and cation types in the zeolite frameworks. Zeolite L, MOR and BEA possess the SiO₂/Al₂O₃ ratios of 6, 17.7 and 41 along with K⁺, Na⁺ and H⁺ cations, respectively. It appears that the electrical conductivity sensitivity decreases with increasing Al content. Zeolite L has the highest aluminium content and thus the highest cation content in its zeolite framework. So H₂ are more favorably adsorbed by the cation in zeolite L relative to other zeolites that have lower Al contents. The increasing H₂ adsorption by the cation in the zeolite leads to the decreasing interaction between H₂ and the polymer chain. Thus the sensitivity is therefore decreased.

To investigate temporal response of our composites, the induction time is defined as the time required for the electrical conductivity to reach an equilibrium value when exposed to H₂. The induction times of Pth_200:1, Pth_200:1/L_20, Pth_200:1/MOR_20 and Pth_200:1/BEA_20 are 105, 28, 45 and 111 minutes, respectively. These are directly related to the accessibility and the number of available attack sites for H₂. The induction time increased with decreasing an amount of Al due to the greater available active sites of the positive charges on the polymer chain. The induction time of Pth_200:1/BEA_20 is longer than those of other composites because of the greater interaction between H₂ and the polaron or the bipolaron species.

FTIR spectra of Pth_200:1 sample was taken and is shown in Figure 6, before Pth_200:1 was exposed to H₂, when Pth_200:1 was exposed in-situ to H₂ for a duration of 45 min, and when Pth_200:1 was evacuated and replaced with N₂. The adsorption peak of the thiophene ring stretching vibration ($\nu = 1396 \text{ cm}^{-1}$) shifted to upward ($\Delta\nu = 8 \text{ cm}^{-1}$). A shoulder of the adsorption peak of C=C at about 1600 cm^{-1} can be clearly observed when exposed to H₂; this corresponds to the interaction between H₂ and the polaron species of Pth_200:1. The peak of C=C before exposure to H₂ has no distinct shoulder; it remains observable after H₂ was removed and replace with N₂. This indicates that the interaction between H₂ and Pth_200:1 is irreversible. We note that the percentage of permanent electrical conductivity changed under N₂ after H₂ removal relative to the initial electrical conductivity values in N₂ is 44.60 %. On the other hand, FTIR spectra of Zeolite L, MOR and BEA, before, under exposure and after exposure to H₂ do not show any distinct peak position shifted. Thus we cannot identify the interaction between H₂ and the zeolite by FTIR. But we note that the electrical conductivity values under N₂ of Pth_200:1/L, Pth_200:1/MOR and Pth_200:1/BEA differ from their initial values under N₂ by 2.97%, 57.70% and 96.86%, respectively.

Electrical conductivity in H₂ of Pth_200:1/MOR: Effect of Cation Types

Zeolite Mordenite was ion-exchanged ions into Li⁺ and K⁺ form about 90 mole% of cation. The electrical conductivity sensitivity of Pth_200:1/MOR_Li[90]_20, Pth_200:1/MOR_Na[100]_20 and Pth_200:1/MOR_K[90]_20 at 20% v/v of zeolite content are $(-7.78 \pm 0.33) \times 10^{-2}$, $(-4.37 \pm 0.59) \times 10^{-1}$, and $(-2.20 \pm 0.12) \times 10^{-1}$ S/cm, respectively. Table 2 shows the sensitivity values of the composite with various cations. The adsorption of H₂ onto the zeolite framework and the cation can be represented via the bonding electron density accumulated between the two H atoms. The gas adsorption properties depend on the electronegativity and the ionic radius [15]. It is known that a strong binding between a cation and its zeolite framework is due to the larger electronegativity values [16]. Electronegativity values of Li, Na and K atoms are 1.0, 0.9, and 0.9, and

the ionic radii are 0.60, 0.95 and 1.33 Å, respectively. In case of Li, the electronegativity is higher than those of Na and K, causing the strongest binding between the cation and H₂ molecules. In addition, the shorter distance between H₂ and the smaller cation Li suggests a strong dipole-dipole interaction. These two factors explain the lower electrical conductivity sensitivity value of Pth_200:1/MOR_Li[90]_20 and H₂. On the other hand, the lower electronegativity value and the larger ionic radius of Na⁺ lead to a loose contact between H₂ molecules and the cation in the zeolite framework. These factors lead to a more favorable interaction between the gas and the conductive polymer. Although K has a similar electronegativity value than Na, but it has a larger ionic radius, therefore the electrical conductivity sensitivity is moderate.

Electrical conductivity in H₂ of Pth_200:1/L: Effect of Cation Concentration

Zeolite L was ion-exchanged into Na⁺ form at various cation concentrations 0, 15, 20, 30 and 50 mole %, as shown in Table 1. At 20% v/v of zeolite contents, the electrical conductivity sensitivity values of Pth_200:1/L_20, Pth_200:1/L_Na[15]_20, Pth_200:1/L_Na[20]_20, Pth_200:1/L_Na[30]_20, and Pth_200:1/L_Na[50]_20 are $(-7.66 \pm 1.33) \times 10^{-2}$, $(-3.51 \pm 1.99) \times 10^{-2}$, $(-1.13 \pm 0.00) \times 10^{-1}$, $(-2.08 \pm 0.07) \times 10^{-1}$ and $(-1.83 \pm 0.00) \times 10^{-1}$, respectively as shown in Figure 7. The electrical conductivity sensitivity increases with increasing Na⁺ content in zeolite framework upto 20% mole, and it decreases beyond that. The increase in Na⁺ cation contents causes a more loosely binding interaction between the cation and H₂ and therefore a more favorable interaction between H₂ and the conductive polymer. However, as a larger amount of Na⁺ is loaded into Zeolite L, the interaction between and the conductive polymer and therefore a lowering of electrical conductivity sensitivity.

Electrical conductivity in H₂ of Pth_200:1/MOR: Effect of Zeolite Contents

Zeolite Mordenite was mixed into Pth_200:1 at various contents: 0, 20, 30, 40 and 50 %v/v. For zeolite content between 0 to 20 %v/v, the electrical conductivity

sensitivity increased from $(-2.19 \pm 0.62) \times 10^{-1}$ to $(-4.37 \pm 0.59) \times 10^{-1}$. For zeolite content from 20 to 50% v/v the electrical conductivity sensitivity decreased from $(-4.37 \pm 0.59) \times 10^{-1}$ to $(-9.05 \pm 0.49) \times 10^{-2}$, as shown in Figure 8. The initial increase in electrical conductivity sensitivity with zeolite content conforms to our expectation that the addition of a mesoporous material into a conductive polymer with appropriate interaction between the zeolite and the gas will induce a greater interaction between the gas and the conductive polymer. The decrease in the electrical conductivity sensitivity at high zeolite contents can be attributed to the available adsorption sites of H_2 on zeolite framework and its cation through the dipole-dipole interaction similar to the study of H_2 adsorption on active sites of Mordenite [15], and a lesser number of active sites available on the conductive polymer.

Conclusions

In the present study, poly(3-thiopheneacetic acid) was synthesized via oxidative polymerization by using ferric chloride as an oxidant and doped with perchloric acid. The composites using poly(3-thiophene acetic acid) as the matrix and mixed with three different zeolites were investigated for their interaction with H_2 towards sensor applications. Zeolite L, Mordenite and Beta were chosen in our study. The effects of zeolite type, zeolite concentration, cations type and cation concentration were investigated.

The negative electrical conductivity response and sensitivity are present due to the weaker interaction between H_2 and the polaron or the bipolaron species than that of N_2 . For the effect of zeolite type, the composite with 20% v/v of BEA has the highest the electrical conductivity sensitivity due to the lowest amount of Al. The interaction between H_2 and the polaron or the bipolaron species also increased. The induction time increased with decreasing an amount of Al due to the greater available active sites of positive charges on the polymer chain. At 20% v/v, MOR was ion-exchanged from Na^+ into Li^+ and K^+ forms. The Li^+ form has a lower electrical conductivity sensitivity than those of the Na^+ and the K^+ forms due to the higher electronegativity and a smaller ionic radius. To investigate cation concentration, Na^+

cations were load into Zeolite L: 0, 15, 20, 30 and 50 mole%. The electrical conductivity sensitivity increased with increasing Na^+ content until 30 mole%. The loading of Na^+ cations causes a more loosely binding interaction between the cation and H_2 and correspondingly a more favorable interaction between H_2 and the conductive polymer. Adding zeolite Mordenite at small contents causes increases in the electrical conductivity sensitivity. At high zeolite contents, the reduction of sensitivity value arises from the diminishing available active sites on the conductive polymer.

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Table 1 Modified and unmodified zeolite MOR and L and the amounts of the cations present as determined by AAS

Sample	No. Exchange	Amount of Na mole/kg of zeolite	Amount of cation mole/kg of zeolite	Mole% of cations
MOR_Na[100]	0	2.02	-	0
MOR_Li[90]	5	0.26	2.16	89.48
MOR_K[90]	5	0.17	2.05	92.36
L_K[100]	0	-	4.38	0
L_Na[15]	1	0.72	4.20	14.83
L_Na[20]	2	0.85	3.40	20.11
L_Na[30]	5	1.19	2.63	31.09
L_Na[50]	19	1.75	1.76	49.80

Table 2 Pth_200:1/zeolite composites and electrical conductivity responses, sensitivities and temporal responses to H₂

Sample	t _i (min)	t _r (min)	σ (S/cm)			Δσ (S/cm)	Δσ/Δσ _{N₂}	Δσ _r (S/cm)
			Air	N ₂	H ₂			
Pth_200:1	105	21	(4.62±1.58) × 10 ⁻¹	(1.00±0.59) × 10 ⁻⁵	(7.62±3.99) × 10 ⁻⁶	(-2.38±1.91) × 10 ⁻⁶	(-2.19±0.62) × 10 ⁻¹	(-2.05±1.40) × 10 ⁻⁶
Pth_200:1/L_20	28	15	(8.44±4.68) × 10 ⁻⁵	(2.20±1.02) × 10 ⁻⁷	(2.04±0.97) × 10 ⁻⁷	(-1.62±0.49) × 10 ⁻⁸	(-7.66±1.33) × 10 ⁻²	(-9.00±7.07) × 10 ⁻⁹
Pth_200:1/MOR_20	45	30	(2.32±1.14) × 10 ⁻²	(6.17±1.16) × 10 ⁻⁶	(3.51±1.02) × 10 ⁻⁶	(-2.66±0.14) × 10 ⁻⁶	(-4.37±0.59) × 10 ⁻¹	(-9.00±2.40) × 10 ⁻⁷
Pth_200:1/BEA_20	111	20	(4.53±2.07) × 10 ⁻²	(5.07±4.76) × 10 ⁻⁴	(1.25±1.04) × 10 ⁻⁴	(-3.82±3.72) × 10 ⁻⁴	(-7.32±0.47) × 10 ⁻¹	(-1.09±0.91) × 10 ⁻⁴
Pth_200:1/MOR_Li[90]_20	25	13	(5.63±1.61) × 10 ⁻²	(3.74±2.02) × 10 ⁻⁶	(3.44±1.85) × 10 ⁻⁶	(-2.94±1.69) × 10 ⁻⁷	(-7.78±0.33) × 10 ⁻²	(-1.10±0.71) × 10 ⁻⁷
Pth_200:1/MOR_K[90]20	46	19	(3.82±2.80) × 10 ⁻⁴	(4.81±2.72) × 10 ⁻⁶	(3.77±2.18) × 10 ⁻⁶	(-1.04±0.54) × 10 ⁻⁶	(-2.20±0.12) × 10 ⁻¹	(-4.70±2.69) × 10 ⁻⁷
Pth_200:1/L_Na[15]_20	29	29	(1.36±0.75) × 10 ⁻³	(2.58±1.03) × 10 ⁻⁶	(2.48±0.94) × 10 ⁻⁶	(-1.01±0.87) × 10 ⁻⁷	(-3.51±1.99) × 10 ⁻²	(-1.85±2.33) × 10 ⁻⁷
Pth_200:1/L_Na[20]_20	25	13	(3.58±0.78) × 10 ⁻⁴	(2.42±0.12) × 10 ⁻⁶	(2.15±1.06) × 10 ⁻⁶	(-2.74±0.14) × 10 ⁻⁷	(-1.13±0.00) × 10 ⁻¹	(-5.00±0.00) × 10 ⁻⁸
Pth_200:1/L_Na[30]_20	28	16	(1.16±0.56) × 10 ⁻³	(2.48±0.76) × 10 ⁻⁶	(1.97±0.59) × 10 ⁻⁶	(-5.18±1.74) × 10 ⁻⁷	(-2.08±0.07) × 10 ⁻¹	(-1.85±0.92) × 10 ⁻⁷
Pth_200:1/L_Na[50]_20	32	18	(3.20±0.03) × 10 ⁻³	(1.82±1.46) × 10 ⁻⁵	(1.49±1.19) × 10 ⁻⁵	(-3.32±2.66) × 10 ⁻⁶	(-1.83±0.00) × 10 ⁻¹	(-1.62±1.39) × 10 ⁻⁶
Pth_200:1/MOR_10	26	38	(2.92±0.73) × 10 ⁻²	(2.04±1.38) × 10 ⁻⁵	(1.34±0.93) × 10 ⁻⁵	(-6.95±4.54) × 10 ⁻⁶	(-3.45±0.11) × 10 ⁻¹	(-1.59±1.57) × 10 ⁻⁶
Pth_200:1/MOR_30	24	23	(9.59±3.06) × 10 ⁻³	(9.77±5.56) × 10 ⁻⁶	(8.45±4.36) × 10 ⁻⁶	(-1.32±1.19) × 10 ⁻⁶	(-1.20±0.29) × 10 ⁻¹	(-6.05±0.07) × 10 ⁻⁷
Pth_200:1/MOR_40	17	21	(2.24±1.27) × 10 ⁻²	(1.75±1.47) × 10 ⁻⁵	(1.60±1.43) × 10 ⁻⁵	(-1.50±0.38) × 10 ⁻⁶	(-1.18±0.77) × 10 ⁻¹	(-1.62±2.66) × 10 ⁻⁶
Pth_200:1/MOR_50	16	37	(1.41±0.16) × 10 ⁻²	(1.33±1.10) × 10 ⁻⁵	(1.18±0.94) × 10 ⁻⁵	(-1.47±1.65) × 10 ⁻⁶	(-9.05±0.49) × 10 ⁻²	(1.35±1.26) × 10 ⁻⁶
L			(1.45±0.42) × 10 ⁻³					
MOR			(5.18±0.54) × 10 ⁻³					
BEA			(9.46±0.24) × 10 ⁻⁴					

t_i=the induction times, t_r=the recovery time, σ=electrical conductivity in air, N₂ and H₂ and the electrical response (Δσ), the electrical conductivity recovery (Δσ_r = σ_{N₂ final} - σ_{H₂}), the electrical conductivity sensitivity (Δσ/σ_{N₂}), at T = 29±1°C and 1.3 atm, data shown are average values taken from at least two samples.

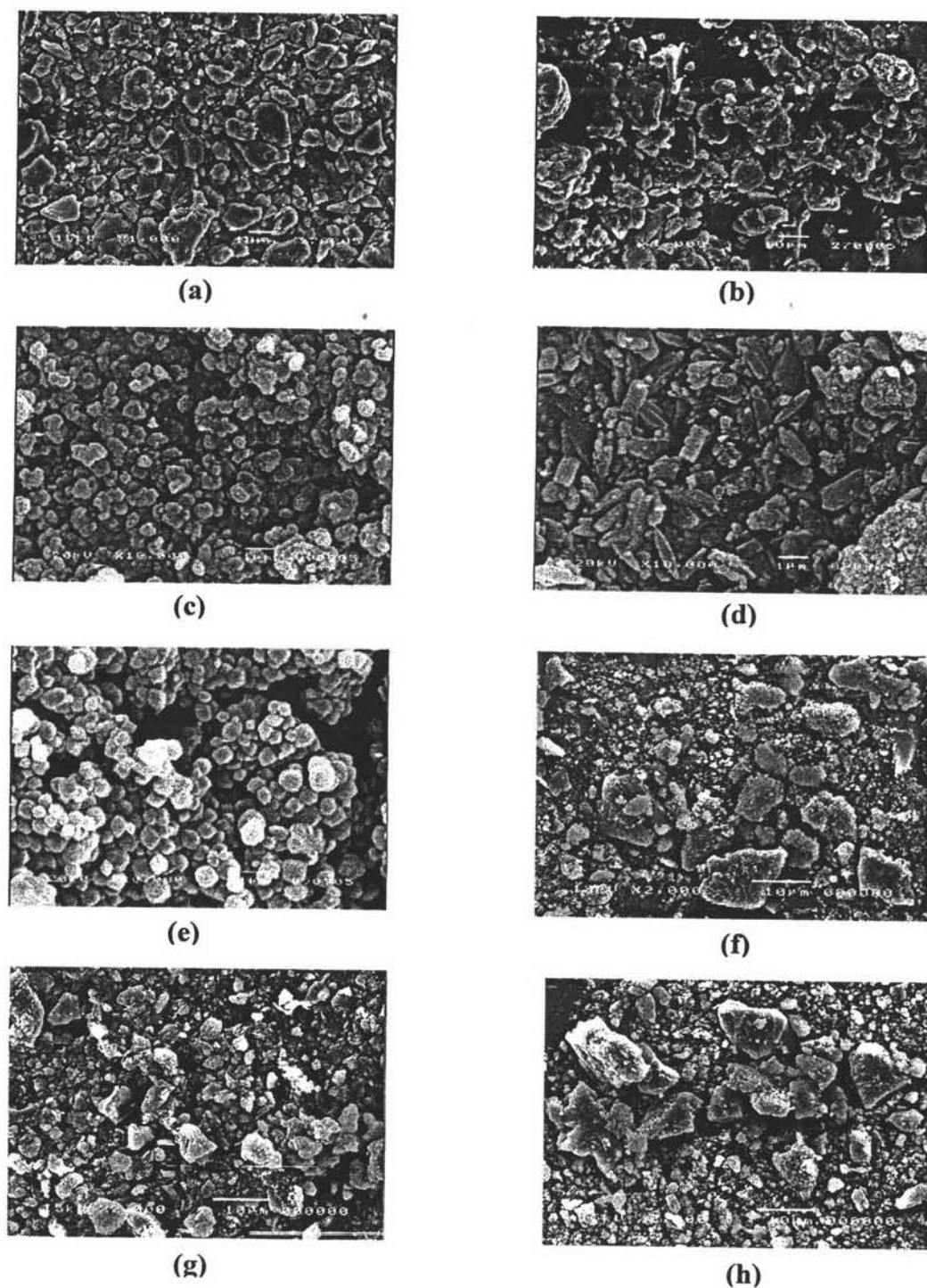


Figure 1 The morphology of polythiophene particles, Zeolite powders and polythiophene/Zeolite composites: a) Pth; b) Pth_200:1 at magnification of 1,000; c) Zeolite L; d) Zeolite Mordenite; e) Zeolite Beta; at magnification of 10,000 f) Pth_200:1/L_20; g) Pth_200:1/MOR_20; and h) Pth_200:1/BEA_20; at magnification of 2000.

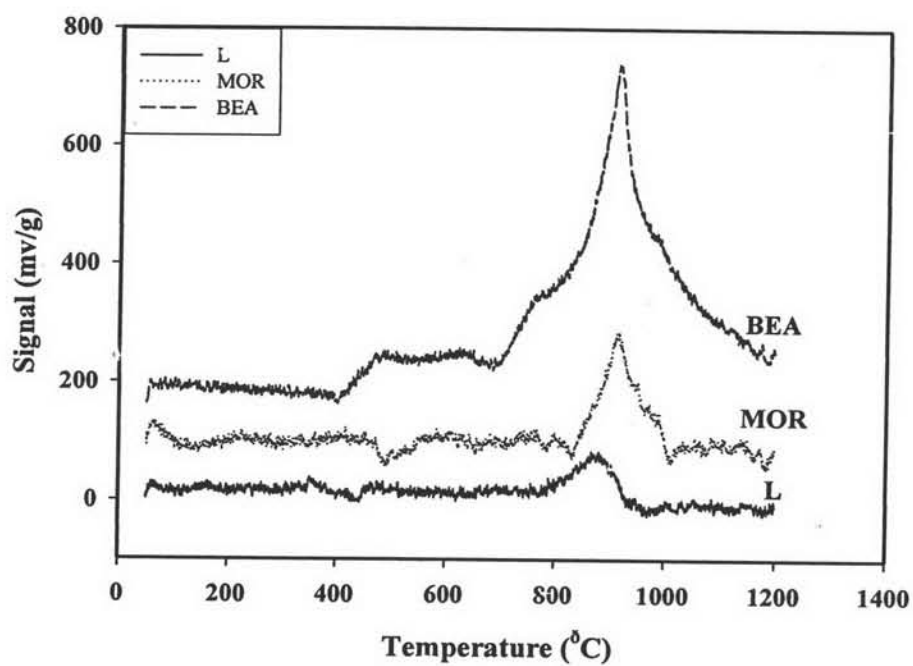


Figure 2 TPD profiles of H_2 adsorbed on L, MOR and BEA.

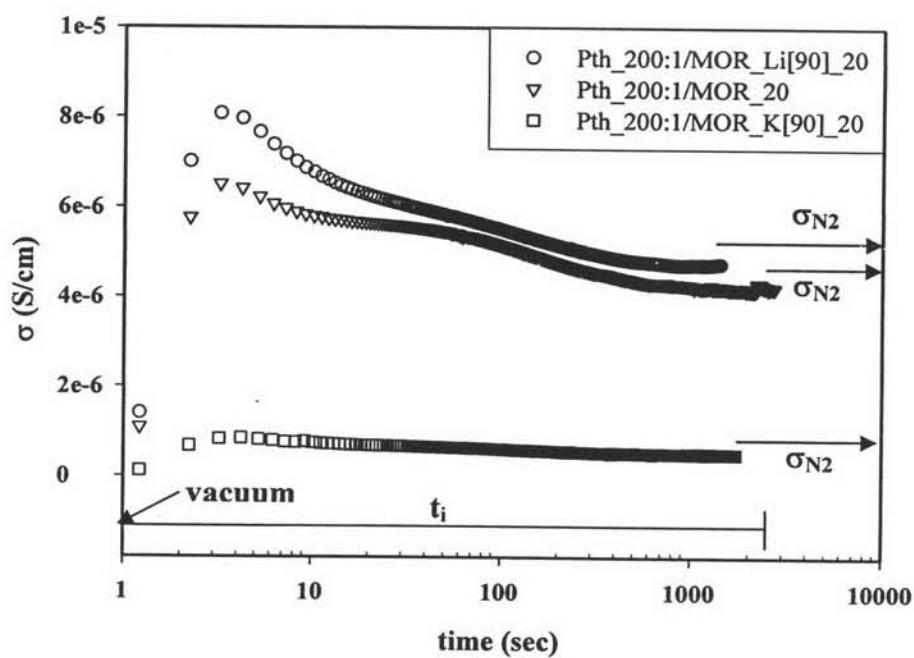


Figure 3 Specific conductivity of Pth_200:1/MOR with various cation types when exposed to H_2 .

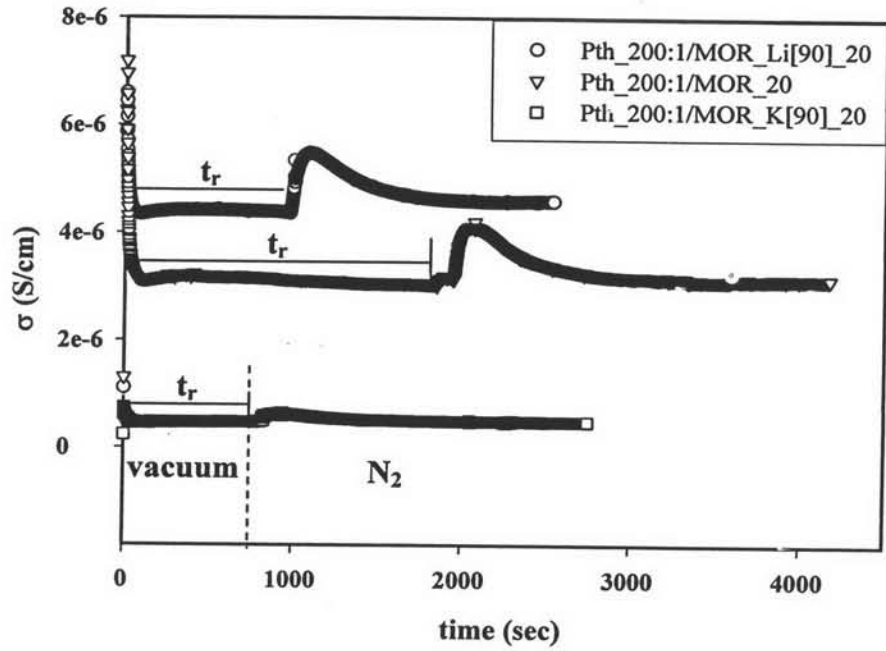


Figure 4 Specific conductivity of Pth_200:1/MOR with various cation types after evacuating H_2 and exposed to N_2 .

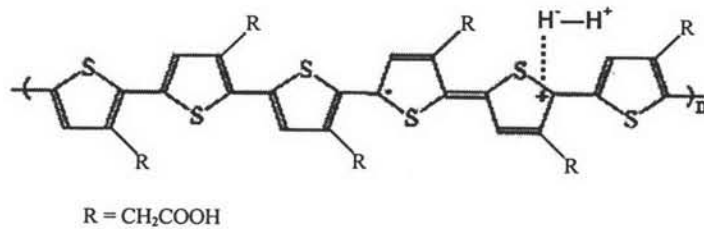


Figure 5 Proposed mechanism of the H_2 -Pth_200:1 interaction.

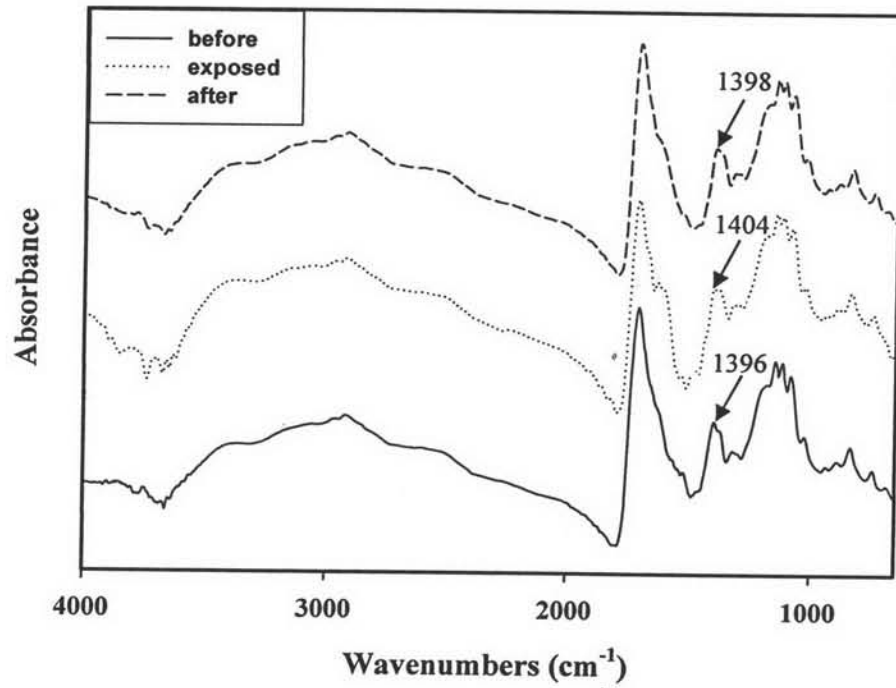


Figure 6 FTIR spectra of Pth_200:1: before, exposed and after exposed with H₂

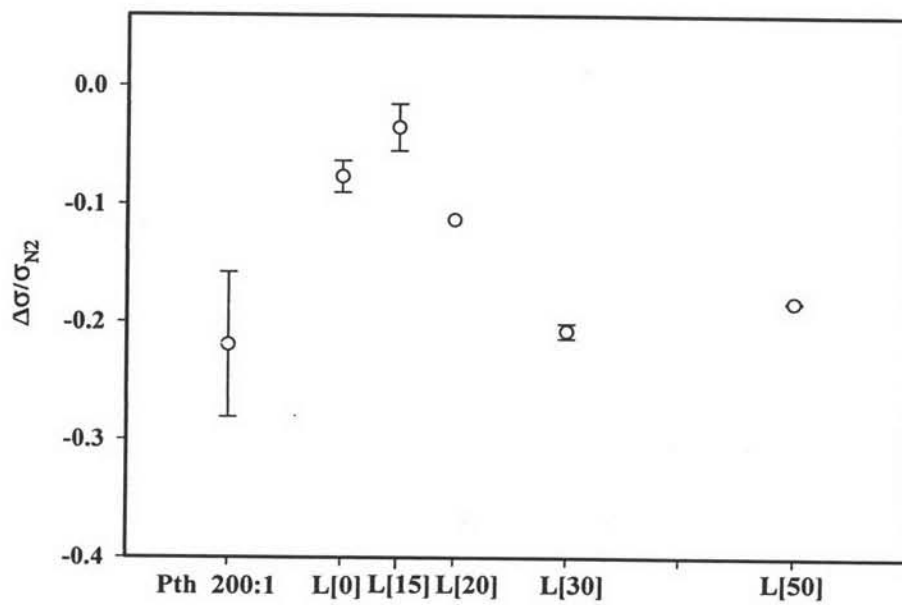


Figure 7 The electrical conductivity sensitivity of Pth_200:1 mixed with Zeolite L at 20%v/v of various Na⁺ cations concentration: 0, 15, 20, 30 and 50 mole% when exposed to H₂ at 29±1°C and 1.3 atm.

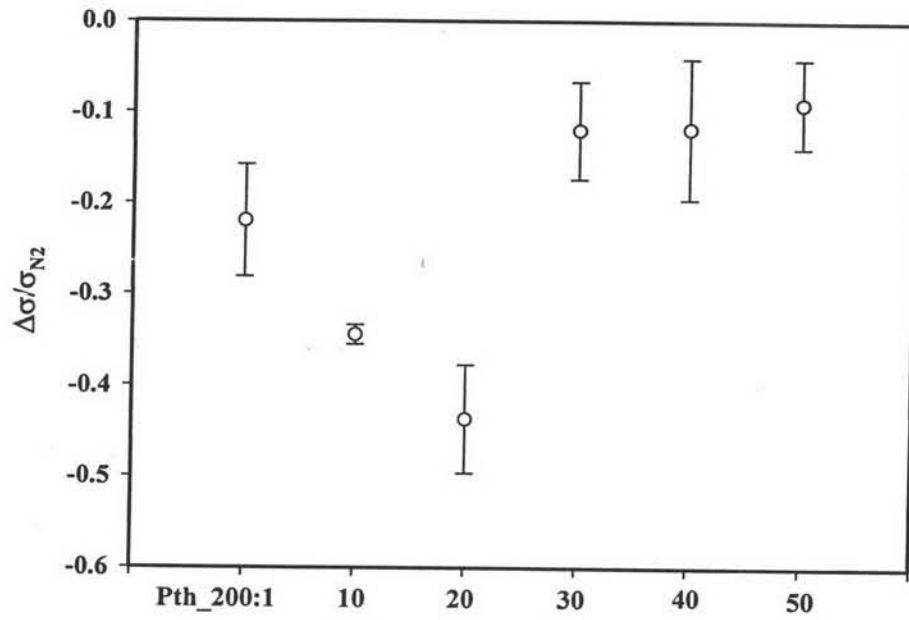


Figure 8 The electrical conductivity sensitivity of Pth_200:1 mixed with Zeolite Mordenite (100% Na^+) at various contents: 0, 10, 20, 30, 40 and 50% v/v when exposed to H_2 at $29\pm 1^\circ\text{C}$ and 1.3 atm.