CHAPTER IV

FABRICATION OF POLY(*P*-PHENYLENE)/ZEOLITE COMPOSITES AS AMMONIA SENSOR

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Abstract

Poly(*p*-phenylene) (PPP) was chemically synthesized via the oxidative polymerization of benzene and doped with $FeCl_3$. Electrical conductivity response of doped PPP (dPPP) towards CO, H_2 and NH_3 was investigated. dPPP shows no response towards CO and H_2, but it shows a definite negative response to NH_3. The electricacl conductivity sensitivity of dPPP increases with increasing NH_3 concentration. In order to improve sensitivity of the sensor, ZSM-5 zeolite is added into the conductive polymer matrix. The sensitivity of the sensor increases with increasing zeolite content up to 30%. Moreover, the effect of cation type residing in the zeolite pore is investigated: including Na^+, K^+, NH_4^+ and H^+. The electrical conductivity sensitivity of the composites with different cations in the zeolite can be arranged in this order; 50:1dPPP(90)/KZ23 <50:1dPPP <50:1dPPP(90)/NaZ23 <50:1dPPP(90)/NH_4Z23 <50:1dPPP(90)/HZ23. The variation in sensitivity with cation type can be described in term of the acid-base interaction. The 50:1dPPP(90)/HZ23 possesses the highest sensitivity of -0.36 since H^+ has the highest acidity which induces more favorable NH_3 adsorption and interaction with the conductive polymer.

Keywords: Conductive polymer, Gas sensor, Poly(*p*-phenylene), Ammonia, ZSM-5

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1. Introduction

Conductive polymers (CPs) have been well-known to be able to be used in several sensing applications such as pH sensors [1], ion selective sensors [2], humidity sensors [3], biosensors [4], and also gas sensors [5]. There are several work related to gas sensing properties: polyaniline (PANi) [6]; poly(thiophene) (PTh) [7]; and polypyrrole (PPy) [8]. Poly(p-phenylene) (PPP) is a conductive polymer which possesses several advantages such as the ease of synthesis, high stability, and chemical resistance. In addition, PPP can be utilized in many other applications; rechargeable batteries, electrodes [9], and etc. PPP can be utilized as a gas sensing material because its optical and electrical properties change when exposed to particular gases [10] [11].

Toxic and flammable gases such as CO, SO_2, NH_3 and H_2 are commonly used and present in many industries. For sensing property, the interaction between those gases called target gases, and CPs can be divided into two types; either conductivity increases or decreases depending on both the undoped/doped state of the CPs and electrophilic/nucleophilic behavior of target gases [6] [11] [12] [13].

To induce or enhance the interaction between CPs and the target gases, zeolite molecular sieves have been used [14] due to their nanometric sized channel system providing a size and shape-selective properties. The adsorption properties of zeolite depend on the zeolite type, the pore size, temperature, and the cation type existing in the pore. There are two propose mechanisms of the zeolite selective adsorption [15]. First, the molecular sieve property, molecules small enough to pass through are adsorbed while larger molecules are not. Second, the zeolite chemical composition; Si/Al ratio is the major factor controlling the hydrophilic/hydrophobic properties of materials. On the other hand, the introduction of specific cations, by using the cation exchange method, can dratically alter gas adsorption properties.

In this work, we systematically investigate the effect of ZSM-5 zeolite content, on the electrical conductivity response of PPP under NH_3, CO and H_2 exposure. The effects of NH_3 concentration, ZSM-5 zeolite content, and their cation type will be reported.

2. Experiment

2.1 Materials

Benzene (AR grade) was supported from Thai aromatic Co., LTD and was freshly distilled before being used as a monomer. Aluminium chloride (AR grade, Riedel-de Haen) and Cupric chloride (AR grade, Riedel-de Haen) were used as the oxidant and the catalyst for the synthesis of poly(*p*-phenylene), respectively. Hydrochloric acid (AR grade, J.T.Baker) was used as the washing solution. Ferric chloride (AR grade, Fisher Scientific) and ethanol (99.5%, CARLO ERBA) were used in the doping of PPP. ZSM-5 zeolite (SiO_2/Al_2O_3: 23) in powder form was purchased from Zeolyst International. Sodium chloride, potassium chloride and lithium chloride, (AR grade, Ajax Finechem), were utilized in the cation exchange processes. Nitrogen (99%, TIG) and ammonia gas (99.99%, Poontaweporn Limited Partnership) were used to investigate the electrical conductivity responses of the composites.

2.2 Poly(p-phenylene) Synthesis

Poly(*p*-phenylene) was chemically synthesized by oxidative polymerization method described elsewhere [16] [17].The reaction between benzene, anhydrous aluminum chloride, and anhydrous cupric chloride in mole ratio of 8:2:1 was carried out at 32-37 °C under nitrogen atmosphere for 3 h. The mixture was subsequently cooled and added to ice-cold 18% hydrochloric acid. After filtration, the PPP particles were washed several times with boiling acid solution and with boiling distilled water and then dried at 110 °C for 3 hr.

2.3 Poly(p-phenylene) Doping

The doping of PPP with $FeCl_3$ in this work was adapted from Shiga *et al.* [18] and performed by suspending the PPP particles in 100 ml of $FeCl_3$-ethanol solutions at 60 °C in the 50:1 mole ratio between dopant and PPP monomer. After the mixture was filtered, the doped PPP was dried at ambient temperature under vacuum for 12 h.

2.4 Preparation of the Zeolitic Materials

The starting ZSM-5 material with SiO_2/Al2O_3 ratios of 23 was in an ammonium form (NH_4ZSM-5). The cation exchange process was carried out by using the conventional method [19], the mixture of 1 g zeolite per 100 ml of 0.3 M NaCl solution was stirred at 90 °C for 1 hr and then filtered, washed with distillation water for several times. After the cation-exchanged zeolite was dried, the zeolite was calcined at 550 °C for 3 hr with heating rate of 1 °C/min.

2.5 Composite Preparation

PPP powder was ground, sieved with 53 μm sieve, and then dried prior to being mechanically mixed with dried zeolite powder at various zeolite amounts: 10, 20, 30, and 40 v% in order to investigate the effect of zeolite content. The dry mixed composites were subsequently pressed into a pellet by using a hydraulic press machine.

2.6 Characterization

In order to ensure the synthesis and doping of PPP were achieved, a FTIR (Nicolet, Nexus 670) was used to identify the PPP's functional groups. The thermal stability of undoped and doped PPP was investigated by using a thermogravimetric analyzer (Dupont, TGA 2950). An XRD (Phillips, Rigaku) was used to examine the crystallinity of PPP and the crystal order of zeolite. SEM (JEOL, JSM 5200) was used to observe the morphology of materials. The surface area and total pore volume of ZSM-5 zeolite were investigated by using a surface area analyzer (Quantachrome, Autosorb-1). An atomic absorption analyzer (Varian, SpectrAA 300) was used to determine the exact amount of silicon-aluminium containing in zeolite and the content of exchangeable cation in the terms of cation exchange level. The NH_3-TPD of zeolite was also carried out with the NH_3 adsorption at room temperature.

2.7 Electrical Conductivity and Gas Measurements

The electrical conductivity of PPP pellets under exposure to air, N_2 and NH_3 were measured by using a custom made two-point probe which was connected to a voltage supplier (Keithley, 6517A) in which its voltage can be changed and the current was measured. Therefore, the electrical conductivity can be calculated by utilizing 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 which can be determined by calibrating the probe with a silicon wafer possessing a known resistivity value. The electrical conductivity response and sensitivity of the composites were determined by following the equations: $\Delta\sigma = \sigma_{NH_3} - \sigma_{N_2\ initial}$ and $\Delta\sigma / \sigma_{N_2\ initial}$, respectively.

3. Results and Discussion

3.1. Characterization of Poly(p-phenylene)

The synthesized PPP shows its characteristic infrared spectra which one very strong band at 805 cm^{-1} and medium intensity bands located at 999, 1396, and 1479 cm^{-1}, corresponding to the *para* aromatic substitution. At 763 and 695 cm^{-1}, absorption peaks are assignable to the mono substitution [16] [20]. For 50:1 doped PPP, new adsorption peaks appears at 1545 and 1180 cm^{-1} are due to the intrinsic vibration of the polymer chain in a doping state. [21] [22] [23].

Thermal behaviour under air atmosphere of both uPPP and 50:1 dPPP displays single transition step decompositions at 569 °C and 480 °C, respectively. It demonstrates that uPPP is thermally and thermooxidatively stable [16]. Even dPPP is likely to be of lesser thermal stability, because doping induces the defect in the polymer chain, dPPP can still withstands heat up to 400 °C.

The XRD patterns reported uPPP have quite high degrees of crystallinity accompanying with the *d*-spacing values of 4.53, 3.63 and 3.24 Å. The most intense *d*-spacing is 4.53 Å which closely corresponds to the length of a phenyl unit [16] [24]. Therefore, it is postulated that the rings are very nearly coplanar. The shape peaks area belonging to the crystalline part decreases after doping. The mean particle size and density of PPP are 33.61 ± 0.18 μm and 1.3273 ± 0.0011 g/cm^3, respectively.

3.2. Characterization of ZSM-5 and Composites

The structure of and crystallinity of ZSM-5 is firstly confirmed by the XRD technique. The peak position and pattern can be matched with the MFI structure. The mean particle size of ZSM-5 from particle size analysis is 5.46 ± 0.01 μm, which is fairly comparable to that obtained from the SEM image. In addition, the density of the zeolite is 1.9739 ± 0.0004 g/cm^3. According to AAS data, the actual mole of Si and Al containing in ZSM-5 is calculated in terms of Si/Al ratio which is equal to 12.67. The amount of incoming cation after cation exchange process is determined under the assumption that 100% cation exchange possesses an identical mole number of incoming cation and Al. The amounts of various cations containing in the zeolite are tabulated in Table 1.

The specific surface area of ZSM-5 with various cation types (Na^+, K^+, NH_4^+ and H^+) are shown in Table 2. It is well-known that if the zeolite contains different cation, the surface area and pore volume of the zeolite are also different due to the various types of cation whose size of cation are not the same. The NH_3-TPD profiles (Fig. 1) indicates the acidic properties of zeolites with different cations. The activity follows this order: $H^+ > Na^+ > K^+$ which is similar to that of another work [25]. Figures 2 (a)-(f) show SEM images of 50:1dPPP, ZSM-5(23), and 50:1dPPP composites at various amounts of zeolite. ZSM-5 zeolite particles possess the irregular shape of crystals and appear to be unevenly dispersed in the polymer matrix.

3.3. Electrical Conductivity in Air and N_2

The specific conductivity measurement of uPPP, 50:1dPPP and its composites under air and N_2 were curried out at 28±1 °C, at 1 atm. The specific conductivity of uPPP under air atmosphere is $(1.17\pm0.07)\times10^{-5}$ S/cm. Doping uPPP contributes several orders magnitude conductivity improvement up to 0.87 ± 0.42 S/cm (Fig. 3) due to the oxidation of the π-conjugated system of the polymer. Not only doping with $FeCl_3$ causes increasing of conductivity, but also converting the brown insulating PPP powder into black conductive PPP. The counter ion or dopant species of dPPP might be $FeCl_4^{2-}$ according to simultaneous occurrence of the reduction of Fe^{3+} to Fe^{2+} and the oxidation of the π-system of PPP [26]. After introducing zeolite into polymer matrix, the conductivity decreases to 0.22 ± 0.13 S/cm with increasing zeolite content from 0% to 40%, because of the reduction of the active sites. Under N_2 atmosphere, it is clearly seen that the specific conductivity is less than that under air surrounding. This could be referred to the absence of moisture which can provide an increase in electrical conductivity [27].

3.4. Electrical Conductivity Response to CO and H_2

The electrical conductivity response ($\Delta\sigma = \sigma_{gas} - \sigma_{N_2}$) is identified by the difference in steady state electrical conductivity of the sample under target gas and N_2 exposure at 28±1 °C and 1 atm. Owing to various composites possessing different initial electrical conductivity values, the sensitivity ($\Delta\sigma / \sigma_{N_2}$), defined as the ratio of the electrical conductivity response and the electrical conductivity under pure N_2 exposure, will be used to instead of the response. The sensitivity toward target gas; CO, H_2 and 10% NH_3 are investigated.

Under CO atmosphere, dPPP shows a very small positive response with less than 5 % sensitivity as tabulated in Table 3. Due to CO behaves an electrophilic gas, CO should withdraw electrons from the polymer causing the conductivity increase [28]. Even then, CO might not be strong enough to increase the conductivity of dPPP resulting in low sensitivity. Therefore, it might be concluded that there is no interaction between dPPP and CO; if there is any interaction it appears to be very weak.

The sensitivity value of dPPP when exposed to H_2 is also very small with almost no difference in sample's conductivity under exposure of N_2 and that of H_2 as shown in Table 3. H_2 is a reducing gas [29], it has weak nucleophilic property thus when doped polymer is under H_2 exposure, H_2 may cause the decrease in conductivity. In some case, H_2 provides the conductivity enhancement [30]. However, it seems dPPP has no interaction with H_2 which may be due to the weakly giving electron of H_2 to dPPP, hence the interaction between dPPP and H_2 was not observed.

3.5. dPPP and Electrical Conductivity Sensitivity to NH_3: Effect of NH_3 Concentration

Fig. 4 shows the electrical conductivity sensitivity against with NH_3 concentration. The sensitivity of 50:1dPPP unsurprisingly increases with increasing NH_3 concentration and the negative response is also shown. Due to dPPP is *p*-type doping and NH_3 is a strong nucleophilic gas [12] which can give electron to dPPP causing the decrease in the number of charge carrier sites and the decrease of electrical conductivity, therefore, the negative response would be observed. The possible mechanism of 50:1dPPP-NH_3 interaction is proposed in Fig. 5. Due to the formations of polaron and biporalon providing dPPP electrons lying at a higher energy and having lesser stability [31] [32] with lack of electrons. When dPPP is treated with the electron rich molecules this might cause a strong interaction. These might be why the conductivity response is partially reversible when NH_3 is replaced by N_2.

3.6. dPPP/ZSM-5(23) Composites and Electrical Conductivity Response to NH_3: Effect of Zeolite Content

The electrical conductivity sensitivity of 50:1dPPP/ZSM-5(23) composites under various NH_3 concentrations versus ZSM-5 zeolite content are shown in Fig. 6. The sensitivity of 50:1dPPP under 0.625, 1.25, and 5%v NH_3 exposure increases from -0.140 ± 0.11 to -0.51 ± 0.02, -0.16 ± 0.02 to -0.79 ± 0.01, and -0.341 ± 0.03 to -0.88 ± 0.01, respectively, as NaZSM-5(23) content increases from 0 to 30%. This is because a higher zeolite content induces more NH_3 molecules to be adsorbed and to diffuse deeper into the composite [28]. Beyond this volume fraction, at 40%v zeolite, the sensitivity decreases to -0.32 ± 0.13, -0.55 ± 0.01 and -0.73 ± 0.01 for 0.625, 1.25 and 5 %v NH_3 exposure, respectively. In the case of mechanically mixed system, the decrease of sensitivity with increasing zeolite content might be due to the reduction of the active sites portion when zeolite content increases.

3.7. dPPP/ZSM-5(23) Composites and Electrical Conductivity Response to NH_3: Effect of Cation Type

In order to investigate the influence of the cation type on the sensitivity of composite, the cation containing in the zeolite was varied. There were four cations being chosen; (1) Na^+, (2) K^+, both cations are very common and was achieved at 100% exchange by the traditional cation exchange process, (3) NH_4^+, which was the purchased form of the zeolite, (4) H^+, this form of ZSM-5(23) was accomplished by the decomposition of ammonium form. To avoid the effect of zeolite content which may be predominant over the effect of cation type, dPPP/zeolite composite at 10%v is preferred to study the effect of cation type. The 50:1 dPPP composites with 10%v of ZSM-5(23) containing different cations of Na^+, K^+, NH_4^+, and H^+, are coded as 50:1dPPP(90)/NaZ23, 50:1dPPP(90)/KZ23, 50:1dPPP(90)/NH_4Z23 and 50:1dPPP(90)/HZ23, respectively. Fig. 7 shows the electrical conductivity sensitivity of 50:1dPPP, 50:1dPPP(90)/KZ23, 50:1dPPP(90)/NaZ23, 50:1dPPP(90)/NH_4Z23 and 50:1dPPP(90)/HZ23 are -0.14±0.01, -0.13±0.005, -0.22±0.003, -0.36±0.016 and -0.36±0.62, respectively. Since Na^+ is very common, Na^+ is used as a basis. The sensitivity of composite is remarkably increased when using H^+ and NH_4^+ as a balancing cation in the zeolite. This is probably due to the adsorption property of NH_3 on the ZSM-5. The sensitivity of the composites increases with the acidity of zeolite which is evidently shown in the NH_3-TPD profiles (Fig. 1). This indicate that the H-ZSM-5 with highest acidity provides a more favorable induction of NH_3 adsorption on the composite, resulting in the highest sensitivity. On the contrary, the addition of KZSM-5 into the dPPP matrix does not improve the sensitivity, but also cause the sensitivity reduction. NH_3 does not appear to adsorb on KZSM-5 because of its lowest acidity. The addition of KZSM-5 into the polymer matrix does not induce NH_3 adsorption, but seems to decrease the portion of dPPP active sites. Hence, the KZSM-5 composite had a lesser sensitivity than that of pure dPPP.

3.8. FTIR Investigations of Interactions of Adsorbed NH_3

The interaction of NH_3 and active sites of dPPP, NaZSM-5(23) and their composite was investigated via FTIR spectroscopy under pressure 1 atm and at room temperature. The FTIR spectra of 50:1dPPP before, during, and after NH_3 exposure are shown in Fig. 8. Under NH_3 exposure for 60 min of duration, FTIR spectra were taken every 5 minutes, FTIR spectra of each time have the same patterns but with different intensities evolving in time. Bands situated at 929.4, 964.3, 1398.5 and 1624.5 cm^{-1} are assigned to the vibrations of NH_3 molecules [33]. After exposed 50:1dPPP to NH_3, there is a remaining IR absorption band in the dPPP/NH_3 spectrum at 1398.5 cm^{-1} which is probably corresponds to the $C^+ \ldots NH_3$ interaction. This indicates that the interaction is irreversible which can be related to the conductivity response when replacing NH_3 by N_2. Fig. 9 shows FTIR spectra of NaZSM-5 before, during, and after NH_3 exposure. There is no significant band pattern between before and after exposed to NH_3 thus there is no irreversible interaction between NH_3 and NaZSM-5.

4. Conclusions

Doped PPP with $FeCl_3$ is utilized as a NH_3 gas sensing material due to the negative response, but it shows no response to CO and H_2. The electrical conductivity sensitivity of 50:1 dPPP toward NH_3 increases with increasing NH_3 concentration and can be then improved by introducing ZSM-5 zeolite into dPPP matrix. The sensitivity increases with zeolite content increases up to 30%. At 40% zeolite content, the positive response is present at the beginning of gas exposure and the negative response is then dominant at later times. The effect of cation type is then investigated, including Na^+, K^+, NH_4^+ and H^+. The sensitivity of the composite with different cation containing in zeolite can be arranged in this order; 50:1dPPP(90)/KZ23 <50:1dPPP <50:1dPPP(90)/NaZ23 <50:1dPPP(90)/NH_4Z23 <50:1dPPP(90)/HZ23. The sensitivity increases with various cation types can be described in term of the acidic properties. The 50:1dPPP(90)/HZ23 possesses the highest sensitivity of -0.36 since H^+ has the highest acidity which can induce the favorable NH_3 adsorption on the composite. From FTIR investigation, the NH_3-dPPP interaction is irreversible while NH_3-zeolite interaction is reversible.

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Table 1 The cation exchange level of NH_4ZSM-5(23) with Na^+ and K^+

Cation	**$[Al_3^+]$ (mmol/g zeolite)**	**[Cation] (mmol/g zeolite)**	**% Exchange**
Na^+	1.0978	1.0674	97.23
K^+	1.0978	1.0576	96.34

Table 2 Surface area and pore volume of zeolite

Zeolite	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**
NH_4ZSM-5(23)	290.1±0.85	0.1819±0.0031
HZSM-5(23)	332.6±6.51	0.2075±0.0006
NaZSM-5(23)	283.1±8.63	0.1759±0.0112
KZSM-5(23)	273.3±1.34	0.1663±0.0074

Table 3 dPPP samples with electrical conductivity responses, sensitivities and temporal responses to CO, and H_2

Samples	t_i	t_{re}	σ (S/cm)			$\Delta\sigma$ (S/cm)	$\Delta\sigma / \Delta\sigma_{N_2}$
	(min)	(min)	Air	N_2	CO		
dPPP	182	17	$(4.37\pm0.13)\times10^{-1}$	$(7.41\pm0.01)\times10^{-2}$	$(7.55\pm0.02)\times10^{-2}$	$(1.37\pm0.25)\times10^{-3}$	$(2.08\pm0.19)\times10^{-2}$

Samples	t_i	t_{re}	σ (S/cm)			$\Delta\sigma$ (S/cm)	$\Delta\sigma / \Delta\sigma_{N_2}$
	(min)	(min)	Air	N_2	H_2		
dPPP	133	10	$(7.56\pm0.21)\times10^{-2}$	$(6.00\pm0.01)\times10^{-2}$	$(6.01\pm0.01)\times10^{-2}$	$(1.66\pm2.27)\times10^{-4}$	$(5.14\pm2.62)\times10^{-3}$

t_i = the induction times, t_{re} = the recovery time, σ = electrical conductivity values in air, N_2, CO, and H_2, and the electrical response ($\Delta\sigma/\Delta\sigma_{N2}$) electrical conductivity sensitivity, at T=28±1 °C, and at atmospheric pressure.

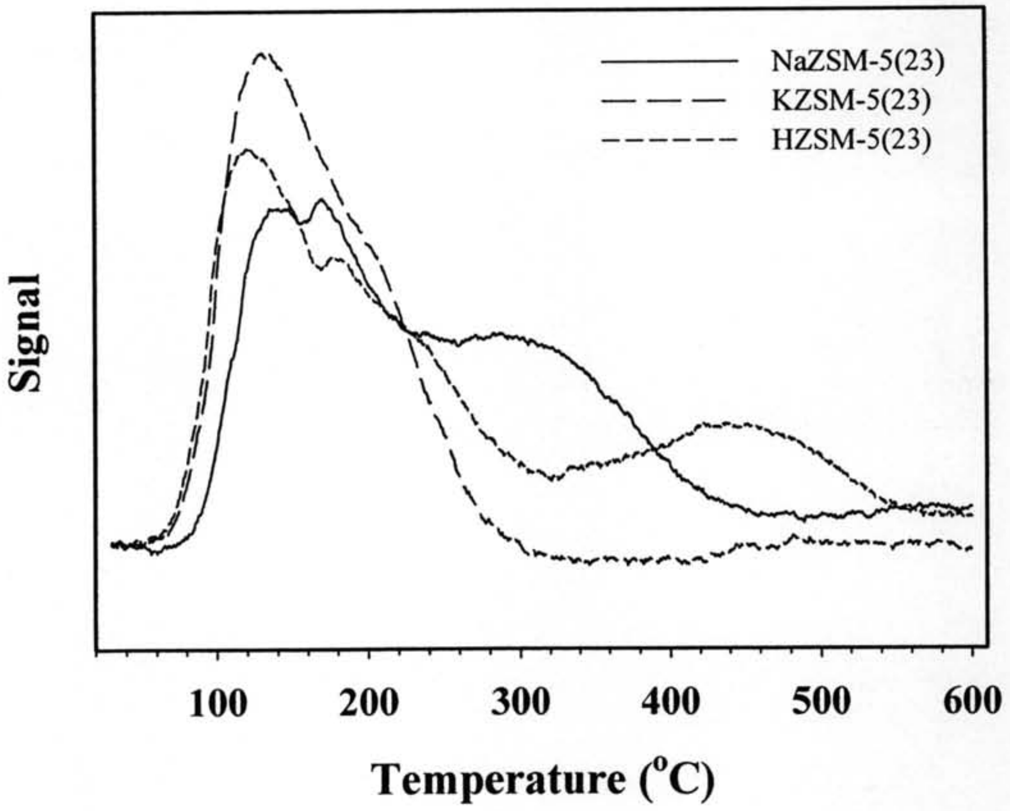
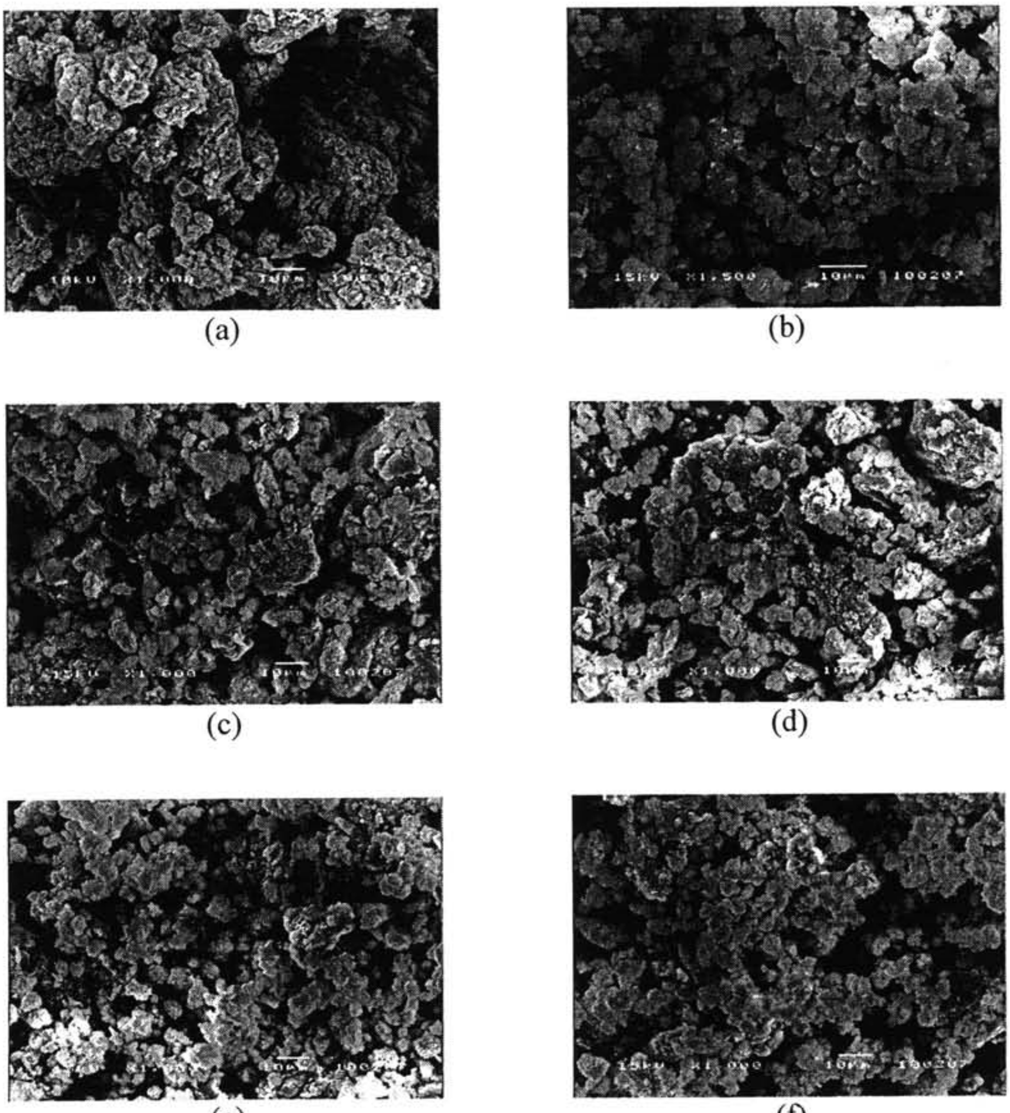


Fig. 1. NH_3-TPD thermogram of ZSM-5(23) with various cation types.



(a) (b) (c) (d) (e) (f)

Fig. 2. The morphology of dPPP particles, ZSM-5(23) powders and dPPP/zeolite composites: a) 50:1dPPP at 1000x; b) ZSM-5(23) at 1500x; c) 50:1dPPP(90)/NaZ23; d) 50:1dPPP(80)/NaZ23; e) 50:1dPPP(70)/NaZ23; f) 50:1dPPP(60)/NaZ23 at 1000x.

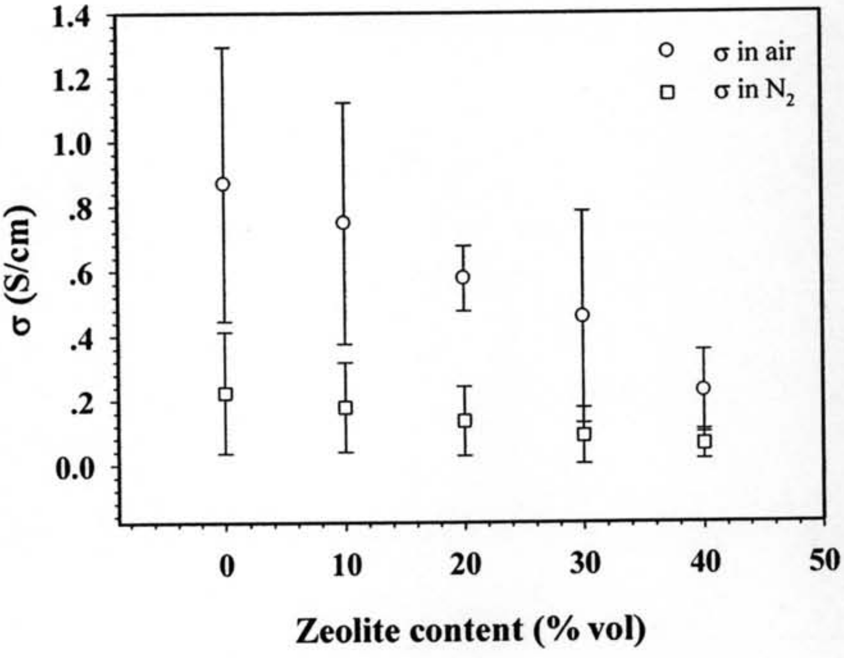


Fig. 3. σ vs. ZSM-5(23) content by volume of 50:1dPPP/NaZSM-5(23) in air and N_2 at 1 atm and 28±1 °C, the shown data are obtained form at least two samples.

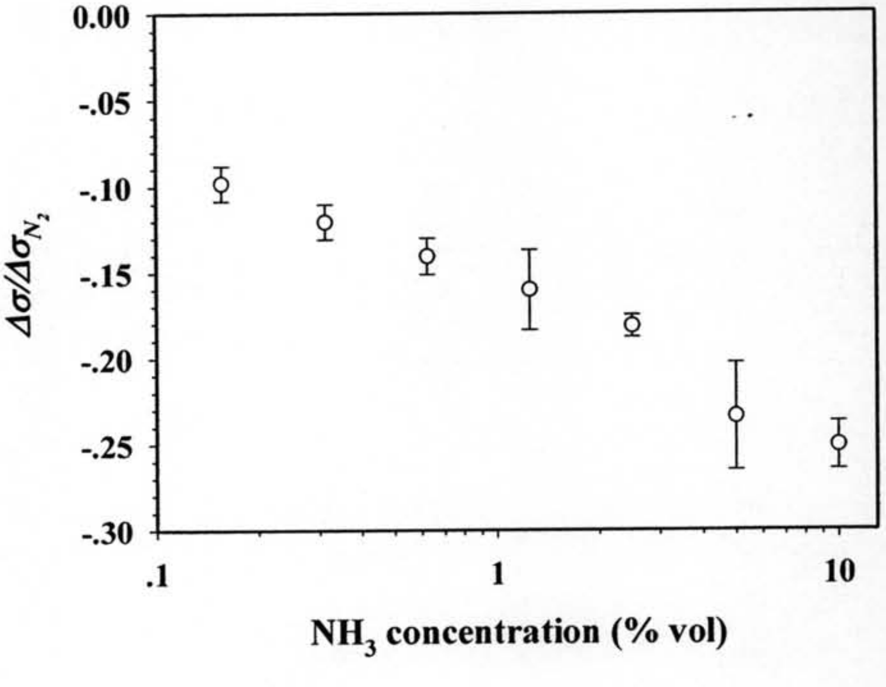


Fig. 4. $\Delta\sigma/\sigma_{N_2}$ of 50:1dPPP at various NH_3 concentrations at 29±1 °C and at 1 atm.

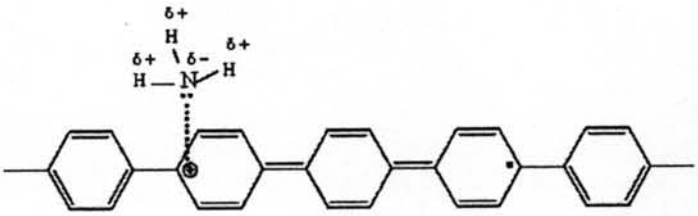


Fig. 5. Proposed mechanism of the 50:1dPPP-NH$_3$ interaction.

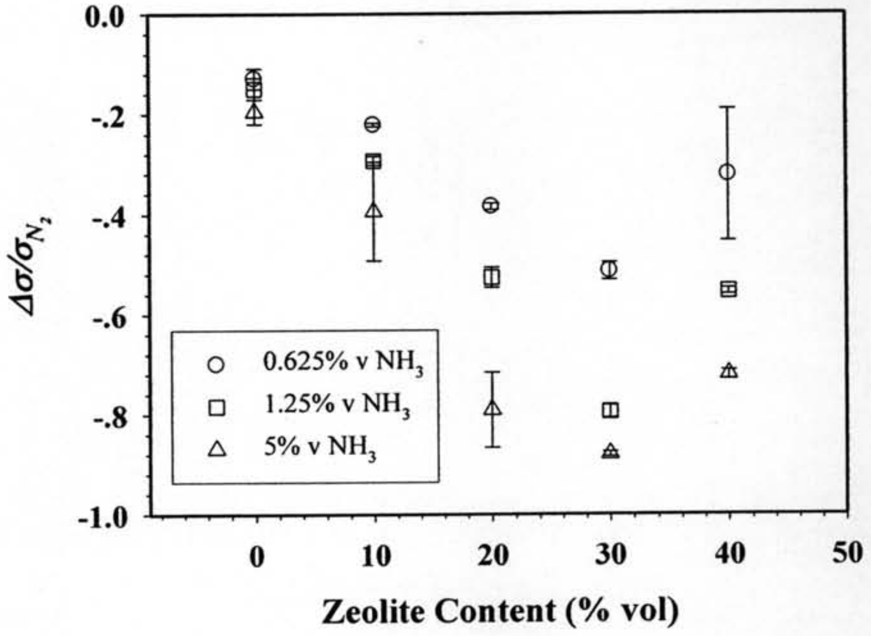


Fig. 6. $\Delta\sigma / \sigma_{N_2}$ of 50:1dPPP/NaZSM-5(23) composites to NH$_3$ at various NaZSM-5(23) contents when exposed to different NH$_3$ concentrations at 28±1 °C and at 1 atm.

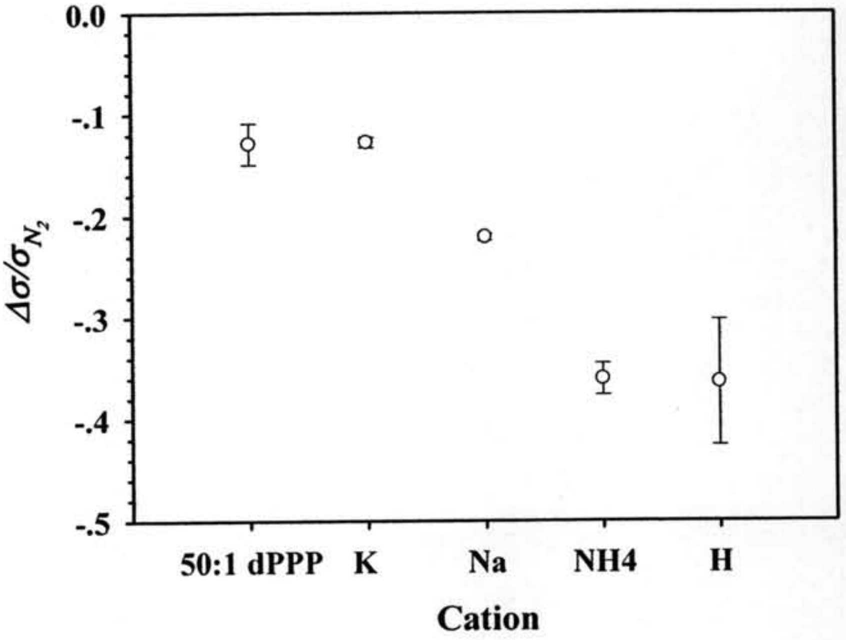


Fig. 7. $\Delta\sigma/\sigma_{N_2}$ of 50:1 dPPP and 50:1 dPPP(90)/ZSM-5(23) composites to 0.625%v NH_3 at various cation types, at 28±1 °C and at 1 atm.

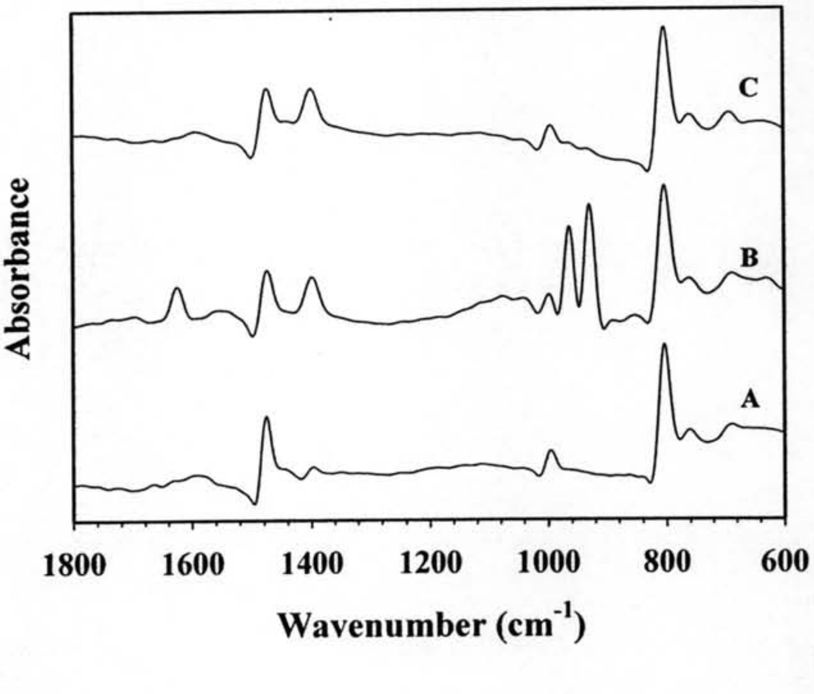


Fig. 8. FT-IR spectra of 50:1 dPPP ; **A** before; **B** during; **C** after NH_3 exposure under . 1 atm and at room temperature.

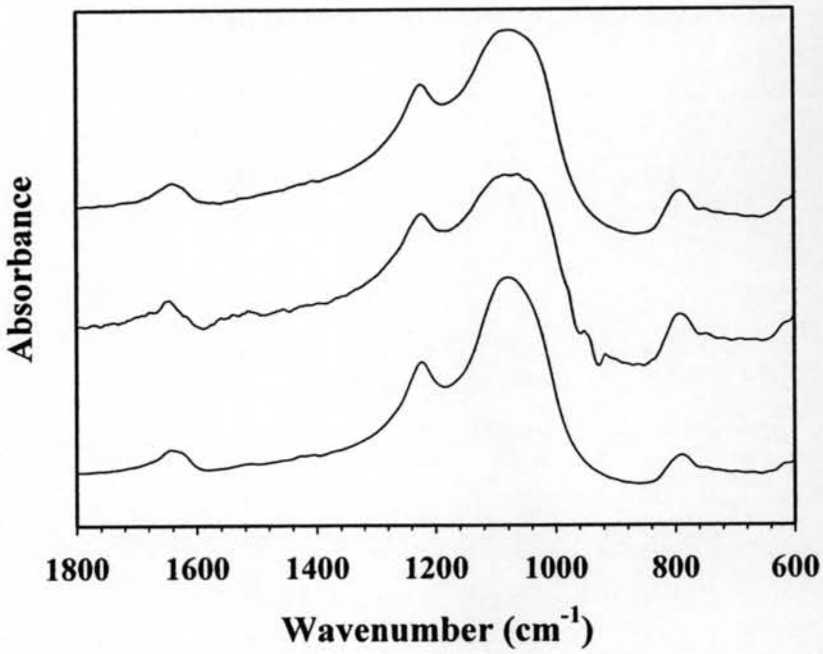


Fig. 9. FT-IR spectra of NaZSM-5(23) ; **A** before; **B** during; **C** after NH_3 exposure under 1 atm and at room temperature.

REFERENCES

[1] H. Kaden, H. Jahn, M. Berthold, Study of the glass/polypyrrole interface in an all-solid-state pH sensor, Solid State Ionics 169 (2004) 129–133.

[2] J. Migdilski, T. Blaz, A. Lewenstam, Conducting polymer-based ion-selective electrodes, Analytica Chimica Acta 322 (1996) 141- 149.

[3] R. Nohria, R.K. Khillan, Y. Su, R. Dikshit, Y. Lvov, K. Varahramyan, Humidity sensor based on ultrathin polyaniline film deposited using layer-by-layer nano-assembly, Sensors and Actuators 114 (2006) 218–222.

[4] K. Grennan, A.J. Killard, C.J. Hanson, A.A. Cafolla, M.R. Smyth, Optimisation and characterisation of biosensors based on polyaniline, Talanta 68 (2006) 1591–1600.

[5] K.C. Persaud, Polymer in chemical sensing, Materials Today 8 (2005) 38-44.

[6] S. Watcharaphalakorn, L. Ruangchuay, D. Chotpattananont, A. Srivat, J. Schwank, Polyaniline/polyimide blends as gas sensors and electrical conductivity response to CO–N_2 mixtures, Polymer International 54 (2005) 1126–1133.

[7] X. Ma, G. Li, H. Xu, M. Wang, H. Chen, Preparation of polythiophene composite film by in situ polymerization at room temperature and its gas response studies, Thin Solid Films 515 (2006) 2700–2704.

[8] L. Ruangchuay, A. Sirivat, J. Schwank, Polypyrrole/poly(methylmethacrylate) blend as selective sensor for acetone in lacquer, Talanta 60 (2003) 25-30.

[9] C. Vamstrom, A. Ivaska, An electrochemical study of poly(paraphenylene) in conductive polymer bilayer electrodes, Journal of Eleclroanalytical Chemistry 421 (1997) 67-78.

[10] D. Blackwood, M. Josowicz, Work function and spectroscopic studies of interaction between conducting polymers and organic vapors, The Journal of Physical Chemistry 95 (1991) 493-502.

[11] K. Yoshino, H.B. Gu, Effect of ammonium gas on electrical property of conductive polymers, Japanese Journal of Applied Physics 25 (1986) 1064-1068.

[12] G.E. Collins, L.J. Buckley, Conductive polymer coated fabrics for chemical sensing, Synthetic Metals 78 (1996) 93-101.

[13] N.V. Bhat, A.P. Gadre, V.A. Bambole, Investigation of Electropolymerized polypyrrole composite film: characterization and application to gas sensors, Journal of Applied Polymer Science **88** (2003) 22-29.

[14] B. Soontornworajit, L. Wannatong, P. Hiamtup, S. Niamlang, D. Chotpattananont, A. Sirivat, J. Schwank, Induced interaction between polypyrrole and SO_2 via molecular sieve 13X, Materials Science and Engineering B 136 (2007) 78–86.

[15] M. Vilaseca, C. Yague, J.Coronas, J. Santamaria, Development of QCM sensors modified by $AlPO_4$-18 films, Sensors and Actuators B 117 (2006) 143-150.

[16] P. Kovacic, and A. Kyriakis, Polymerization of benzene to p-polyphenyl by aluminum chloride-cupric chloride, Journal of the American Chemical Society 85 (1963) 454-458.

[17] P. Kovacic, J. Oziomek, p-Polyphenyl from benzene-Lewis acid catalyst-oxidant reaction scope and investigation of benzene-aluminum chloride-cupric chloride system, Journal of Organic Chemistry 29 (1964) 100-104.

[18] T. Shiga, A. Okada, T. Kurauchi, Electroviscoelastic effect of polymer blends consisting of silicone elastomer and semiconducting polymer particles, Macromolecules 26 (1993) 6958-6963..

[19] Y. Kuroda, Y. Yoshikawa, Characterization of specific N_2-adsorption site existing on CuZSM-5 type zeolite: effect of ion-exchange level on adsorption properties, The Journal of Physical Chemistry B 103 (1999) 2155-2164.

[20] S. Aeiyach, P. Soubiran, P. Lacaze, Influence of the temperature on the structure of poly(p-phenylene) (PPP) films formed by electropolymerization of benzene on platinum electrodes in sulphur dioxide medium. Polymer Communications 29 (1988) 130-131.

[21] P. Yli-Lahti, H. Stubb, H. Isotalo, P. Kuivalainen, L. Kalervo, IR behaviour, conductivity and stability of FeCl3-doped polyparaphenylene $(p\text{-}C_6H_4)_x$, Molecular Crystals and Liquid Crystals 118 (1985) 305-308.

[22] L.W. Shacklette, H. Eckhardt, R.R. Chance, G.G. Miller, D.M. Ivory, R.H. Baughman, Solid-state synthesis of highly conducting polyparaphenylene from crystalline oligomers. The Journal of Chemical Physics 73 (1980) 4098-4102.

[23] S.I. Yaniger, D.J. Rose, W.P. McKenna, E.M. Eyring, Photoacoustic infrared spectroscopy of doped and undoped poly(*p*-phenylene), Macromolecules 17 (1984) 2579-2583.

[24] C.S. Marvel, G.E. Hartzell, Preparation and aromatization of poly-1,3-cyclohexadiene, Journal of the American Chemical Society 81 (1959) 448-452.

[25] R. Kumar, W. C. Cheng, K. Rajagopalan, A. W. Peters, and P. Basu, The Effect of Exchange Cations on Acidity, Activity, and Selectivity of Faujasite Cracking Catalysts. Journal of Catalysis, 143 (1993) 594-600.

[26] A. Pron, I. Kulszewicz, D. Billaud, J. Pryluski, Organic metals reaction of $FeCl_3$ with Polyacetylene, $(CH)_x$, and poly-(p-phenylene), $(p\text{-}C_6H_4)_x$. Journal of the Chemical Society, Chemistry Communications (1981) 783-784.

[27] C. Chuapradit, L.R. Wannatong, D. Chotpattananont, A. Sirivat, J. Schwank, Polyaniline/zeolite LTA composites and electrical conductivity, Polymer 46 (2005) 947–953.

[28] N. Densakulprasert, W. Ladawan, C. Datchanee, P. Hiamtup, A. Sirivat, and J. Schwank, Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO, Materials Science and Engineering B 117 (2005) 276-282.

[29] I. Kosacki, and H.U. Anderson, Nanostructured oxide thin films for gas sensors, Sensors and Actuators B 48 (1998) 263–269.

[30] V.S. Shabnam, R.B. Kaner, and B.H. Weiller, Hydrogen sensors based on conductivity changes in polyaniline nanofibers, The Journal of Physical Chemistry 110 (2006) 22266-22270.

[31] J.R. Bredas, Theoritical studies of charged defect states in doped polyacetylene and polyparaphenylene, Molecular Crystals and Liquid Crystals 77 (1981) 319-332.

[32] J.R. Bradas, Comparative theoretical study of the doping of conjugated polymer: polarons in polyacetylene and polyparaphenylene, Physical Review, 26 (1982) 5843-5854.

[33] F. Yin, L. Blumenfeld, V. Gruver, and J.J. Fripait, NH_3 as a probe molecule for NMR and IR study of zeolite catalyst acidity. The Journal of Physical Chemistry, 101, (1997) 1824-1830.