



CHAPTER IV

DEVELOPMENT OF POLY(3-THIOPHENEACETIC ACID)/ZEOLITE Y AS A GAS SENSOR MATERIAL FOR AMMONIA

Sansanee Konkayan^a, Anuvat Sirivat^{a#}

^a*The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok,
10330 Thailand.*

Abstract

Poly(3-thiopheneacetic acid) was synthesized and doped from an insulating state to a conducting state using perchloric acid. The electrical conductivity sensitivity towards ammonia is further improved by introducing Y zeolite into the doped P3TAA matrix. For the effect of zeolite content, the composite with 10 %v/v of Y zeolite has the highest electrical conductivity sensitivity ($\Delta\sigma/\sigma_{N_2}$) values when exposed to NH_3 . The electrical conductivity sensitivity ($\Delta\sigma/\sigma_{N_2}$) increases with increasing Si/Al ratio. The highest electrical conductivity sensitivity of all composites is obtained with the doped P3TAA/Zeolite Y (Si/Al = 80) at the value of $7.46 \pm 3.56 \times 10^2$.

Keywords: Conductive Polymer/Polythiophene/Polymer composites/Ammonia sensors/Gas sensor/Zeolite Y

*Corresponding author. Tel.: +66 2218 4131; fax: +66 2611 7221.

E-mail address: anuvat.s@chula.ac.th (A. Sirivat).

1. Introduction

Ammonia gas has been known to be hazardous to both humans and the environment. Due to its high toxicity, even low level concentrations (ppm) pose a serious threat. The industrial processes, including fertilizer manufacturing, chemical manufacturing, livestock farms as well as its use as a refrigerant involve the use of

ammonia gas. Existing ammonia gas-sensing devices show low selectivity and sensitivity. A new approach is desirable to increase the sensor selectivity and sensitivity towards ammonia gas [1].

One method for dealing with this problem is the use of conductive polymers in gas sensing applications. In comparison with most of the commercially available sensors, based usually on metal oxides which are operated at high temperatures, the sensors made of conducting polymers have many favorable characteristics. They have high sensitivities and moderately short response times; especially, these features are ensured at room temperature. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations. Furthermore, conducting polymers have moderately good mechanical properties, which allow a facile fabrication of sensors [2]. Polythiophene has several advantages over other semiconducting polymer particles; it can be easily polymerized by an oxidative polymerization at relatively low temperature to giving a high yield, and it can be doped from an insulating state to a conducting state by using simple protonic acids [3]. A polythiophene film can be expected to show a highly sensitive response to ammonia and that the response can be easily recovered with N_2 . Furthermore, with the proven reproducibility, it has a number of important applications as gas sensors, such as electronic noses [4]. Therefore this work is aimed to investigate Poly(3-thiopheneacetic acid)(P3TAA) as NH_3 gas sensor.

Zeolites are naturally and synthetically occurring aluminosilicate minerals with three-dimensional structure based on $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ polyhedral [5]. Due to the size-and-shape selectivity of zeolite crystals, zeolites of type Y are utilized to promote or to demote one species of gas interaction via the size selection and the cationic interaction.

The objectives of this work are to investigate the effects of zeolite contents and Si/Al mole ratios on the electrical conductivity response of P3TAA/Zeolite Y composites. The scope of this research covers as follows: the synthesis a conductive polymer, polythiophene, and the fabrication with commercial zeolites of type Y forming composite sensing materials, and the use as a selective NH_3 gas sensor. The

electrical conductivity sensitivity of P3TAA/zeolite Y composites when exposed to NH₃ gas are investigated.

2. Experimental

2.1. Materials

3-thiopheneacetic acid, 3TAA (AR grade, Fluka) was used as the monomer and anhydrous ferric chloride, FeCl₃ (AR grade) was used as the oxidant as received. Chloroform, CHCl₃ (AR grade, Lab-Scan), methanol, CH₃OH (AR grade, Lab-Scan), and dimethyl sulfoxide, DMSO (AR grade, Lab-Scan) were dried over CaH₂ for 24 h under the nitrogen atmosphere and then distilled, prior to be used as solvents. Hydrochloric acid, HCl (AR grade, Lab-Scan) was used to neutralize and to precipitate the polymer synthesized. Sulfuric acid, H₂SO₄ was used to protect the oxidative decomposition of the monomer. Diethyl ether, C₄H₁₀O and distilled water were used to extract and to wash materials. Sodium hydroxide, NaOH was used as the hydrolyzing agent. Perchloric acid, HClO₄ (AR grade, Panreac Quimica) was used as received as the dopant.

Zeolite Y with different Si/Al ratios were purchased from Zeolyst International (USA).

Nitrogen (99 %, TIG) was used as the carrier gas of ammonia (99.99 %, Poontaweporn Limited Partnership) was used to investigate the electrical conductivity responses of the composites.

2.2. Synthesis of poly(3-thiopheneacetic acid)(P3TAA)

The reaction was by the oxidative-coupling polymerization according to the method of Kim et al. [6]. Poly(3-thiopheneacetic acid) was prepared by a reflux of 10.0 g of 3-thiopheneacetic acid (3TAA) in 50 ml of dry methanol with 1 drop of concentrated H₂SO₄ for 24 h. Then, methanol was evaporated and the residue was extracted with diethyl ether. The extract was washed with distilled water, dried with anhydrous MgSO₄, and filtered. The 3-thiophene methyl acetate (3TMA) was recovered after diethyl ether was evaporated.

The prepared monomer, 3-thiophenemethyl acetate (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 ± 0.5 °C for 24 h. The mixture was precipitated by pouring the solution in an excess amount of methanol. Then the precipitate was washed with methanol and distilled water. Finally, poly(3-thiophenemethyl acetate)(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) (Pth) was obtained by neutralization and precipitation in a dilute HCl solution. Pth was repeatedly washed with distilled water before vacuum drying at room temperature for 2 days.

2.3. Preparation of doped poly(3-thiopheneacetic acid)

Pth particles was stirred in 2.0 M HClO₄ at room temperature for 3 days. The doping ratio of HClO₄/3TAA were varied from 1:1 to 300:1. Doped Pth was filtered and vacuum-dried [7].

2.4. Preparation of the PTH/Zeolite Composites

Before mechanical mixing, poly(3-thiopheneacetic acid) was grinded and sieved with mesh size of 38 µm. Then, a zeolite was grinded and dried before mixing with Pth grinding. After mixing, the composites were pressed into a pellet form by a hydraulic press machine.

2.5. Characterization methods

Undoped and doped poly(3-thiophene acetic acid) (Pth) powders were investigated 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 was used as the background material and the polymers were mixed with dried KBr at a ratio 1:20. In order to investigate the spectrum of Pth₁₀:1 and zeolites Y, before exposure, under exposure, and after exposure with NH₃ gas, a gas cell with ZnSe window was used.

A thermal gravimetric analyzer (Perkin Elmer) was used to characterize the thermal property of the undoped and the doped poly(3-thiopheneacetic acid) (Pth) at 10:1 mole ratio of dopant to monomer unit. Measurements were carried out with the temperature scan from 30 to 800 °C and a heating rate of 10 °C/min. The samples were weighed in the range of 5-20 mg and loaded into a platinum pan, and then it was heated under N₂ flow.

The average particle size of poly(3-thiophene acetic acid) and the zeolites were determined by a particle size analyser (Malvern, Mastersizer X Version 2.15). The samples were grounded and sieved with mesh size 38 µm before measurements were taken. A X-ray Diffractometer (XRD) (D/MAX 2200) was used to identify the crystallinity and structure of poly(3-thiopheneacetic acid) and the zeolites. Powders of polymer and the zeolites were packed onto a glass plate and data were collected after X-ray passed through the sample.

Morphology of undoped and doped poly(3-thiopheneacetic acid), the zeolites, and the composites were observed by the scanning electron microscopy (SEM)(JEOL, JSM-5410LV). Surface area and pore size of zeolite Y were measured by using a surface area analyzer (Physisorption) (Quantachrome, Autosorb-1MP). Zeolite powder was weighed and out gassed at 300 °C over night before the adsorption and the desorption with He and N₂ gases. During the operation, zeolite powder was cooling by liquid N₂. A custom-built two-point probe with a linear geometric array (Keithley, Model 6517A) was used to measure the specific conductivity of each sample. Current used was in the linear Ohmic regime.

2.6. Electrical conductivity measurement

The specific electrical conductivity values, σ (S/cm), of the poly(3-thiopheneacetic acid) and the composites were measured by using a custom-built two-point probe. The specific electrical conductivity was calculated from;

$$\sigma = (1/Rt)(1/K) \quad (1)$$

where t is the pellet thickness, and K is the geometric correction factor which is equal to the ratio w/l , where w and l are the width and the length of probe,

respectively. The value of K was determined by calibrating the two-point probe with semi-conducting silicon sheet of known resistivity value.

A custom-built two-point probe consists of two chambers of equal volume. All measurements were taken at 26 ± 1 °C and 1.1 atm in the linear Ohmic regime. The procedure was as follows. Initially the sample was measured the specific electrical conductivity in air. Then the chambers were evacuated of air and moisture by using a vacuum pump and the steady state electrical conductivity value in vacuum was measured. Nitrogen gas was injected until the pressure reached 1.2 atm, to prevent leakage, and the steady state electrical conductivity value was measured as $\sigma_{N_2\text{ initial}}$. Then the chambers were re-evacuated. Ammonia gas was injected until the pressure reached 1.1 atm and the steady state electrical conductivity (σ_{NH_3}) was measured. Finally ammonia gas was evacuated then nitrogen gas was injected and the steady state electrical conductivity value was measured as $\sigma_{N_2\text{ final}}$. From the procedure of measurement, the electrical conductivity response can be calculated from;

$$\Delta\sigma = \sigma_{NH_3} - \sigma_{N_2\text{ initial}} \quad (2)$$

and the sensitivity ($\Delta\sigma/\sigma_{N_2\text{ initial}}$) of poly(3-thiopheneacetic acid) and composites were recorded.

3. Results and discussion

3.1. Characterization of poly(3-thiopheneacetic acid) and zeolite

From the FTIR spectrum of Pth, the characteristic peak appears at 3200-3000 cm^{-1} and can be assigned to the stretching vibration of the C-H bond on the thiophene ring; peaks between 3000-2800 cm^{-1} represent the aliphatic C-H bonds; a peak at 1700 cm^{-1} represents the C=O stretching vibration; a peak at 1400 cm^{-1} represents the thiophene ring stretching vibration; and peaks between 1300-1200 cm^{-1} represent the C-O stretching vibration. The important feature peak is the extremely broad O-H absorption occurring in the region from 3400 to 2400 cm^{-1} , which can be attributed to the strong hydrogen bonding of the dimer. After doping with perchloric

acid, some characteristic peaks of acid appear on FT-IR spectra: a lower absorbance at $3400\text{-}2400\text{ cm}^{-1}$ and a sharp peak at 1200 cm^{-1} .

The TGA thermogram of synthesized P3TAA shows two transitions at $219\text{ }^{\circ}\text{C}$ and $474.7\text{ }^{\circ}\text{C}$. The first transition can be referred to as the side chain degradation. The other transitions can be referred to as the backbone degradation [8]. The doped P3TAA with perchloric acid has lower thermal stability, its degradation temperature is $120.7\text{ }^{\circ}\text{C}$.

The mean particle diameter of undoped and doped poly(3-thiopheneacetic acid) is $39.28 \pm 0.26\text{ }\mu\text{m}$ and $39.53 \pm 0.41\text{ }\mu\text{m}$, respectively. These were obtained by grinding and sieving through mesh size $38\text{ }\mu\text{m}$. The mean particle diameter of zeolite Y is $30.07 \pm 1.16\text{ }\mu\text{m}$.

The X-ray diffraction pattern of synthesized undoped and doped P3TAA shows broad peak at 2θ equal to 23.30° and 22.15° , respectively. This can be identified as the amorphous part and attributed to the stacking distance of successive thiophene ring between two polymers, as shown in Figure 1a [9]. The structure of zeolite can be considered from the position of each peak, as shown in Figure 1b [10]. The density of undoped P3TAA and zeolite Y is equal to 1.5974 g/cm^3 and 1.7931 g/cm^3 , respectively.

The morphology of undoped and doped P3TAA, zeolite Y, and the composites was observed and investigated using scanning electron microscopy (SEM). Both undoped and doped P3TAA particles were quite irregular in shape. The shape of zeolite has uniform in both size and shape. Figure 2 and Figure 3 show SEM monographs of undoped P3TAA, doped P3TAA 10:1, Zeolite Y, Pth_10:1/Y_10%, and Pth_10:1/Y_20% composites in which a nonuniform distribution of zeolite particles within the matrix can be observed.

3.2 Electrical conductivity in Air and N_2

The specific electrical conductivity values of the undoped and doped P3TAA 10:1 are $1.16 \times 10^{-4}\text{ S/cm} \pm 0.14 \times 10^{-4}\text{ S/cm}$ and $1.31 \times 10^{-4}\text{ S/cm} \pm 0.55 \times 10^{-4}\text{ S/cm}$, respectively. Due to the doped P3TAA has the repulsion force of the positive charges of the counter anions (ClO_4^-) along back bone, so the extended chains were

obtained. The specific electrical conductivity of the doped P3TAA 10:1 is higher than the undoped P3TAA because the electrons can move easily along the polymer chain. The electrical conductivity values of Zeolite NaY, NH₄Y, HY are $(3.48 \pm 2.34) \times 10^{-4}$ S/cm, $(1.30 \pm 0.73) \times 10^{-4}$ S/cm, and $(3.55 \pm 4.45) \times 10^{-4}$ S/cm, respectively. The electrical conductivity of P3TAA 10:1 in N₂ decreases to $(3.68 \pm 0.12) \times 10^{-9}$ S/cm, as shown in Table 1. The greater electrical conductivity values in air can be attributed to the interaction of moisture and O₂ with the polaron and the bipolaron species [5].

3.3 Electrical conductivity sensitivity of Doped P3TAA and Composites in NH₃: Effect of zeolite content

The electrical conductivity sensitivities of the composites versus zeolite content are shown in Figure 4. Zeolite Y was mixed into Pth 10:1 at various contents: 0, 10, 20, 30, 40 and 50 %v/v. For the zeolite content between 0 to 10 %v/v, the electrical conductivity sensitivity increases from $(1.02 \pm 41.43) \times 10^2$ to $(7.39 \pm 2.35) \times 10^2$. For the zeolite content from 20 to 50 %v/v, the electrical conductivity sensitivity decreases from $(4.68 \pm 241.95) \times 10^2$ to $(1.16 \pm 4.86) \times 10^2$ S/cm, as shown in Figure 4. The highest electrical conductivity sensitivity is obtained with the 10 %v/v composite the composite allows more NH₃ molecules to adsorb and diffuse into the composite thus promoting the NH₃-dP3TAA interaction. The decrease in the electrical conductivity sensitivity at higher zeolite contents (from 20 to 50 %v/v) is due to the reduction in the number of available active sites on the polymer chains for NH₃ to interact as zeolite content increases [14]. Various polythiophene/copper phthalocyanine (PT-CuPc) polymers were studied by Radhakrishnan and Deshpande [11]. The sensitivity increased initially with increasing phthalocyanine content to about 3% concentration for ammonia vapor but then decreased for higher concentration of phthalocyanine. Pure PT is an amorphous polymer; the diffusion of a gas would be expected very easy. As the phthalocyanine content in the polymer increases, the polymer became more crystalline. The diffusion of the gas molecules through this well ordered crystal lattice was more difficult. Polyaniline films were employed as a sensing material for the optical

detection of aqueous ammonia; they possessed a fast response time and a fast regeneration time of less than 10 s at room temperature [12].

3.4 Electrical conductivity sensitivity of Doped P3TAA and Composites in NH₃: Effect of Si/Al ratio

The electrical conductivity sensitivity of doped P3TAA is the interaction of doped P3TAA with ammonia molecules. The zeolite HY at various Si/Al ratios: 5.1, 30, 60, 80 were used to investigate the effect of Si/Al ratio on the electrical conductivity sensitivity towards NH₃. All composites contain 10 %v/v of zeolite. The electrical conductivity sensitivities of the composites versus Si/Al ratio are shown in Figure 5. For Si/Al ratio increase from 5.1 to 80, the electrical conductivity sensitivity increases from $(4.88 \pm 0.94) \times 10^0$ to $(7.46 \pm 3.56) \times 10^2$ S/cm. The highest electrical conductivity sensitivity is obtained with Si/Al 80 of $(7.46 \pm 3.56) \times 10^2$ S/cm is due to the increase in the number of Si in the Zeolite Y structure that facilitates the electrostatic interaction between oxygen on the Si molecule in the Zeolite Y and NH₃. The increasing electrostatic interaction between target gas and zeolite improves the electrical conductivity sensitivity of the P3TAA/ZeoliteY composites [13]. From the specific surface area of zeolite in Table 2, zeolite Y with Si/Al 80 has the highest surface area. The higher surface area induces the target gas to reside in the cavity so the electrical conductivity sensitivity increases with increasing the surface area [14]. Table 1 shows the temporal response times of the composites studied: Pth_10:1/Y_H(5.1)_10, Pth_10:1/Y_H(30)_10, Pth_10:1/Y_H(60)_10, and Pth_10:1/Y_H(80)_10. Their temporal response times are 27, 20, 17, and 13 min, respectively. This indicates that a zeolite with more Si can interact with and trap NH₃ molecules more effectively through the dipole–dipole interaction resulting in a shorter response time [15]. The response of PANI films to ammonia was studied. The resistance of the sample increases with the increasing ammonia concentration, but decreases with the increasing temperature. The humidity effect on the PANI film's sensitivity is much smaller compared with that of ammonia gas [16]. For the novel conducting polymer nanojunctions sensor elements for detection of ammonia in human breath at ppb levels is faster and more sensitive than those using microscale polymer materials, and largely immune of variations in

3.5 FTIR Investigations of Interactions of Adsorbed NH₃

The interaction of the active sites of Pth_10:1 and zeolite NaY with NH₃ were investigated by FTIR spectroscopy at 26 ± 1 °C and under pressure 1.1 atm. FTIR spectra were taken by the KBr pellet technique. The sample pellet was placed on a sample holder and put it into the gas cell. The spectrums of samples were recorded, before NH₃ exposure, when exposed to NH₃, and after the NH₃ exposure, in order to study the interaction between these samples and NH₃, as shown in Figures 6 and 7.

When exposed to NH₃, FTIR spectra were taken every 5 minutes for a duration of 45 min, each FTIR spectrum has the same patterns but with different intensities evolving in time. Peaks at 948.8 and 1619.0 cm⁻¹ can be assigned to the vibrations of NH₃ molecules, and a peak at 1396.5 cm⁻¹ belongs to the vibration of NH₄⁺ molecules [17]. After replacing NH₃ with N₂, the bands at 948.8, 1396.5, and 1619.0 cm⁻¹ disappear from the FTIR spectra. Therefore, the interaction of NH₃ and doped Pth is reversible, as shown in Figure 7.

From the FTIR spectra of NaY before, during, and after the NH₃ exposure. The bands at 963.2 cm⁻¹ appears when the exposed to NH₃, but it disappears when NH₃ is replaced by N₂. This peak shift from 968.09 cm⁻¹ represents the Lewis sites of NH₃ molecules [11]. The IR spectrum shows a new peak at 3332 cm⁻¹ which can be assigned to NH₄⁺ interacting with oxygen on zeolite Y [18]. Figure 8 show that there is no significant difference in the band patterns before and after the exposure to NH₃ so the interaction between NH₃ and NaY is reversible based on the FTIR spectrum. For the sensitivity of polyaniline (PANI) films to ammonia has been investigated. When PANI is interacting with ammonia, ammonia molecules take up protons from PANI, forming ammonium, NH₄⁺. However, in air, ammonium decomposes into ammonia and protons which restore the initial level of doping. In such a way, reversibility of the ammonia effect on PANI layers occurs [15].

4. Conclusions

The effects of acid dopant ratio, zeolite content, and Si/Al ratio on the electrical conductivity response of poly(3-thiopheneacetic acid)(Pth) and composites when exposed to NH₃ were investigated. Doped Pth at 10:1 has the highest electrical

conductivity. The electrical conductivity sensitivity of the composites towards NH_3 is improved with the addition of zeolite Y up to 10 %v/v. From 20 to 50 %v/v of zeolite Y, the electrical conductivity sensitivity decreases due to the diminishing of the active sites that available for the interaction between NH_3 and the polaron or the bipolaron species. The electrical conductivity sensitivity ($\Delta\sigma/\sigma_{\text{N}_2}$) increases linearly with increasing Si/Al ratio. Because the number of Si in the zeolite Y structure facilitates the electrostatic interaction between oxygen on the Si molecule in the zeolite Y and NH_3 . The interaction of NH_3 and doped Pth is reversible based on the FTIR spectra.

Acknowledgements

The author is grateful for the scholarship and funding of the thesis work as provided by the Petroleum and Petrochemical College, and by the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand. The authors acknowledge the financial support from the Thailand Research Fund (TRF-BRG), the Conductive and Electroactive Research Unit of Chulalongkorn University, and the Royal Thai Government (Budget of Fiscal Year 2552).

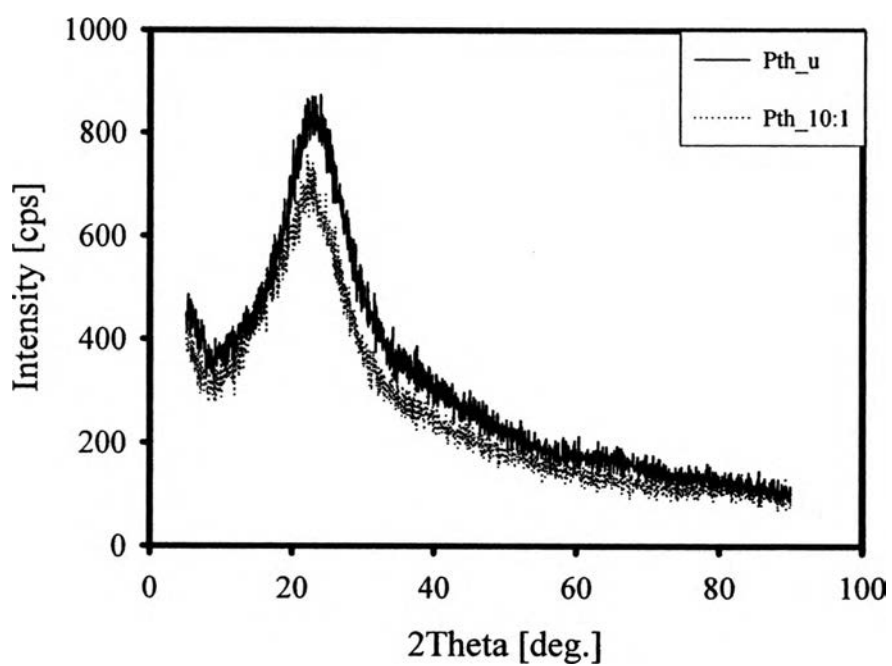
Table 1 The electrical conductivity responses ($\Delta\sigma$) and the electrical conductivity sensitivities ($\Delta\sigma/\sigma_{N_2}$) in NH_3 at 26 ± 1 °C and 1.1 atm, data shown are average values taken from at least two samples

Sample	t_i (min)	t_r (min)	σ (S/cm)			$\Delta\sigma$ (S/cm)	$\Delta\sigma/\sigma_{N_2}$	$\Delta\sigma_r$ (S/cm)
			Air	N_2	NH_3			
Pth_10:1	30	13	$(1.31 \pm 0.55) \times 10^{-4}$	$(3.68 \pm 0.12) \times 10^{-9}$	$(3.87 \pm 5.04) \times 10^{-7}$	$(3.84 \pm 5.04) \times 10^{-7}$	$(1.02 \pm 41.43) \times 10^2$	$(-3.84 \pm 5.04) \times 10^{-7}$
Pth_10:1/Y_Na_10	19	16	$(1.32 \pm 1.06) \times 10^{-6}$	$(4.59 \pm 1.42) \times 10^{-9}$	$(3.23 \pm 0.01) \times 10^{-6}$	$(3.23 \pm 0.01) \times 10^{-6}$	$(7.39 \pm 2.35) \times 10^2$	$(-3.23 \pm 0.01) \times 10^{-6}$
Pth_10:1/Y_Na_20	15	15	$(2.39 \pm 1.21) \times 10^{-8}$	$(3.70 \pm 0.004) \times 10^{-9}$	$(1.73 \pm 0.10) \times 10^{-6}$	$(1.73 \pm 0.10) \times 10^{-6}$	$(4.68 \pm 241.95) \times 10^2$	$(-1.73 \pm 0.10) \times 10^{-6}$
Pth_10:1/Y_Na_30	20	14	$(2.78 \pm 3.05) \times 10^{-6}$	$(3.83 \pm 0.12) \times 10^{-9}$	$(6.40 \pm 1.80) \times 10^{-7}$	$(6.36 \pm 1.80) \times 10^{-7}$	$(1.66 \pm 15.82) \times 10^2$	$(-6.36 \pm 1.80) \times 10^{-7}$
Pth_10:1/Y_Na_40	25	23	$(1.51 \pm 0.14) \times 10^{-6}$	$(4.42 \pm 0.27) \times 10^{-9}$	$(7.77 \pm 3.86) \times 10^{-7}$	$(7.72 \pm 3.86) \times 10^{-7}$	$(1.72 \pm 15.14) \times 10^2$	$(-7.72 \pm 3.87) \times 10^{-7}$
Pth_10:1/Y_Na_50	41	26	$(2.84 \pm 2.78) \times 10^{-6}$	$(5.59 \pm 0.85) \times 10^{-9}$	$(6.23 \pm 3.44) \times 10^{-7}$	$(6.17 \pm 3.45) \times 10^{-7}$	$(1.16 \pm 4.86) \times 10^2$	$(-6.14 \pm 3.42) \times 10^{-7}$
Pth_10:1/Y_H(5.1)_10	27	13	$(1.02 \pm 0.72) \times 10^{-8}$	$(3.85 \pm 0.09) \times 10^{-9}$	$(2.26 \pm 0.31) \times 10^{-8}$	$(1.88 \pm 0.32) \times 10^{-8}$	$(4.88 \pm 0.94) \times 10^0$	$(-1.91 \pm 0.31) \times 10^{-8}$
Pth_10:1/Y_H(30)_10	20	13	$(3.02 \pm 0.21) \times 10^{-8}$	$(4.91 \pm 0.47) \times 10^{-9}$	$(9.20 \pm 6.14) \times 10^{-9}$	$(4.28 \pm 5.67) \times 10^{-9}$	$(8.20 \pm 10.76) \times 10^1$	$(-5.64 \pm 5.99) \times 10^{-9}$
Pth_10:1/Y_H(60)_10	17	10	$(2.67 \pm 2.76) \times 10^{-9}$	$(3.74 \pm 0.14) \times 10^{-9}$	$(2.64 \pm 1.29) \times 10^{-8}$	$(2.27 \pm 1.31) \times 10^{-8}$	$(6.13 \pm 3.72) \times 10^0$	$(-2.28 \pm 1.30) \times 10^{-8}$
Pth_10:1/Y_H(80)_10	13	12	$(7.46 \pm 9.96) \times 10^{-7}$	$(3.48 \pm 0.14) \times 10^{-9}$	$(2.59 \pm 1.22) \times 10^{-6}$	$(2.59 \pm 1.22) \times 10^{-6}$	$(7.46 \pm 3.56) \times 10^2$	$(-2.59 \pm 1.22) \times 10^{-6}$
Y_Na			$(3.48 \pm 2.34) \times 10^{-4}$					
Y_NH ₄			$(1.30 \pm 0.73) \times 10^{-4}$					
Y_H(5.1)			$(3.55 \pm 4.45) \times 10^{-4}$					
Y_H(30)			$(4.43 \pm 2.42) \times 10^{-4}$					
Y_H(60)			$(4.34 \pm 5.91) \times 10^{-2}$					
Y_H(80)			$(1.22 \pm 1.64) \times 10^{-2}$					

t_i = the induction time, t_r = the recovery time, σ = the electrical conductivity in air, N_2 , and NH_3 and the electrical response ($\Delta\sigma$), the electrical conductivity recovery ($\Delta\sigma_r = \sigma_{N_2 \text{ final}} - \sigma_{NH_3}$), the electrical conductivity sensitivity ($\Delta\sigma/\sigma_{N_2 \text{ initial}}$).

Table 2 Surface area of zeolite Y

Cation type	Si/Al ratios	Surface area (m ² /g)		
		1	2	AVG
Na ⁺	5.1	611.0	640.0	625.5 ± 20.5
NH ₄ ⁺	5.1	594.3	583.2	588.8 ± 7.8
H ⁺	5.1	601.2	633.3	617.3 ± 22.7
H ⁺	30	634.9	742.6	688.8 ± 76.1
H ⁺	60	713.9	748.1	731.0 ± 24.2
H ⁺	80	768.4	763.8	766.1 ± 3.2

**Figure 1a** XRD pattern of: a) undoped and; b) doped poly(3-thiophene acetic acid) with HClO₄.

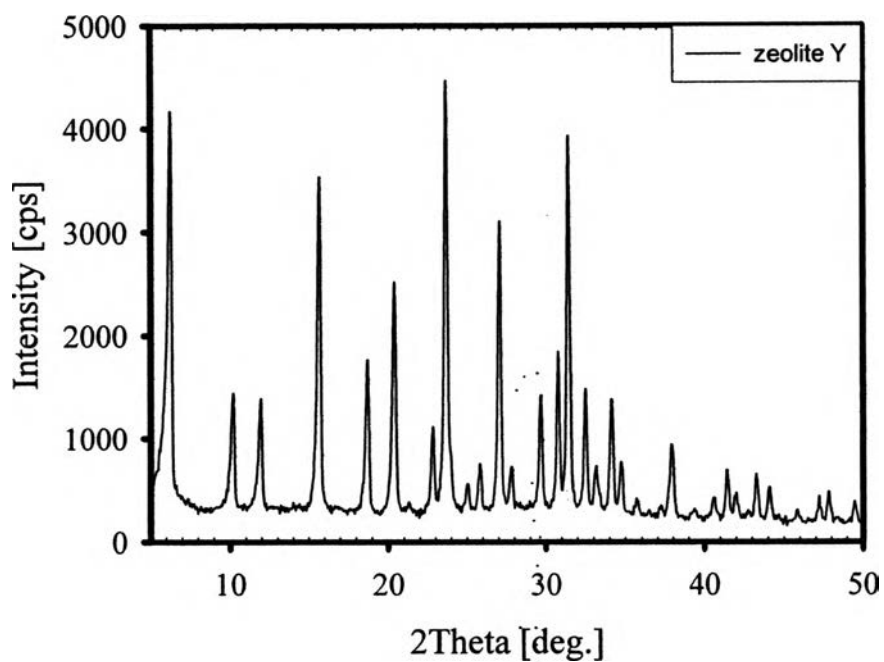


Figure 1b XRD pattern of Zeolite y.

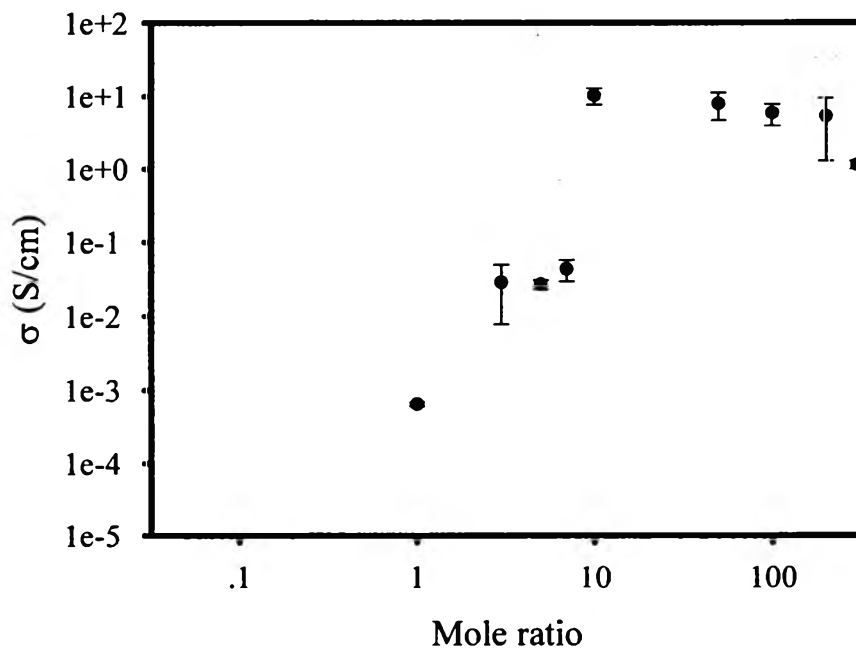
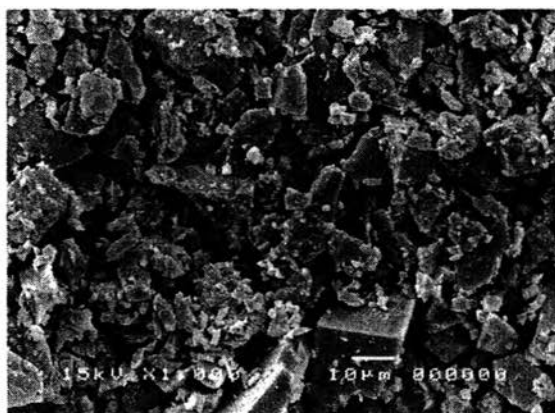
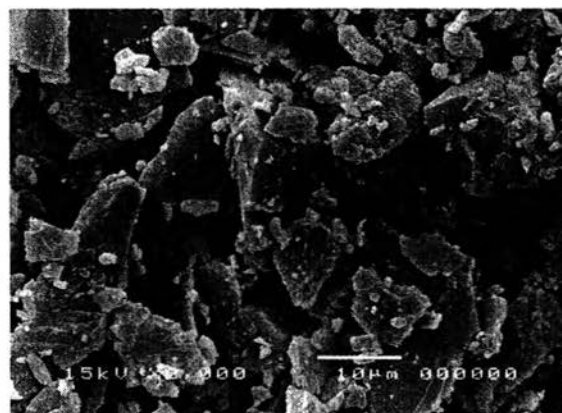


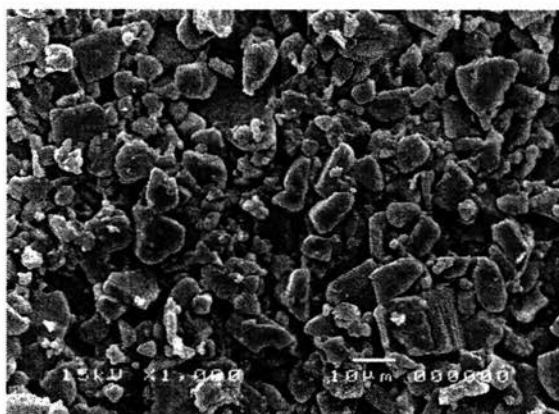
Figure 2 The specific conductivity (S/cm) of undoped and doped poly(3-thiopheneacetic acid) with different mole ratio of HClO_4 to monomer unit.



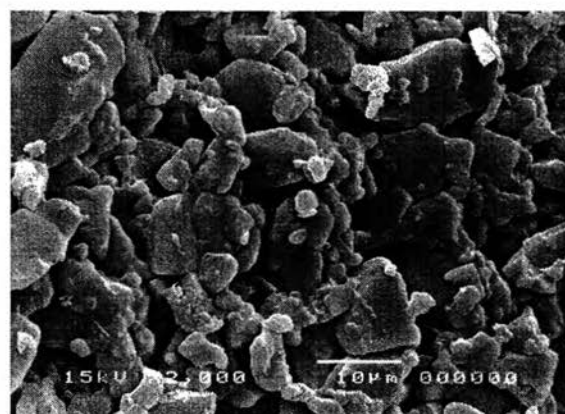
(a)



(b)

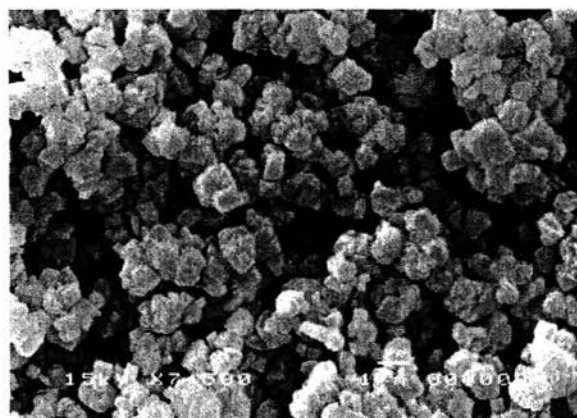


(c)

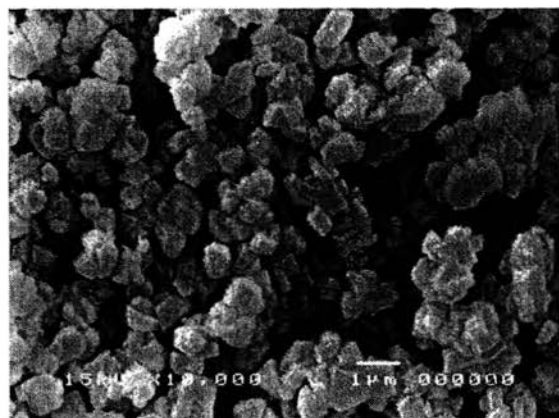


(d)

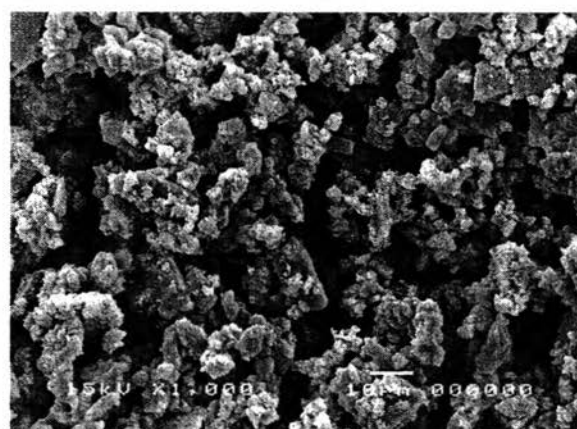
Figure 3 SEM photographs of undoped poly(3-thiopheneacetic acid) at magnifications of: (a)1000; and (b)2000 and doped poly(3-thiopheneacetic acid) 10:1 at magnifications of: (c)1000; and (d)2000.



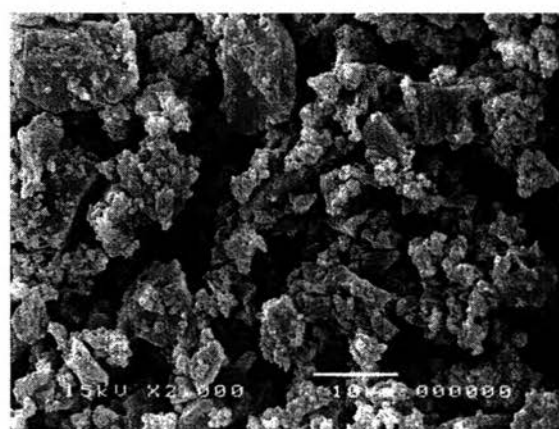
(a)



(b)



(c)



(d)

Figure 4 SEM photographs: Zeolite Y at magnifications of: (a) 7500; and (b) 10000 and Pth_10:1/Y_10% at magnifications of: (a) 1000; and (b) 2000.

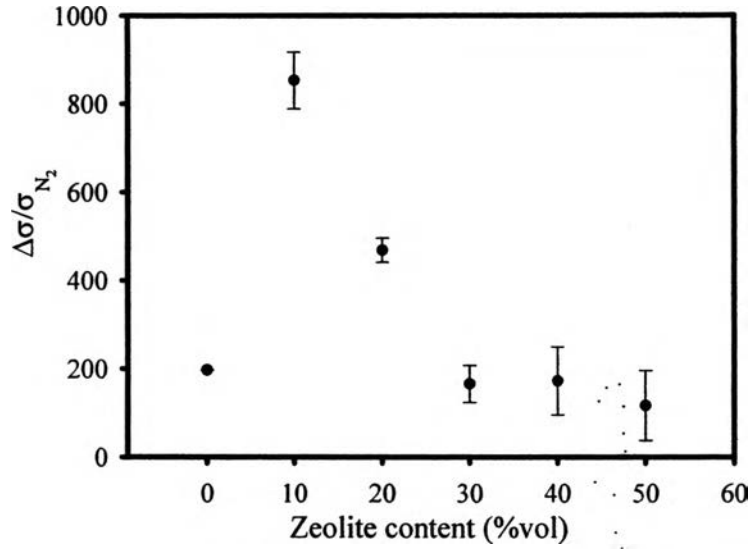


Figure 5 The electrical conductivity sensitivity ($\Delta\sigma/\sigma_{N_2}$) versus zeolite content (%vol) of 10:1 dPth/NaY composites when exposed to NH_3 at 26 ± 1 °C and at 1.1 atm; data shown were obtained from at least two samples.

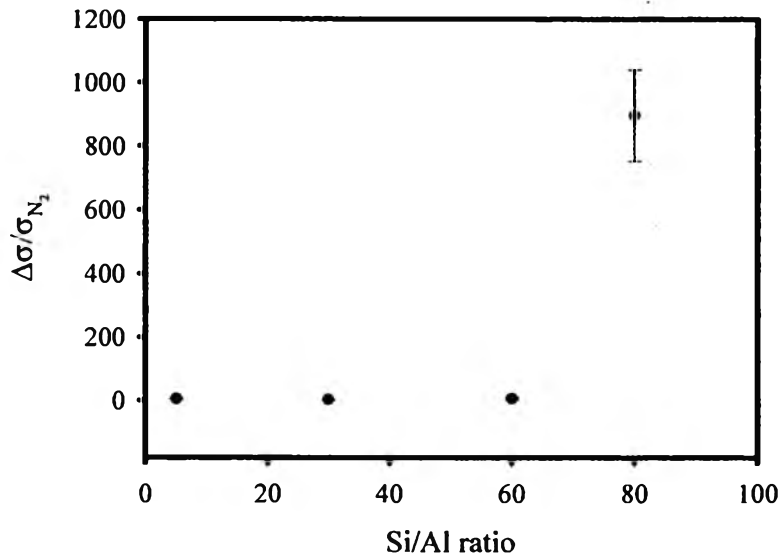


Figure 6 The electrical conductivity sensitivity ($\Delta\sigma/\sigma_{N_2}$) versus Si/Al ratios of 10:1 dPth/HY composites when exposed to NH_3 at 26 ± 1 °C and at 1.1 atm; data shown were obtained from at least two samples.

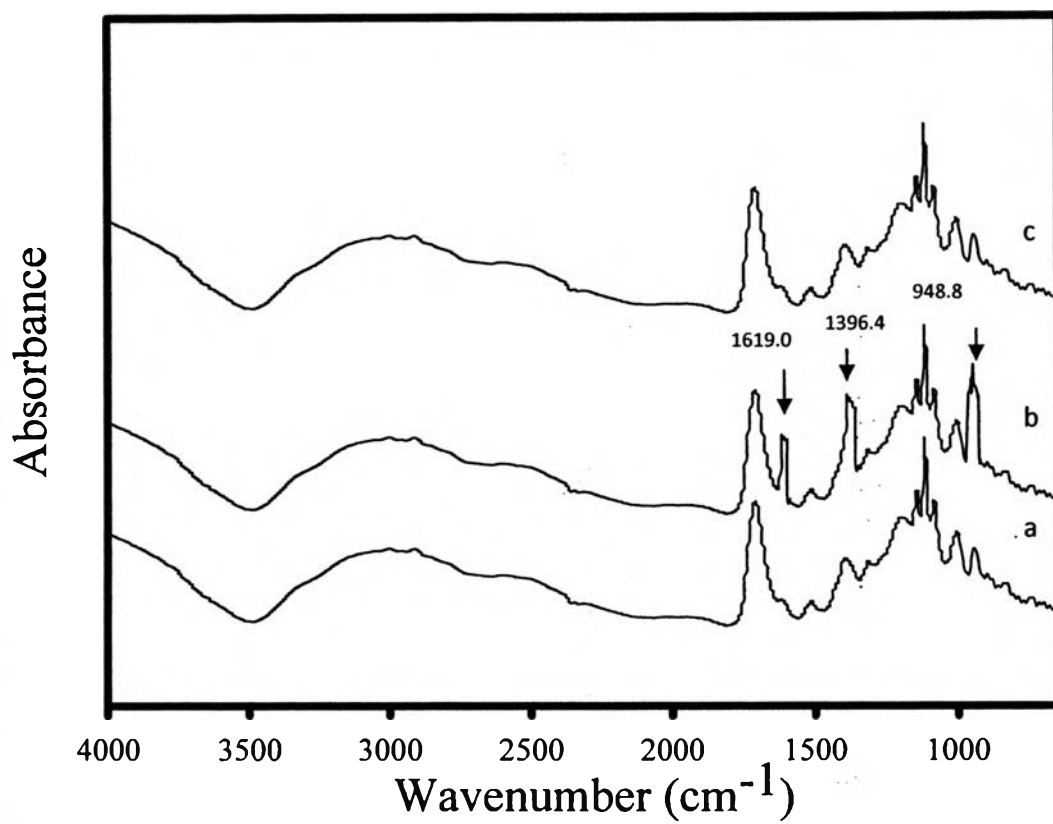


Figure 7 The FT-IR spectra of Pth_10:1: (a) before; (b) during; and (c) after the exposure to NH_3 .

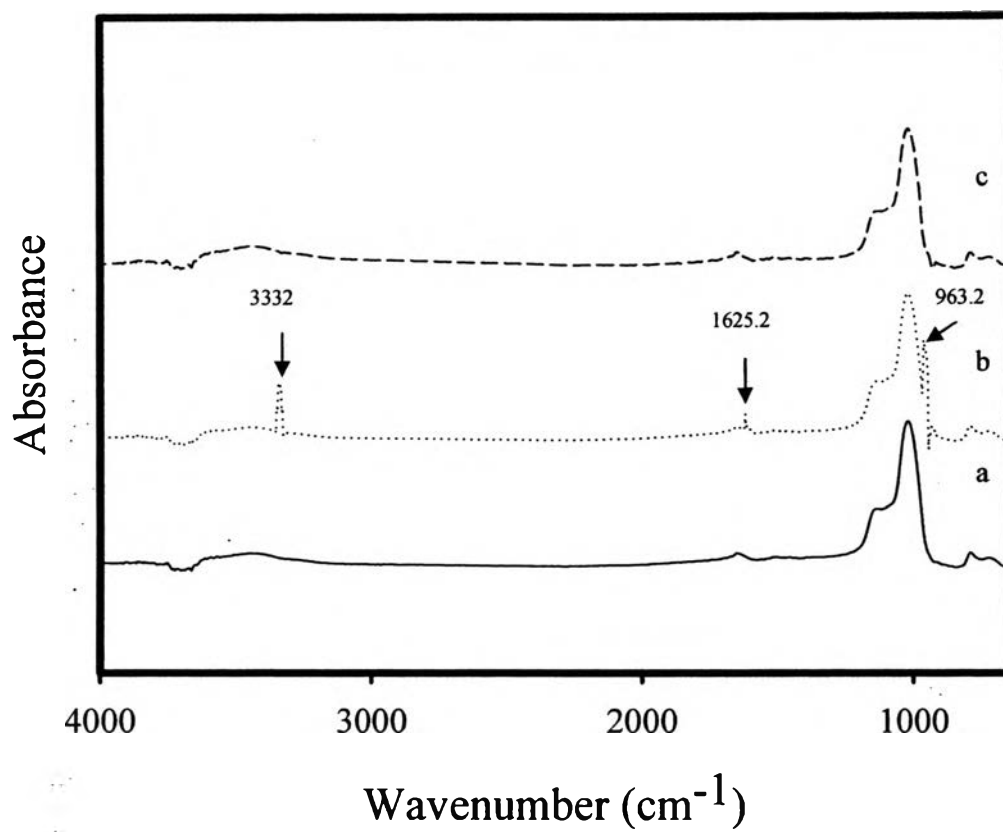


Figure 8 The FT-IR spectra of zeolite NaY: (a) before; (b) during; and (c) after exposure to NH_3 .

References

- [1] Brantley B. Characterization of nanocomposite materials for ammonia gas sensor application. USF 2004.
- [2] Bai H, and Shi G. Gas sensors based on conducting polymers. *Sensors*, 2007; 7: 267-307.
- [3] Puvanattvattana T, Chotpattananont D, Hiamtup P, Niamlang S, Kunanuruksapong R, Sirivat A, and Jamieson AM. Electric field induced stress moduli of polythiophene/polyisoprene suspensions: Effects of particle conductivity and concentration. *Materials Science and Engineering C*, 2008; 28: 119–128.
- [4] Ma XF, Li G, Xu H, Wang M, and Chen H. Preparation of polythiophene composite film by in situ polymerization at room temperature and its gas response studies. *Thin Solid Films*, 2006; 515: 2700–2704.
- [5] Chuapradit C, Wannatong R, Chotpattananont D, Hiamtup P, Sirivat A, and Schwank J. Polyaniline/zeolite LTA composite and electrical conductivity response toward CO. *Polymer*, 2005; 46: 947-953.
- [6] Kim BS, Chen L, Gong J, Osada Y. Titration behavior and spectral transitions of water-soluble polythiophene carboxylic acids. *Macromolecules*, 1999; 32: 3964-3969.
- [7] Thuwachaowsoan K, Chotpattananont D, Sirivat A, Rujiravanit R, Schwank JW. Electrical conductivity responses and interactions of poly(3-thiopheneacetic acid)/zeolites L, mordenite, beta and H₂. *Materials Science and Engineering B*, 2007; 140: 23–30.
- [8] Chotpattananont D, Sirivat A, and Jamieson AM. Electrorheological properties of perchloric acid-doped polythiophene suspensions. *Colloid Polym Sci*, 2004; 282: 357-365.
- [9] Chen TA, Wu X, and Rieke, RD. *J. Am. Chem. Soc.*, 1995; 117: 233-244.
- [10] Norma B, Castagnola and Dutta PK. Spectroscopic Studies of Colloidal Solutions of Nanocrystalline Ru(bpy)₃²⁺-Zeolite Y. *J. Phys. Chem. B*, 2001; 105: 1537-1542.

- [11] Phumman P, Niamlang S, Sirivat A. Fabrication of poly(p-phenylene)/Zeolite composites and their responses towards ammonia. *Sensors*, 2009; 9: 8031-8046.
- [12] Yahiro H, Konda Y, Okada G. Conductivity of zeolite/PTFE composite membrane in the presence of water vapor. *Phys. Chem. Chem. Phys.*, 2003; 5: 620–623.
- [13] Soontornworajit B, Wannatong L, Hiamtup P, Niamlang S, Chotpattananont D, Sirivat A, Schwank J. Induced interaction between polypyrrole and SO₂ via molecular sieve 13X. *Materials Science and Engineering B*, 2007; 136: 78–86.
- [14] Shirazi L, Jamshidi E, Ghasemi MR. The effect of Si/Al ratio of ZSM-5 zeolite on its morphology, acidity and crystal size. *Cryst. Res. Technol.* 43, 2008; 12: 1300 – 1306.
- [15] Zecchina A, Marchese L, Bordiga S, Paze C, Gianotti E. Vibrational Spectroscopy of NH₄⁺ Ions in Zeolitic Materials. An IR Study, 1997; 101: 10128-10135.
- [16] Densakulprasert N, Wannatong L, Chotpattananont D, Hiamtup P, Sirivat A, Schwank J. Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. *Materials Science and Engineering B*, 2005; 117: 276–282.
- [17] Yin F, Blumenfeld L, Gruver V, Frippait JJ. NH₃ as a probe molecule for NMR and IR study of zeolite catalyst acidity. *J Phys Chem B*, 1997; 101: 1824-1830.
- [18] Zecchina A, Geobaldo F, Lamberti C, Ricchiardi G, Bordiga S, Turnes Palomino P.G., Reply to Comments on "N₂ Adsorption at 77 K on H-Mordenite and Alkali-Metal-Exchanged Mordenites: An IR Study", *J. Phys. Chem*, 1996; 48: 18883.