

Article

Electrical Conductivity Response of Poly(Phenylene-vinylene)/Zeolite Composites Exposed to Ammonium Nitrate

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Abstract: Poly(*p*-phenylenevinylene) (PPV) was chemically synthesized via the polymerization of *p*-xylene-bis(tetrahydrothiophenium chloride) monomer and doped with H₂SO₄. To improve the electrical conductivity sensitivity of the conductive polymer, Zeolites Y (Si/Al = 5.1, 30, 60, 80) were added into the conductive polymer matrix. All composite samples show definite positive responses towards NH₄NO₃. The electrical conductivity sensitivities of the composite sensors increase linearly with increasing Si/Al ratio: with values of 0.201, 1.37, 2.80 and 3.18, respectively. The interactions between NH₄NO₃ molecules and the PPV/zeolite composites with respect to the electrical conductivity sensitivity were investigated through the infrared spectroscopy.

Keywords: conductive polymer; gas sensor; poly(*p*-phenylenevinylene); ammonium nitrate; zeolite Y

1. Introduction

The combustion of petroleum products such as diesel oil, heating oil, and heavy fuel oil generates pollutant emissions in the environment. Carbon monoxide (CO) causes chest pain in heart patients, headaches, nausea and reduced mental alertness. Sulfur dioxide (SO₂) can induce lung disease and breathing problems for asthmatics. Emissions of sulfur dioxide also lead to the deposition of acid rain and other acidic compounds. Such deposition can change the chemical balance of soils which leads to the leaching of trace minerals and nutrients critical to trees and plants. In addition to those toxic gases present in atmosphere, terrorist bomb explosions are of main concern. A safe method is required to detect in advance the potential explosion via tailored gas sensors which can sense various volatiles of typical bomb chemicals: cyclotrimethylenetrinitramine (RDX), trinitrotulene (TNT), and ammonium nitrate [1-4].

Conducting polymers such as poly(*p*-phenylenevinylene) (PPV) can serve as a potential sensing material because PPV possesses good optical and electrical properties, and it can be synthesized by a relative simple technique. To obtain an analyte-specific material, the sensors should have very narrow chemical specificity with high sensitivity towards polar chemicals [5,6]. A zeolite is chosen as a selective microporous adsorbent to be introduced into the polymer matrix in order to increase sensitivity towards NH₄NO₃ [7-9]. PPV and their oligomers have been shown to be useful as active sensing materials. PPV has been shown to detect eight organic solvents (chloroform, acetone, ethanol, ethyl acetate, toluene, hexane, acetic acid, methanol, diethyl ether); their sensitivity values were between 10–40% [10]. In our work, we demonstrate further that PPV can detect NH₄NO₃ vapor, commonly found in fertilizers and explosive material industries [11]. In this paper, PPV/zeolite Y composites were prepared and electrical conductivity sensitivities of the composites under the NH₄NO₃ exposure were investigated, and data were compared with those of pristine PPV and zeolite Y. Influence of Si/Al ratios of the zeolite Y on the electrical conductivity sensitivities was studied. Based on IR spectroscopy studies, interactions between NH₄NO₃ molecules and PPV, zeolite Y, and the PPV/zeolite Y composites are proposed.

2. Experimental

2.1. Materials

α,α' -Dichloro-*p*-xylene, tetrahydrothiophene and methanol (Aldrich) were used to synthesize *p*-xylene-bis(tetrahydrothiophenium chloride) monomer. Sodium hydroxide (Merck) and hydrochloric acid (Merck) were used as the basic and the acidic reagents, respectively. Sulfuric acid (Merck) was used as the oxidant. Zeolites: CVB400 (Si/Al = 5.1, H⁺), CVB720 (Si/Al = 30, H⁺), CVB760 (Si/Al = 60, H⁺) and CVB780 (Si/Al = 80, H⁺) (all from Zeolyst) were used as the adsorbents. Ammonium hydroxide (Suksapan, Thailand) and nitric acid (Fluka) were used to make ammonium

nitrate (NH_4NO_3) as the target chemical. Nitrogen (N_2 , TIG) was used as the surface cleaning gas and to vaporize ammonium nitrate. All chemicals were used without further purification.

2.2. Poly(*p*-phenylenevinylene) Synthesis and Doping Process

Synthesis of the *p*-xylene-bis(tetrahydrothiophenium chloride) monomer was achieved by reacting α,α' -dichloro-*p*-xylene with tetrahydrothiophene [12]. The precursor sulfonium polyelectrolyte was prepared in an aqueous solution by the base induced polymerization of an appropriate *bis*-sulfonium monomer. The polymerization reaction was terminated by the addition of dilute aqueous hydrochloric acid to the reaction mixture which was then dialyzed 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. Poly(*p*-phenylenevinylene) (PPV) was obtained by heating pol[*p*-xylene-bis(tetrahydro-thiophenium chloride)] under vacuum at 180 °C for 6 hours [12]. 18 M sulfuric acid was used as a dopant solution at the mole ratios between PPV repeating unit per sulfuric acid equal to 1:300. The doping process occurred after adding the dopant solution to a polymeric powder, and it was monitored by observing the color changes of the powder from bright yellow to black [13].

2.3. Composite Preparation

dPPV/zeolite composites were prepared by dry mixing doped PPV particles with the zeolites at a volume ratio equal to 10:90. The composites were compressed into a disc form by using a hydraulic press at a pressure of 6 kN.

2.4. Characterization

FT-IR spectrometry (Bruker, model FRA 106/S) was used to characterize functional groups. A scanning electron microscope (SEM, JEOL, model JSM-5200) was used to study the morphology of PPV, doped PPV, the zeolites, and PPV/zeolite composites at magnifications of 1,500 and 5,000 and at 15 kV. BET (Sorptomatic-1990) was used to measure the pore sizes and the surface areas of the zeolites. A custom made two-point probe with a linear geometric array was used to measure the specific electrical conductivity of samples.

2.5. Electrical Conductivity and Gas Measurements

The electrical conductivity of the PPV pellets under exposures to air, N_2 , and NH_4NO_3 were measured using a custom made two-point probe which was connected to a voltage supplier (Keithley, 6517A), in which its voltage was varied and the resultant current was measured. The electrical conductivity was calculated by using the equation: $\sigma = (I/KVt)$, where I is the measured current (A), V is the applied voltage (V), t is the thickness, and K is the geometric correction factor of the two-point probe as determined by calibrating the probe with a silicon wafer with a known resistivity value. The electrical conductivity response and sensitivity of the composites were determined by following the equations: $\Delta\sigma = \sigma_{\text{NH}_4\text{NO}_3} - \sigma_{\text{N}_2, \text{initial}}$ and $\Delta\sigma/\sigma_{\text{N}_2, \text{initial}}$, respectively. $\Delta\sigma$ is the difference in the specific electrical conductivity (S/cm), $\sigma_{\text{N}_2, \text{initial}}$ is the specific electrical

conductivity in N_2 before exposure (S/cm), and $\sigma_{NH_4NO_3}$ is the specific electrical conductivity under NH_4NO_3 exposure (S/cm).

3. Results and Discussion

3.1. Electrical Conductivity Sensitivity of PPV, dPPV and Zeolite Y Exposed to NH_4NO_3

The electrical response ($\Delta\sigma = \sigma_{NH_4NO_3} - \sigma_{N_2\text{initial}}$ [S/cm]) of each sample was calculated by the difference between the saturated electrical conductivity when exposed to NH_4NO_3 and the steady state conductivity value when exposed to pure N_2 at 1 atm and 30 ± 2 °C. Due to appreciable differences in initial conductivity between various composites, the sensitivity (sensitivity = $\Delta\sigma/\sigma_{N_2}$), defined as the electrical conductivity response divided by the electrical conductivity when exposed to pure N_2 , will be used for comparison purposes.

When PPV and dPPV is exposed to NH_4NO_3 at 377 ppm, its electrical conductivity increases and the corresponding electrical conductivity sensitivity values are 5.55×10^{-2} and 9.65×10^{-1} , respectively. The positive increment of the sensitivity upon exposed to NH_4NO_3 implies that NH_4NO_3 molecules act as a primary and secondary dopants for PPV and dPPV, respectively, resulting in a greater number of charges along the polymer backbone.

In this study, the zeolites Y having different Si/Al ratios (Si/Al = 5.1, 30, 60, 80, H^+) were selected to investigate the effect of Si/Al ratios on the electrical conductivity sensitivity towards NH_4NO_3 . Figures 1(a)–(d) show that the zeolites have nearly the same morphology. In addition, the zeolites Y with different Si/Al ratios possess nearly the same surface areas, pore sizes, and densities. When the zeolites Y are exposed to NH_4NO_3 at 377 ppm, the electrical conductivity values increase by one order of magnitude, relative to the values when exposed to nitrogen. The electrical conductivity sensitivity, $\Delta\sigma/\sigma_{N_2}$, increases with the increasing Si/Al ratios as shown in Table 1.

A higher Si content of the zeolite Y, as accompanied by a greater amount of cations present, appears to facilitate the static interaction between oxygen on the Si molecule on the zeolite Y and NH_4NO_3 [14,15]. The dPPV/zeolite Y composites were fabricated by mixing of the dPPV and zeolite Y having different Si/Al ratios (Si/Al = 5.1, 30, 60, 80, H^+). All composites contain 90% by volume of the zeolites Y. Zeolite Y particles appear to possess the irregular shape of crystals and appear to be inhomogeneously dispersed in the polymer matrix [15].

Figures 2(a)–(c) show the response of the doped PPV, Zeolite Y (Si/Al = 5.1, H^+) and dPPV/zeolite Y (Si/Al = 5.1, H^+) composite when exposed to NH_4NO_3 . It is obvious that the doped PPV and the dPPV/zeolite Y composite show comparable increases in electrical conductivity when exposed to NH_4NO_3 whereas the zeolite Y exhibits a slight increase in its electrical conductivity. Table 2 tabulates the electrical conductivity sensitivities and the induction times of the doped PPV/zeolite Y composites having different Si/Al ratios. It can be seen from the Table 2 that a higher sensitivity is observed for the composite containing a higher Si/Al ratio. A similar trend is observed for the induction times; a longer induction time is required for the composite with a higher Si/Al ratio. The composite with a higher Si/Al ratio corresponds with the zeolite containing a greater amount of cations which induces a more favorable interaction between NH_4NO_3 molecules and the active sites on the conductive polymer chain [16].

Figure 1. SEM micrographs of the dPPV/zeolite Y composites having different Si/Al ratios (magnification 1,500, 15 kV).

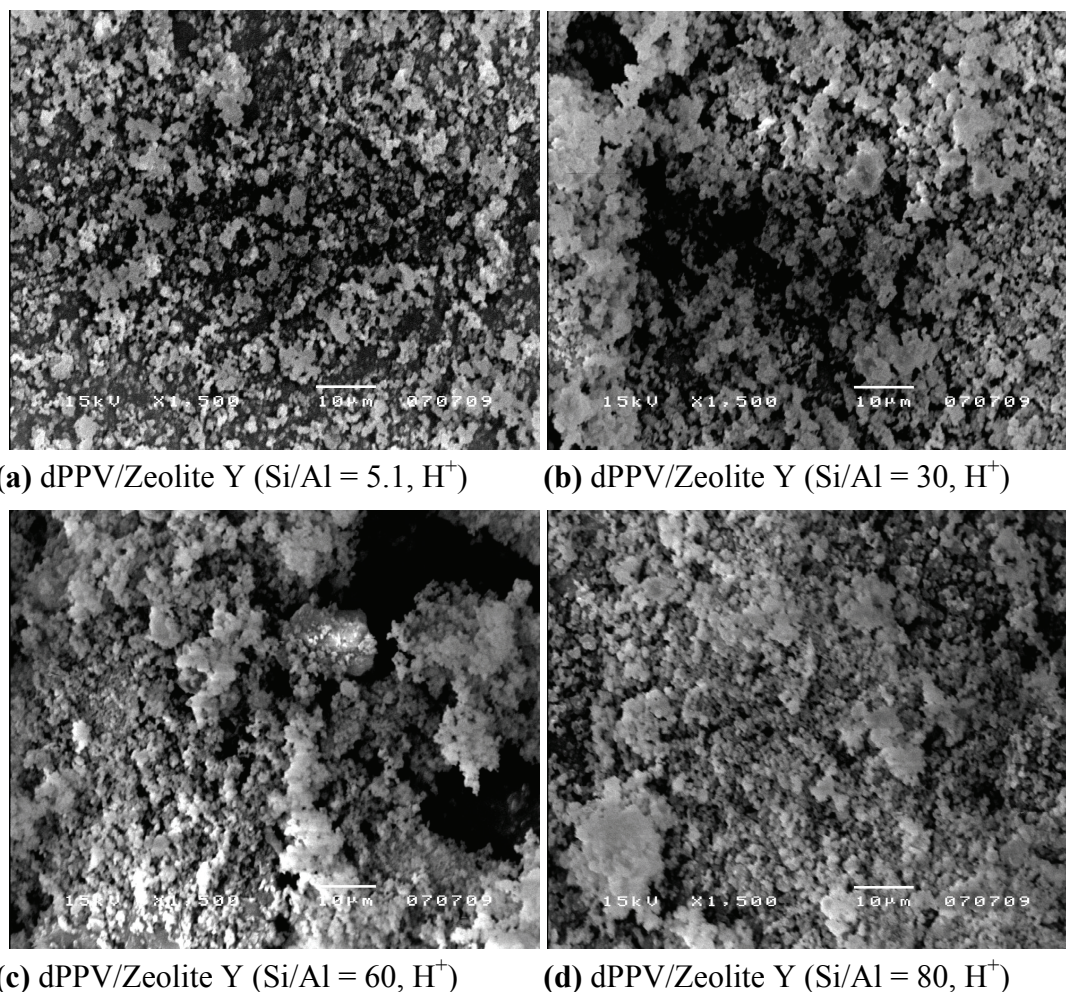


Table 1. Surface areas, pore size and electrical conductivity sensitivity of the zeolites and the electrical conductivity sensitivity when exposed to NH₄NO₃.

Zeolite	BET surface area (m ² /g)	Median Pore width (°A)	Apparent Density (g/cm ³)	Sensitivity ($\Delta\sigma/\sigma_{N_2}$)
Zeolite Y (Si/Al = 5.1, H ⁺)	864 ± 5.65	10.75 ± 0.0025	2.0046 ± 0.34	1.21 × 10 ⁻¹ ± 7.88 × 10 ⁻³
Zeolite Y (Si/Al = 30, H ⁺)	780 ± 0.35	9.56 ± 0.0982	1.8331 ± 0.27	1.98 × 10 ⁻¹ ± 1.81 × 10 ⁻²
Zeolite Y (Si/Al = 60, H ⁺)	740 ± 28.99	10.74 ± 0.0254	2.0102 ± 0.07	3.83 × 10 ⁻¹ ± 2.55 × 10 ⁻³
Zeolite Y (Si/Al = 80, H ⁺)	728 ± 4.35	10.10 ± 0.0212	2.0048 ± 0.36	4.64 × 10 ⁻¹ ± 2.15 × 10 ⁻²

Figure 2. The responses of: (a) doped PPV; (b) Zeolite Y (H^+ , Si/Al = 5.1); and (c) dPPV/Zeolite Y (H^+ , Si/Al = 5.1).

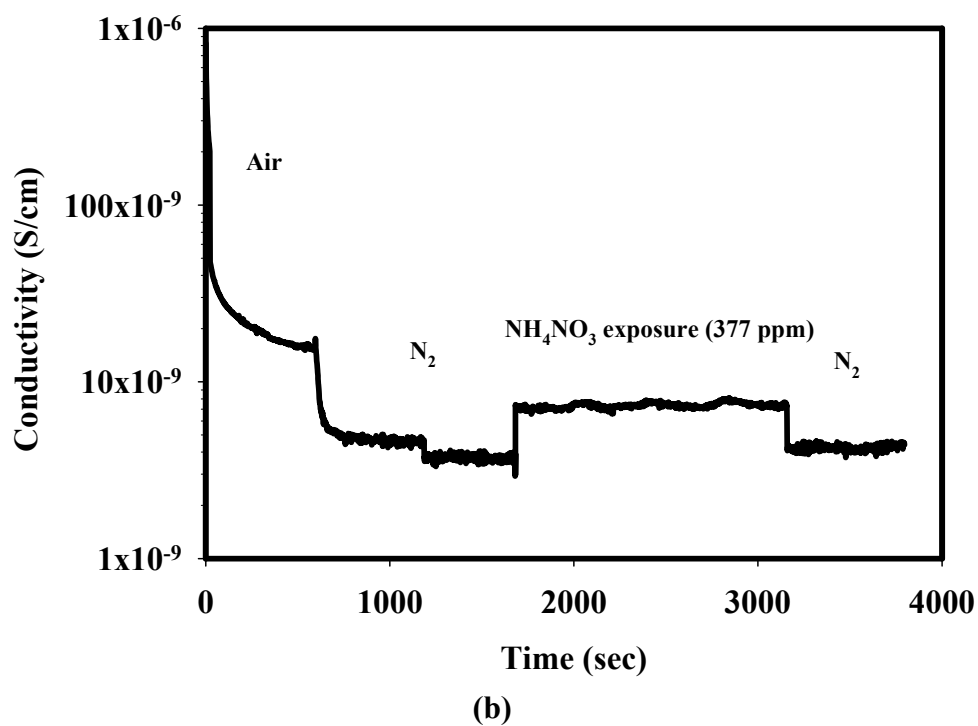
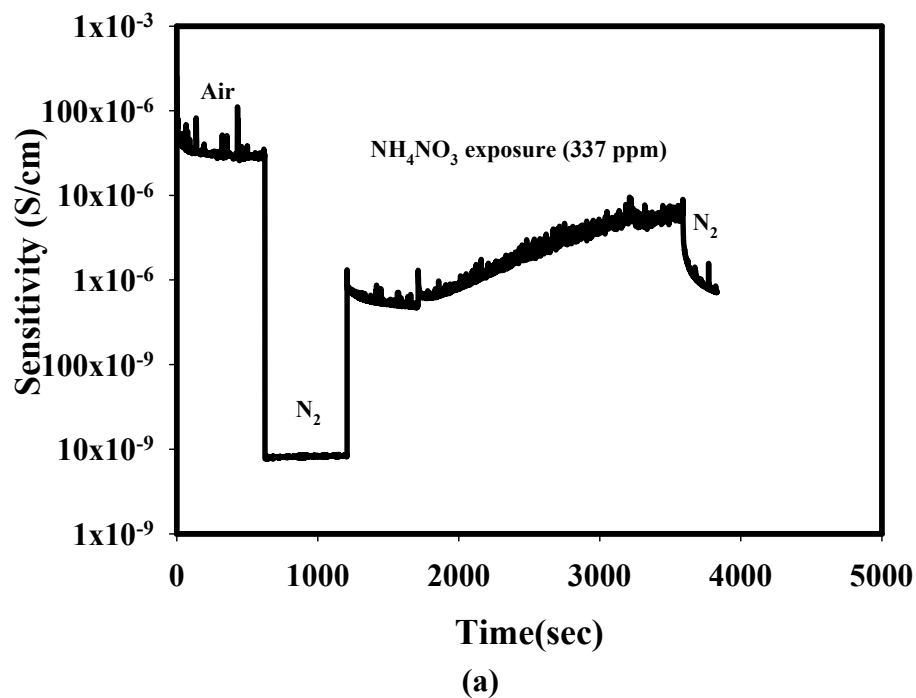


Figure 2. Cont.

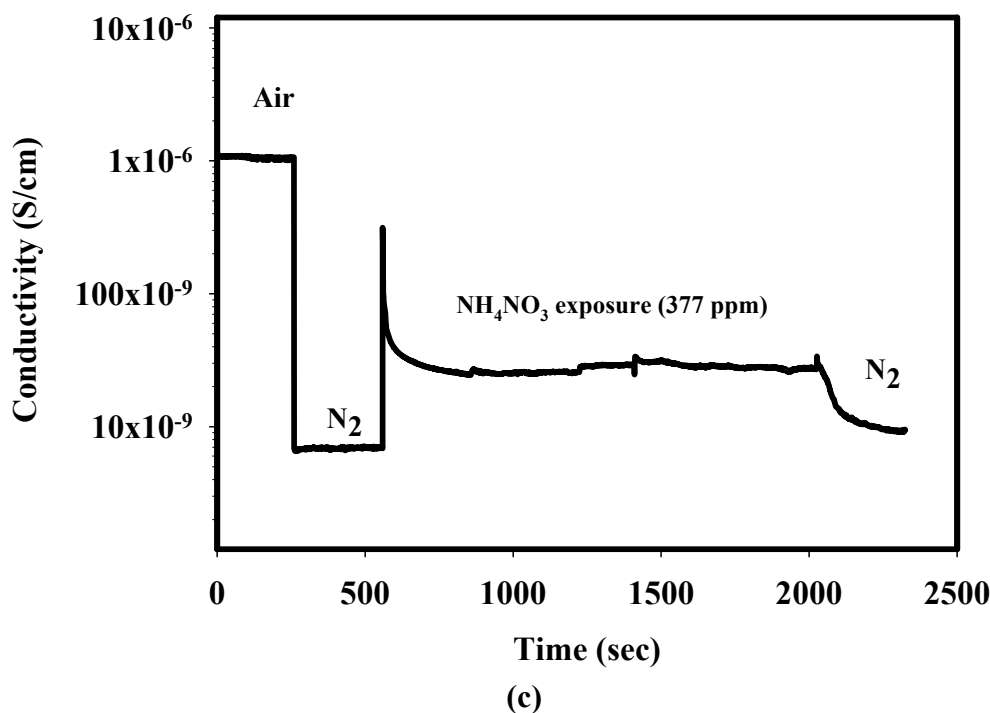


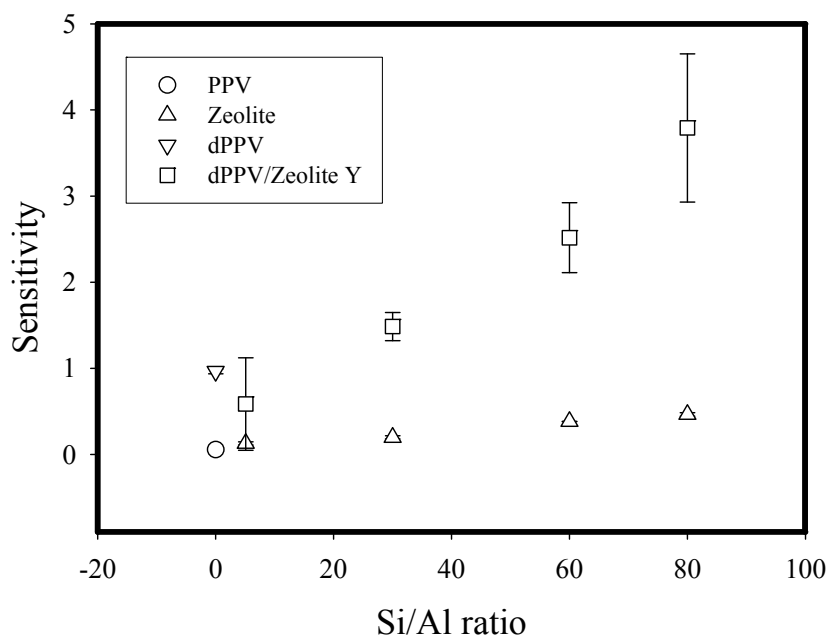
Table 2. The electrical conductivity sensitivity and the induction and recovery times the dPPV/90%Zeolite Y composites when exposed to NH_4NO_3 .

Sample	$\Delta\sigma$ ($\sigma_{\text{NH}_4\text{NO}_3} - \sigma_{\text{N}_2}$) (S/cm)	Sensitivity ($\Delta\sigma/\sigma_{\text{N}_2}$)	Induction time (minutes)	Recovery time, t_r (minutes)
dPPV/90% Zeolite Y (Si/Al = 5.1, H^+)	$2.60 \times 10^{-3} \pm 3.57 \times 10^{-3}$	$5.86 \times 10^{-1} \pm 5.37 \times 10^{-1}$	41 ± 11	23 ± 8
dPPV/90% Zeolite Y (Si/Al = 30, H^+)	$1.73 \times 10^{-4} \pm 1.64 \times 10^{-4}$	$1.48 \times 10^0 \pm 1.64 \times 10^{-1}$	34 ± 11	47 ± 14
dPPV/90% Zeolite Y (Si/Al = 60, H^+)	$1.61 \times 10^{-3} \pm 2.20 \times 10^{-3}$	$2.52 \times 10^0 \pm 4.06 \times 10^{-1}$	91 ± 23	38 ± 6
dPPV/90% Zeolite Y (Si/Al = 80, H^+)	$9.73 \times 10^{-5} \pm 2.02 \times 10^{-5}$	$3.79 \times 10^0 \pm 8.60 \times 10^{-1}$	118 ± 38	20 ± 10

σ = electrical conductivity values, $\Delta\sigma$ = the electrical conductivity response, and $\Delta\sigma/\Delta\sigma_{\text{N}_2}$ = electrical conductivity sensitivity, at $T = 28 \pm 1$ °C, and at atmospheric pressure.

Figure 3 shows that all of the composites have larger sensitivity values than that of the pristine PPV and the doped PPV with the corresponding sensitivity values of 5.55×10^{-2} , 9.65×10^{-1} , respectively. The increase in the sensitivity values of PPV/zeolite composites relative to those of the pristine PPV and the doped PPV reflects the fact that NH_4NO_3 molecules can adsorb into the zeolites by the electrostatic interaction. Therefore, under this condition, a larger amount of NH_4NO_3 molecules are available to interact with dPPV chains.

Figure 3. Electrical conductivity sensitivity of PPV, dPPV, Zeolite Y, and dPPV/zeolite Y composites of different Si/Al ratios.



3.2. FTIR Investigations of Reactions of Adsorbed NH_4NO_3 .

FTIR spectra of a dPPV, a zeolite Y and a dPPV/zeolite Y composite were taken. The spectra of samples were collected before, during at 15 minutes interval, and after the NH_4NO_3 exposure, in order to study the interaction between the samples and NH_4NO_3 . The IR spectrum of NH_4NO_3 recorded in the $700\text{--}3,500\text{ cm}^{-1}$ region (not shown here) exhibits the vibrational stretching frequencies of the free NH_4^+ molecules at $3,330, 3,300\text{ cm}^{-1}$ [16,17] and of the free NO_3^- molecules at $1,300\text{--}1,350\text{ cm}^{-1}$, $815\text{--}840\text{ cm}^{-1}$ [18].

Figure 4 shows the IR spectra of the zeolite Y ($\text{Si/Al} = 5.1, \text{H}^+$) before the NH_4NO_3 exposure, during the NH_4NO_3 exposure, and after the NH_4NO_3 exposure. Before the NH_4NO_3 exposure, the IR spectrum shows a peak at $3,640\text{ cm}^{-1}$ which can be assigned to the silanol group [19]. During NH_4NO_3 exposure, the IR spectrum shows two new peaks at $3,334$ and $1,625\text{ cm}^{-1}$; they can be assigned to the interaction between NH_4^+ and the oxygen molecules of the zeolite [14,17]. The peak at $1,380\text{ cm}^{-1}$ can be assigned to the interaction between NO_3^- and the oxygen molecules of the zeolite [18]. These three peaks disappears after the NH_4NO_3 exposure, and the peak at $3,663\text{ cm}^{-1}$, the stretching vibration of the silanol group, reappears. This suggests that no interaction between the zeolite and NH_4NO_3 remains and the interaction is reversible. Overall, there is no significant difference in the zeolite spectra before and after exposure to NH_4NO_3 [20-22].

Figure 4. IR spectra of the zeolite Y (Si/Al = 5.1, H^+) exposed to NH_4NO_3 ($NH_4NO_3 = 377$ ppm, pressure at 1 atm, and at $T = 25$ °C).

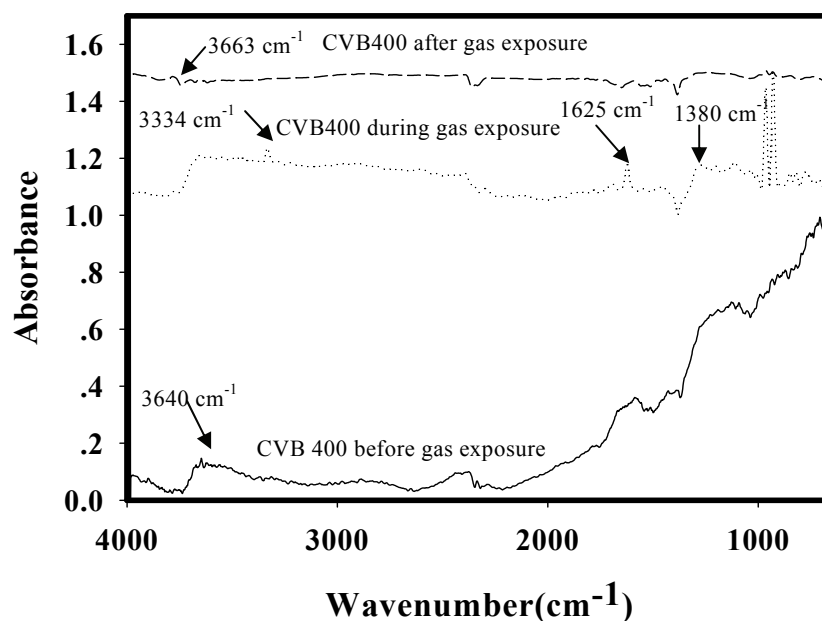


Figure 5 shows the structure of NH_4^+ , the zeolite Y structure and the interaction between NH_4^+ and the zeolite Y. Zeolite Y (Si/Al = 80) and zeolite Y (Si/Al = 5.1) have comparable specific surface areas: 728 and 868 g/cm^2 . The higher surface area induces more easily the target gas to reside in the cavity [14]. With increasing Si/Al ratio, it appears that the increase in Si in the zeolite Y structure facilitates the static interaction between NH_4NO_3 and oxygen on the Si molecule in the zeolite Y. Increasing the static interaction between the target gas and zeolite in turn improves the sensitivity of the PPV/zeolite Y composites as described previously [23,24].

Figure 5. The structures of: (a) NH_4NO_3 ; (b) Zeolite Y structure; and; (c) the interaction between NH_4NO_3 and a zeolite.

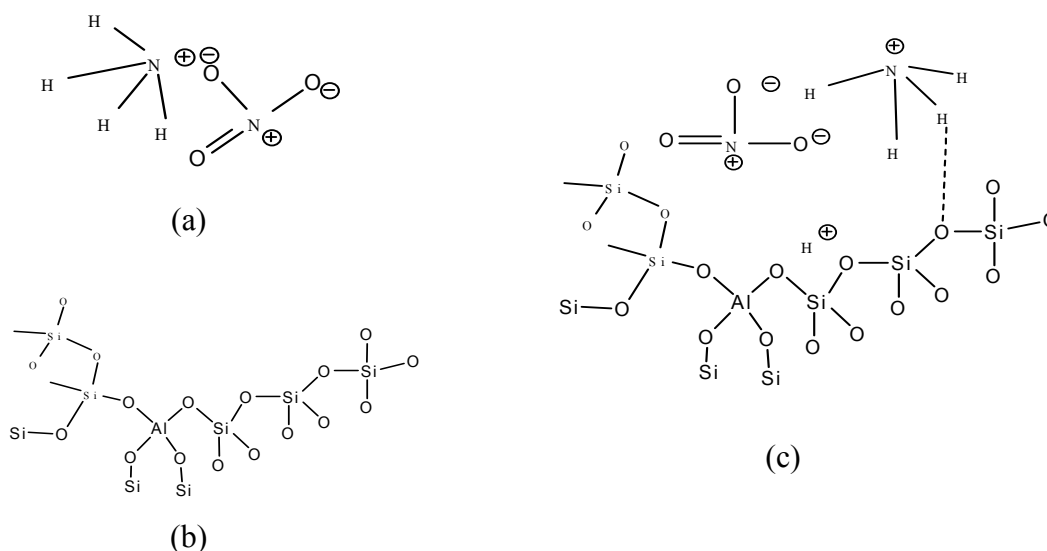


Figure 6 shows the IR spectrum of a dPPV before the NH_4NO_3 exposure, during the NH_4NO_3 exposure, and after the NH_4NO_3 exposure. Before the NH_4NO_3 exposure, the IR spectrum shows a peak at $1,170\text{ cm}^{-1}$ which can be assigned to the quinoid structure, peaks at $1,519$ and $3,022\text{ cm}^{-1}$ can be assigned to the phenylene characteristics [10,25]. During the NH_4NO_3 exposure, the IR spectrum shows a new peak at $3,336\text{ cm}^{-1}$ which can be assigned to the vibration of NH_4^+ . The two new peaks at $1,333$ and 830 cm^{-1} can be assigned to the vibration of NO_3^- interacting with the cation on the quinoid structure of doped PPV [18]. Increasing peak intensity at $1,172\text{ cm}^{-1}$ during the NH_4NO_3 exposure is caused by the increase in the quinoid structures in the doped PPV. The intensities of peaks at $3,019$, $1,517\text{ cm}^{-1}$ decrease after the NH_4NO_3 exposure and the peaks at $3,336$, $1,333\text{ cm}^{-1}$ disappear. The decreases in the intensities at $3,019$, $1,517\text{ cm}^{-1}$ after the NH_4NO_3 exposure suggest that NH_4NO_3 molecules may act as a secondary dopant and the number of the quinoid structures of DPPV increases [18]. From the FTIR result shown in Figure 6, the interaction between the doped PPV and a zeolite Y may be proposed as shown in Figure 7.

Figure 8 shows the IR spectra of NH_4NO_3 (pressure at 1 atm and at room temperature) adsorbed on dPPV/zeolite-Y (Si/Al = 80, H^+) before the NH_4NO_3 exposure, during the NH_4NO_3 exposure, and after the NH_4NO_3 exposure.

Figure 6. IR spectra of the doped PPV exposed to NH_4NO_3 ($\text{NH}_4\text{NO}_3 = 377\text{ ppm}$, pressure at 1 atm, and at $T = 25\text{ }^\circ\text{C}$).

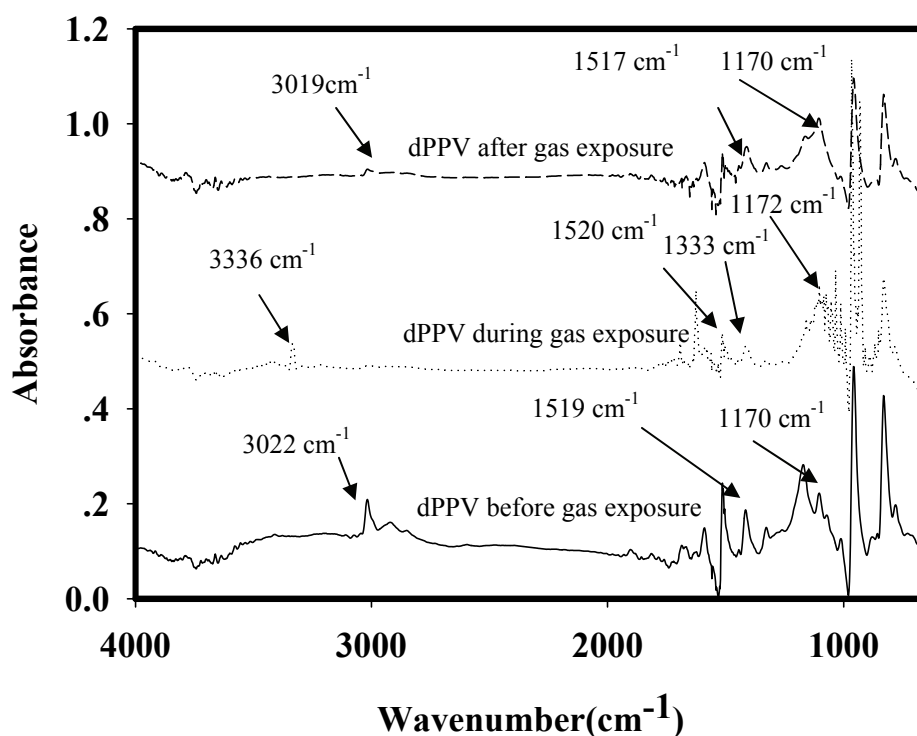


Figure 7. Schematic of the proposed mechanism of the NH_4NO_3 -dPPV.

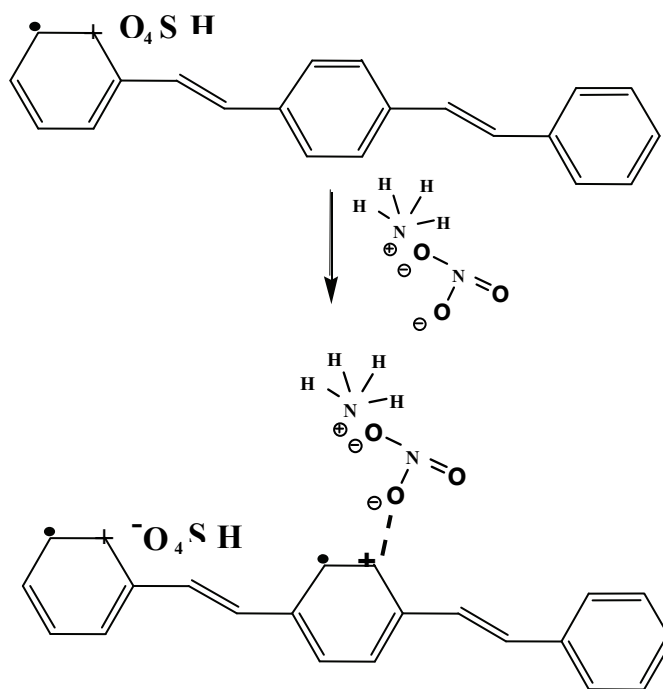
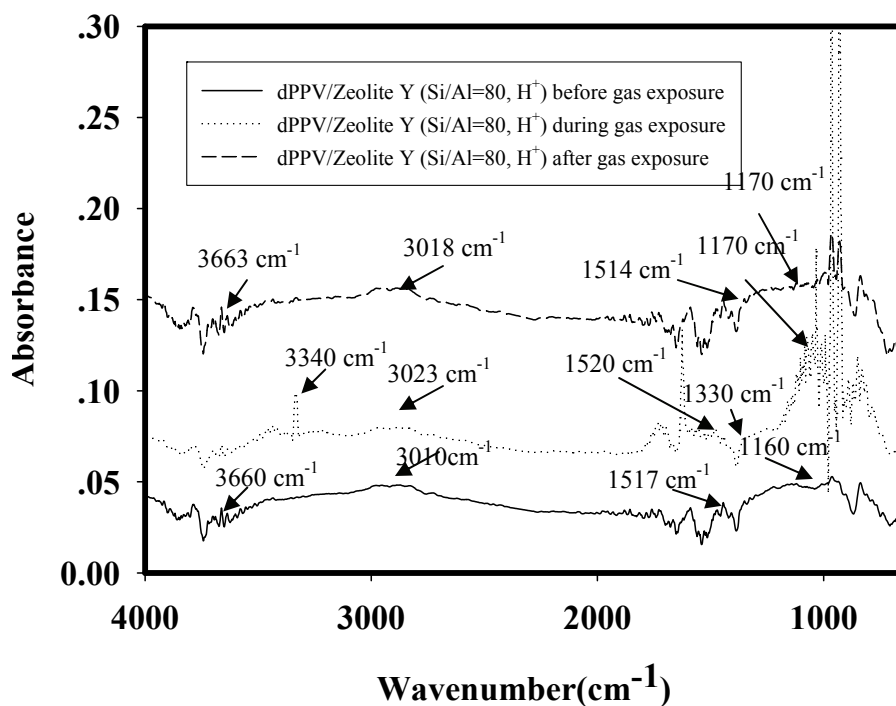


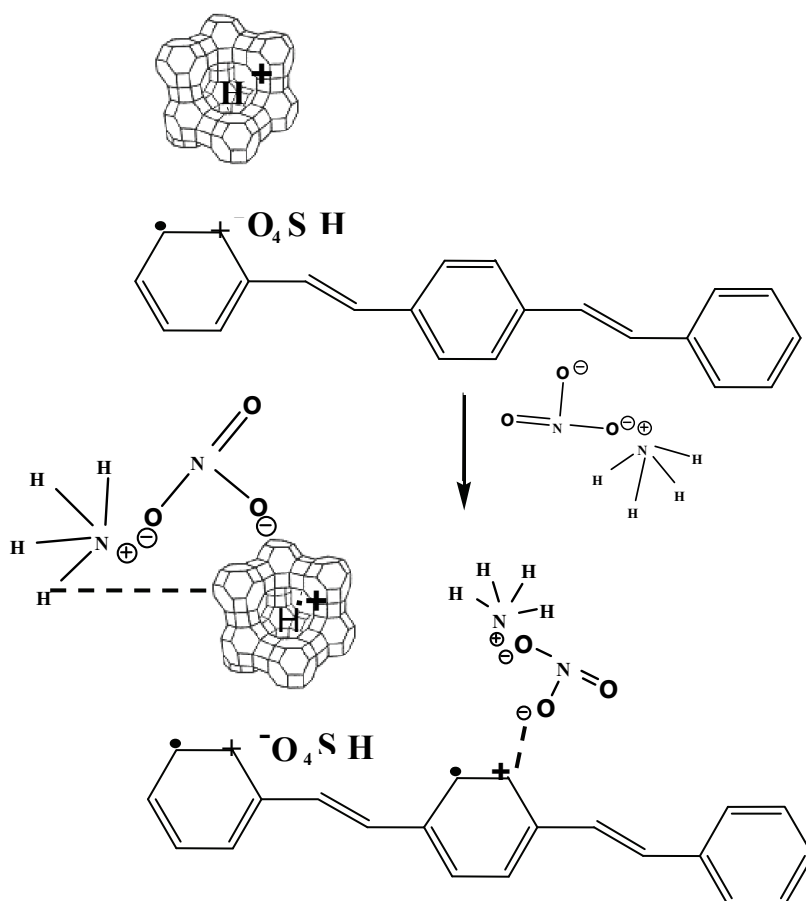
Figure 8. IR spectra of dPPV/zeolite Y (Si/Al = 80, H^+) exposed to NH_4NO_3 ($\text{NH}_4\text{NO}_3 = 377$ ppm, pressure at 1 atm and at $T = 25$ °C).



Before the NH_4NO_3 exposure, the IR spectrum shows a peak at $1,160\text{ cm}^{-1}$ which can be assigned to the quinoid structure, peaks at $1,517$ and $3,010\text{ cm}^{-1}$ can be assigned to the phenylene characteristic [10,25], and the peak at $3,660\text{ cm}^{-1}$ can be assigned to the silanol group [19]. During the NH_4NO_3 exposure, the IR spectrum shows a new peak at $3,340\text{ cm}^{-1}$ which can be assigned to NH_4^+

interacting with oxygen on Si molecule [14,17]. The new peak at $1,330\text{ cm}^{-1}$ can be assigned to NO_3^- interacting with the cation on dPPV and oxygen on Si molecule [18]. The intensities of the peaks at $3,023, 1,520\text{ cm}^{-1}$ decrease during and after the exposure. The decreases in the intensities at $3,023, 1,520\text{ cm}^{-1}$ during and after the exposure suggest that NH_4NO_3 molecules may act as a secondary dopant. The number of the quinoid structures increases in the doped PPV structure corresponding to the intensity increase at $1,170\text{ cm}^{-1}$ during the NH_4NO_3 exposure. After the NH_4NO_3 exposure, the peaks at $3,340, 1,330\text{ cm}^{-1}$ disappear. A peak at $3,663\text{ cm}^{-1}$ is characteristic of the zeolite after the NH_4NO_3 exposure, suggesting that no interaction between zeolite and NH_4NO_3 remains [17,22]. This is the FTIR evidence for the previously proposed mechanism that zeolite Y induces a larger volume of NH_4NO_3 vapor to interact with the doped PPV and NH_4NO_3 molecules act as a secondary dopant. A previous study also suggested the interactions between a target gas and a zeolite were further induced by the presence of the zeolite [14]. Figure 9 shows a schematic of the proposed interactions between NH_4NO_3 and the dPPV/zeolite Y composites.

Figure 9. Schematic of the proposed interactions between NH_4NO_3 and the dPPV/zeolite Y composite.



4. Conclusions

Doped PPV with H_2SO_4 is utilized as a NH_4NO_3 gas sensing material due to the positive electrical conductivity response. Electrical conductivity sensitivity of the doped PPV towards NH_4NO_3 can be improved by introducing the zeolites Y into the doped PPV matrix. The effect of Si/Al ratio was

investigated at the ratios of 5.1, 30, 60, and 80. The sensitivity increases monotonically with Si/Al ratio up to 80. The increases in electrical conductivity sensitivity with increasing Si/Al ratio can be described in terms acidity or the amount of cations present on the zeolites. The dPPV/zeolite Y (Si/Al = 80, H⁺) possesses the highest sensitivity of 3.79 since zeolite Y (Si/Al=80, H⁺) has the highest acidity; it can induce a more favorable NH₄NO₃ vapor adsorption onto the composite. From FTIR investigations, the NH₄NO₃-dPPV interaction is irreversible while NH₄NO₃-zeolite interaction is reversible.

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References

1. Collins, G.E.; Buckley, L.J. Conductive polymer coated fabrics for chemical sensing. *Synth. Met.* **1996**, *78*, 93-101.
2. Heeger, A.J.; Maria, A.D. Semiconducting polymers as a material for photonic device. *Solid State Sci.* **1998**, *3*, 16-22.
3. Heeger, A.J. Semiconducting and metallic polymers: the fourth generation of polymeric materials. *Synth. Meth.* **2002**, *125*, 23-42.
4. Persaud, K.C. Polymer in chemical sensing. *Mat. Today* **2005**, *8*, 38-44.
5. Babudri, F.; Farinola, G.M.; Giancane, S.; Naso, F.; Rella, R.; Scarpa, A.; Valli, L. Deposition and application in gas sensors of thin films of a bridged chain dialkoxo PPV derivative. *Mater. Sci. Eng. C* **2002**, *22*, 445-448.
6. Bouchet, R.; Rosiri, S.; Vitter, G.; Siebert, E. Solid state hydrogen sensor based on acid doped polybenzimidazole, *Sens. Actuat. B* **2001**, *76*, 610-616.
7. Graham, S.C.; Fung, S.; Moratti, S.C.; Friend, R.H. High sensitivity radiation sensing by photo induced doping in PPV derivatives. *Synth. Met.* **1999**, *102*, 1169-1170.
8. Hagen, G.; Dubbe, A.; Retting, F.; Jerger, A.; Birkhofer, T.; Muller, R.; Rlog, C.; Moos, R. Selective impedance based gas sensors for hydrocarbons using ZSM-5 zeolite films with chromium (3) oxide interface. *Sens. Actuat. B* **2006**, *119*, 441-448.
9. Vilaseca, M.; Coronas, J.; Cirera, A.; Cornet, A.; Morante, R.J.; Santamaria, J. Gas detection with SnO₂ sensors modified by zeolite films. *Sens. Actuat. B* **2007**, *124*, 99-110.
10. Cirpan, A.; Kucukyavuz, Z.; Kucukyavuz, S. Synthesis, characterization and electrical conductivity of poly (paraphenylene vinylene). *Turk. J. Polym.* **2003**, *27*, 135-143.
11. Peres, L.O.; Mauro, R.; Fernandes, B.; Jarem, R.; Garcia, B.; Wang, S.H.; Francisco, C.; Nart, B. Synthesis and characterization of chloro and bromo substituted *p*-phenylene vinylene homopolymers and alternating copolymers. *Synth. Met.* **2006**, *156*, 529-536.

12. Wessling, R.A.; Zimmerman, R.G. Polyelectrolytes from bis-sulfonium salts. *U.S. Patent 3,401,152*, 3 November, 1966.
13. Ahlskog, M.; Reghu, M.; Noguch, T.; Ohnishi, B. Doping and conductivity studies on poly(p-phenylene vinylene). *Synth. Met.* **1997**, *89*, 11-15.
14. Zecchina, A.; Marchese, L.; Bordiga, S.; Paze, C.; Gianotti, E. Vibrational spectroscopy of NH_4^+ ions in zeolitic materials: An IR study. *J. Phys. Chem. B* **1997**, *101*, 10128-10135.
15. Break, D.W. *Zeolite Molecular Sieves*; Robert E. Krieger Publishing: Malabar, Florida, USA, 1973.
16. Densakulprasert, N.; Ladawan, W.; Datchanee, C.; Hiamtup, P.; Sirivat, A.; Schwank, J. Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. *Mater. Sci. Eng. B* **2005**, *117*, 276-282.
17. Geobaldo, F.; Lamberti, C.; Ricchiardi, G.; Bordiga, S.; Zecchina, A.; Palomino, T.; Arean, C.O. Reply to comments on “ N_2 adsorption at 77 K on H-mordenite and alkali-metal-exchanged mordenites: An IR study”. *J. Phys. Chem.* **1996**, *99*, 11167-11177.
18. Matsumoto, A.; Kitajima, T.; Tsutsumi, K. Adsorption characteristics and polymerization of pyrrole on Y-zeolites. *Langmuir.* **1999**, *15*, 7626-7631.
19. Venkatathri, N., Synthesis and characterization of high silica content silicoaluminophosphate SAPO-35 from non-aqueous medium. *Catal. Commun.* **2006**, *7*, 773-777.
20. Yang, J.C.; Dutta, P.K. Promoting selectivity and sensitivity for a high temperature YSZ-based electrochemical total NO_x sensor by using a Pt loaded zeolite Y filter. *Sens. Actuat. B* **2007**, *125*, 30-39.
21. Angell, C.L. Carbon dioxide adsorbed on Linde X and Y zeolites. *J. Phys. Chem.* **1996**, *70*, 2420.
22. Carmen, C.; Thomas, S.; Elke, L.; Alexander, B.; Wolfgang, B. Preparation and structure of In-ZSM 5 catalysts for the selective reduction of NO by hydrocarbon. *J. Phy. Chem. B* **2002**, *106*, 4085-4097.
23. Thuwachawsoan, K.; Chotpattananont, D.; Sirivat, A.; Rujiravanit, R.; Schwank, J. Electrical conductivity responses and interactions of poly(3-thiopheneaceticacid)/zeolites L, mordenite, beta and H2. *Mater. Sci. Eng. B* **2007**, *140*, 23-30.
24. Soontornworajit, B.; Wannatong, L.; Hiamtup, P.; Niamlang, S.; Chotpattananont, D.; Sirivat, A.; Schwank, J. Induced interaction between polypyrrole and SO_2 via molecular sieve 13X. *Mater. Sci. Eng. B* **2007**, *136*, 78-86.
25. Gagnon, D.R.; Capistran, J.D.; Karasz, F.E.; Lenz, R.W.; Antoun, S. Synthesis, doping, and electrical conductivity of high molecular weight poly(p-phenylene vinylene). *Polymer* **1987**, *28*, 567-573.