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Polyaniline/zeolite LTA composites and electrical conductivity response towards CO

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Abstract

Electrical conductivity response of polyaniline/zeolite composites towards CO is investigated in terms of dopant type, dopant concentration, zeolite LTA content and zeolite pore size. Both MA and HCl doped polyanilines respond with comparable magnitudes towards CO; the latter responses are slightly smaller for the same doping level. Addition of zeolite 4A reduces the electrical conductivity response but improves the sensitivity towards CO with increasing zeolite concentration up to 40% w/w. This concentration is evidently below the percolation threshold value, which is estimated to be above 50% w/w. Composite with zeolite 3A has a comparable sensitivity value relative to that of pure polyaniline. Composites of 4A and 5A have greater sensitivity values over that of the pure polyaniline at the CO concentration range between 16 and 1000 ppm. Zeolite 5A is the most effective mesoporous material in promoting interaction between CO and polyaniline because of its largest pore size of 5 Å, relative to the zeolite 3A and 4A which have the pore sizes of 4 and 3 Å, respectively.

Keywords: Polyaniline; Zeolite LTA; Composite

1. Introduction

There has been considerable interest in using conductive polymers as alternatives to metal or metal oxide sensors [1,2]. Conductive polymers have several advantages for sensor applications over metallic or ceramics counterparts: low cost and relatively simple fabrication. Polyaniline (PANI) is often chosen because of its ease of synthesis and environmental stability [3]. Polyanilines deposited on a quartz substrate [4] and an alumina substrate [5] exhibit fast reversible electrical conductivity responses when exposed to gases or vapors at room temperature. Ultra thin films of polyaniline/isopolymolybdic acid have been developed as humidity and gas sensors (NH_3 and NO_2) [6]. A simple polyaniline film was employed as a sensor material to detect different vapors such as methanol, ethanol, acetone, and benzene [7]. A three-sensor array consisting of Langmuir Blodgett (LB) polyaniline films has been fabricated to detect and differentiate between vapors of water, propan-2-ol, ethyl acetate, and acetone based on pattern recognition [1]. Other LB films have also been developed based on polypyrrole (PPy) to improve sensitivity towards alcohol vapor [8], and polythiophene (PT) to detect NO_2 [9].

Zeolites are naturally and synthetically occurring aluminosilicate minerals with three-dimensional structure based on $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ polyhedra. Their corners link these polyhedra to produce an open structure that has internal cavities in which molecules of various sizes can be trapped [10]. Due to the size-and-shape selectivity of zeolite crystals and their Lewis and Bronsted acid sizes, zeolite is used for molecular gas separation and purification. Zeolite has also been used as template synthesis of polyaniline to produce nanocomposite devices [11–13]. A siliceous zeolite was used as an ethanol filtering material, coated on a CO sensing layer, to depress a high sensitivity towards C_2H_5OH

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[14]. Recently metal-substituted zeolite was used as a catalyst for the decompositions of NO_x and CO [15]. In particular, CO has been frequently used as a probe molecule on the active site of the Cu-ZSM5 zeolite [16].

Zeolite A (LTA) is normally synthesized in the Na^+ form, $Na_{12}Al_{12}Si_{12}O_{48}27H_2O$ and it has a three-dimensional pore structure. The pore diameter is defined by an eight-member oxygen ring and it is about 2.3–4.2 Å depending on the cation type. Zeolite A has a cavity with a minimum free diameter of 11.4 Å, large enough to allow CO molecules to adsorb but too small for larger molecules to enter. In this work, we investigate the influence of Zeolite A on the electrical conductivity response of polyaniline to CO exposure. The effects of zeolite amount and pore size will be reported.

2. Experimental

2.1. Materials

Aniline monomer (Aldrich) was purified by distillation under the vacuum at 50–60 °C and kept at 5 °C prior to use. Ammonium peroxydisulphate (Merck) was used as an oxidant without further purification. Analytical grade hydrochloric acid (Aldrich) and maleic acid (Fluka) was used as the dopants. Zeolites LTA (Aldrich) of three window sizes (3, 4 and 5 Å), namely 3A, 4A and 5A, were obtained in powder form. Nitrogen (TIG) was used as the carrier gas. Carbon monoxide (TIG) stock was a mixture of CO and nitrogen at 1000 ppm.

2.2. Synthesis of polyaniline emeraldine base

In this work, we followed the chemical synthesis procedure of MacDiarmid et al. [17]. 7.67 g of aniline (0.082 mol) were mixed with 89.06 ml of a 1 M HCl aqueous solution. The solution mixture was kept at 0 °C for 1 h and 98.44 ml of ammonium peroxydisulfate in 1 M HCl solution was added dropwise. Polymerization was carried out at 0 °C for 3 h. The mixture color changed from clear through a blue to a dark green. The precipitated polyaniline was then filtered and washed with a methanol/water (20:80) solution until the filtrate was completely colorless. The precipitated polyaniline (emeraldine salt, ES) was converted to the emeraldine base form (EB) by a treatment with an aqueous 0.1 M ammonium hydroxide solution at room temperature for 4 h. The polyaniline base form was washed with a methanol/water (20:80) solution and dried in a vacuum oven at 60 °C for 48 h. Finally, the polyaniline emeraldine base powder was ground with a ball mill for 3 h and sieved with a fine mesh (mesh no. 270, pore size 53 μm). The polyaniline emeraldine base powder was stored in a dessicator at room temperature for later use.

2.3. Preparation of polyaniline emeraldine salt

Powder of polyaniline emeraldine base (EB) was doped or converted into the emeraldine salt (ES) at various acid-dopant/EB mole ratios. EB powder was weighted and immersed in 1 M acid dopant solution at a particular volume. The mixture was then stirred and allowed to reach equilibrium at room temperature after a period of 48 h. Two acids were used as the dopants: hydrochloric acid (HCl) and maleic acid (MA) with the corresponding pK_a values of −6.10 and 3.19, respectively. The ES powder was filtered and then dried in a vacuum oven at 60 °C for 48 h to eliminate moisture [18].

2.4. Preparation of polyaniline emeraldine salt and composite pellets

Polyaniline particles were ground by a ball mill for a period of 3 h and sieved with a fine mesh (mesh no. 270, pore size 53 μm). 0.075 ± 0.002 g of doped polyaniline powder was pressed into a disc form under the pressure between 3 and 4 tons by a hydraulic press (Graseby) using a stainless steel die of 2.5 cm in diameter. Pellets, having a thickness about 0.01 cm, were obtained. All pellet samples were stored in a dessicator for later use. Polyaniline/zeolite LTA composites were obtained by a dry mixing method. Polyaniline powder was ground together with zeolite LTA powder which had been previously dried at 120 °C for few hours prior to the mixing. Three types of zeolite LTA were used in making our composites: 3A, 4A and 5A with the corresponding pore size diameters of 3, 4 and 5 Å, respectively. 0.075 g of polyaniline and zeolite powder was pressed into a disc form under the pressure between 3 and 4 tons be the hydraulic press using the stainless steel die of 2.5 cm in diameter. The percolation threshold for electrical conductivity of polyaniline/zeolite composites prepared by this method is approximately 50% w/w of zeolite powder.

2.5. Characterization

Elemental analysis data (Perkin–Elmer, PE2400 Series II) were obtained in the CHNS/O mode to determine the contents of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) atoms in polyaniline. The ratio of H_{acid}/N indicates the apparent doping levels of PANI-HCl and PANI-MA, the HCl-doped and MA doped polyanilines, respectively. A thermalgravimetric analyzer (DuPont, TGA 2950) was used to measure thermograms under nitrogen atmosphere 30–700 °C at a heating rate of 10 °C/min. FT-IR spectra of polyaniline pellets were taken with a spectrometer (Bruker, EQUINOX55/S) in the absorption mode with 32 scans at a resolution of 4 cm^{-1} covering the wavelengths between 400 and 4000 cm^{-1}. UV–visible spectra were recorded with a spectrometer (Perkin Elmer, Lamda 10) in the wavelength range of 290–900 nm.

Scanning electron micrographs (JOEL, 5200-2AE) were taken with magnifications of 1500 and 3000. X-ray diffraction patterns (Phillips, PW 1830/00 No. DY 1241) were recorded between 2θ 5–50°. Size distribution functions of polyaniline and zeolite samples were determined by a particle sizer (Malvern, Masterizer X).

2.6. Conductivity measurement

Custom made four-point probe and associated electrical units [19] were used to measure the electrical conductivity of synthesized polyaniline and composite pellets under atmospheric condition or when exposed to carbonmonoxide. The four-point probe built was of a linear array geometry. The voltage drop measured was converted to the electrical conductivity of polymer by using equation as following: σ $(1/\rho)$ $(1/Rt)$ $(1/K)$, where R is sheet resistivity (Ω), t is pellet thickness (cm) and K is the geometric correction factor. K was determined by using standard materials whose specific resistivity values were known. All measurements were taken at 1 atm and at 27 ± 1 °C in the linear Ohmic regime; the DC current used was between 15 and 20 mA. To study the effect of CO concentration, measurements of electrical conductivity response were made by using a specially constructed gas cell. Electrical conductivity responses ($\Delta\sigma = \sigma_{CO} - \sigma_{Final\ N2}$) were measured at CO concentrations of 1000, 500, 250, 125, 62.5, 31.25, 15.63, and 7.86 ppm through successive serial dilutions.

3. Results and discussion

3.1. Characterization of polyanilines and zeolites

Elemental analysis data of polyaniline emeraldine base (EB) give the following compositions: C, 73.8%; H, 5.31%; N, 14.2% and residual, 6.729%. The chemical formula of EB has the following compositions: C, 79.56%; H, 4.97%; and N, 15.47. The raw elemental analysis data of EB suggest some amount of oxygen, which can be attributed to small amounts of oxidant and free or bound water molecules present [18]. For the doped polyanilines, Table 1 tabulates % apparent doping levels of PANI-1HCl, PANI-10HCl, PANI-1MA, and PANI-10MA which are 64, 97, 57 and 96%, respectively. PANI-1HCl refers to HCl-doped polyaniline with the acid-emeraldine base molar ratio of 1, and vice versa.

Thermal analysis data of EB show two major step weight losses. The first step loss around 60–100 °C can be attributed to the release of free and bound dopant [20]. The second step is the decomposition of EB backbone around 510 °C [18]. The thermograms of PANI-1HCl and PANI-1MA showed a three-step weight loss behavior. The first step can be attributed to the loss of water between 50 and 90 °C. The second step weight loss appearing continuously from 190 to 250 °C is due to the loss of the dopant. The amount of

Table 1
PANI/Zeolite samples and their % apparent doping levels (DL), % degrees of crystallinity (DC), the response times (Δt_r) to CO at 1000 ppm, electrical conductivity values in air (σ_{air}), electrical conductivity values in N_2 (σ_{N2}), and the responses in electrical conductivity ($\Delta\sigma \equiv \sigma_{CO} - \sigma_{N2}$) upon exposed to 1000 ppm CO/NO_2 mixture at 27 °C, at atmospheric pressure

Samples	DL	DC	Δt_r [min]	σ_{air} [S/cm]	σ_{N2} [S/cm]	$\Delta\sigma$ [S/cm]	$\Delta\sigma/\sigma_{N2}$	a	b
PANI-1HCl	64	46	10	4.02 ± 0.32	2.66 ± 0.04	0.75 ± 0.14	0.28	2.47×10^{-2}	0.43
PANI-10HCl	97	54	35	2.93 ± 0.27	1.51 ± 0.10	0.54 ± 0.04	0.36	5.86×10^{-3}	0.74
PANI-1MA	57	43	17	$(4.10 \pm 0.02) \times 10^{-2}$	$(9.52 \pm 5.18) \times 10^{-3}$	$(4.91 \pm 0.36) \times 10^{-3}$	0.52	1.50×10^{-2}	0.51
PANI-10MA	96	56	30	3.65 ± 0.55	2.48 ± 0.32	0.54 ± 0.13	0.22	4.52×10^{-2}	0.34
PANI-10MA/ 10Zeolite 4A	96	56	30	1.85 ± 0.21	1.13 ± 0.08	0.43 ± 0.12	0.38	9.50×10^{-2}	0.22
PANI-10MA/ 20Zeolite 4A	96	56	45	1.29 ± 0.43	$(9.15 \pm 0.32) \times 10^{-1}$	0.37 ± 0.11	0.40	1.08×10^{-2}	0.52
PANI-10MA/ 40Zeolite 4A	96	56	30	0.421 ± 0.08	$(1.56 \pm 0.05) \times 10^{-1}$	$(8.15 \pm 4.95) \times 10^{-2}$	0.52	1.03×10^{-2}	0.34
PANI-10MA/ 20Zeolite 3A	96	56	30	2.21 ± 0.38	1.72 ± 0.33	$(2.12 \pm 0.18) \times 10^{-1}$	0.12	5.82×10^{-2}	0.19
PANI-10MA/ 20Zeolite 5A	96	56	45	1.52 ± 0.19	$(7.01 \pm 0.17) \times 10^{-1}$	$(4.66 \pm 0.08) \times 10^{-1}$	0.67	4.21×10^{-2}	0.34

a and b are the prefactor and the scaling exponent of the relation $\Delta\sigma$ $a[CO]^b$.

weight loss due to evaporation of moisture in PANI-1HCl (∼12%) is greater than that of PANI-1MA (∼4%). Water molecules would adsorb on two possible sites on polyaniline chain: (i) the positive charge species ($=NH^+–$) of the polymer backbone; and (ii) on dopant anions (X-site) at which water molecules would prefer to absorb than those at ($=NH^+–$) [21–23].

FT-IR spectra of PANI-HCl (of various molar ratios) show distinct absorption peaks at 825, 1161, 1297, 1493, 1586, and 3300 cm^{-1}. These peaks can be attributed to the C–H bending vibration of *para*-couple benzenoid ring, the vibration mode of, quinoid ring, the stretching vibration of C–N, the stretching vibration of *N*-benzenoid ring, the stretching vibration of *N*-quinoid ring, and the NH stretching, respectively [22,24]. The intensity peaks between 1493 and 1586 cm^{-1} increase with increasing doping level. The intensity of the absorption peak at 1161 cm^{-1} increases relative to that of the peak at 1493 cm^{-1}, evidently suggesting that some of the quinoid structure units are converted to the benzenoid structure units. For FT-IR spectra of PANI-MA (of various molar ratios), the stretching vibration bands of the *N*-quinoid ring (1586 cm^{-1}) and the *N*-benzenoid ring (1493 cm^{-1}) could not be clearly observed due to the stretching vibration of the C=C group of maleic acid between 1480 and 1600 cm^{-1}.

The UV–vis spectra of PANI-HCl in NMP solutions show peaks at 325 and 627 nm when N_A/N_{EB} is less than 2. The peak at 325 nm can be assigned to the $\pi–\pi^*$ transition. The peak at 633 nm has been assigned to the creation of a localized molecular excitation with an electron on a quinoid part and a hole on the neighboring two-benzenoid part [17, 25]. When N_A/N_{EB} is greater than 2, two new absorption peaks appear at 450 and 900 nm, which can be identified as the bipolaron and polaron species, respectively.

The X-ray diffraction pattern of EB indicates that it is typically an amorphous polymer, consisting of a compact coil structure resulting from the H-bonding between amine and imine positions. The diffraction patterns of PANI-HCl and PANI-MA consist of two components: a sharp peak corresponds to the crystalline domain and a broad band as the amorphous domain [26]. The degree of crystallinity is determined from the ratio of the sharp peak area divided by the broad-band area, assuming they were of Gaussian profile. For the lowly doped PANI-1HCl, the degree of crystallinity is 46. For the highly doped PANI-10HCl, the degree of crystallinity increases to 54. The corresponding values of the degree of crystallinity of our MA-doped polyanilines are tabulated in Table 1. Here the symbol PANI-10MA/10Zeolite 3A refers to the composite consisting of the MA doped polyaniline with the aniline monomer and MA mole ratio equal to 10, and with 10% w/w of Zeolite 3A added.

SEM micrographs show that the morphology of undoped polyaniline, PANI-HCl and PANI-MA are similar; they possess globular structures. This is because the electrostatic repulsive force between positive charges along the polymer chains is smaller than the intramolecular hydrogen bonding force between amine and imine positions. Particle size analyzer data indicate that PANI particles have a mean diameter of about 23.8 ± 1.8 μm.

The unit cell contents of zeolite 3A, 4A and 5A are $K_6Na_6Al_{12}Si_{12}O_{48}27H_2O$, $Na_{13}Al_{13}Si_{13}O_{48}27H_2O$, $Ca_{2-}Na_7Al\ _{11}Si_{11}O_{48}27H_2O$ with the corresponding quoted window sizes of 3, 4, and 5 Å, respectively. Particle size analysis data indicate that Zeolites 3A, 4A and 5A have mean particle diameters of 15.2 ± 0.14, 3.65 ± 0.02 and 7.36 ± 0.07 μm, respectively. Zeolite A samples contain some amounts of adsorbed water varying between 15 and 19% as determined by the weight loss between 120 and 200 °C from the thermogram data. The adsorbed water molecules within the zeolite structures were removed prior to mixing with PANI.

Fig. 1(a)–(c) show SEM monographs of PANI-10MA, PANI-10MA/20Zeolte 4A and PANO-10MA/40Zeolite 4A particles in the pellet form. Zeolite 4A particles appear in the monographs as white particles as can be seen in Fig. 1(b) and (c), at the weight fractions of 20 and 40%, respectively. Zeolite 4A particles appear to be moderately dispersed in the PANI matrix. Same levels of the zeolite dispersion are obtained for other composite systems: PANI-10MA/Zeolite 3A and 5A of various zeolite concentrations.

3.2. Electrical conductivity in air and N_2

In the electrical conductivity measurements of PANI and PANI/Zeolite samples in vacuum, air, pure N_2, and CO–N_2 mixtures, temperature was maintained between 27 and 28 °C. Table 1 tabulates electrical conductivity values of our samples in air. Electrical conductivity values of PANI-1HCl and PANI-1MA are 4.02 and 4.10×10^{-2} S/cm, respectively; even though % degrees of crystallinity are comparable, they differ by nearly two orders of magnitude because of differing % doping levels: 64 and 57, respectively. As the mole ratio N_A/N_{EB} increases to 10, the electrical conductivity values become comparable: 2.93 and 3.65 S/cm. Here, % doping levels and % degrees of crystallinity of the highly doped polyanilines are nearly the same as shown in Table 1. As zeolite 4A is added to PANI-10MA, its electrical conductivity value in air decreases from 3.65 S/cm for pure polyaniline to 1.85, 1.29 and 0.421 S/cm for the composites with zeolite contents of 10, 20 and 40% w/w, respectively. Fig. 2 shows the electrical conductivity in air of PANI-10MA/*x*Zeolite 4A vs. zeolite content, *x*, which varies between 0 and 50% w/w; it decreases monotonically with increasing zeolite content but still remains of order one, suggesting that the percolation threshold is above 50% w/w. For the effect of zeolite type at a fixed zeolite content of 20% w/w, the electrical conductivity values are 2.21, 1.29 and 1.52 S/cm for the composites with zeolites 3A, 4A and 5A added, respectively. The variations in the pore size and the particle size appear to have small effect on electrical conductivity of our composites fabricated.

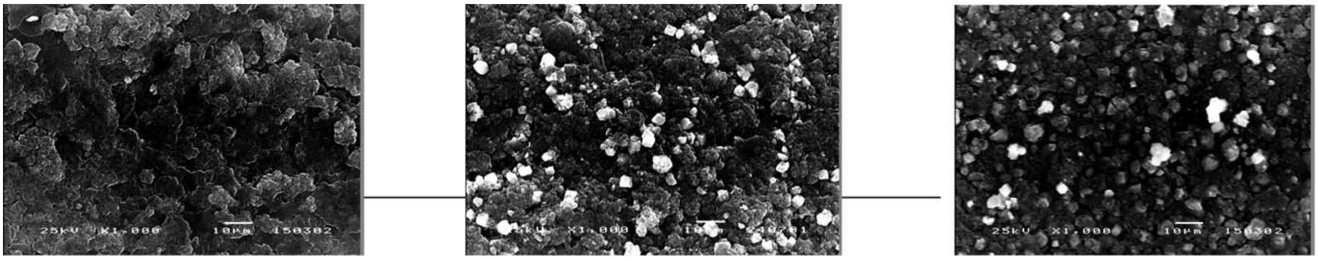

Fig. 1. SEM monographs of: (a) PANI-10MA particles: (b) PANI-10MA/20Zeolite 4A; and (c) PANI-10MA/40Zeolite 4A.

When PANI-HCl, PANI-MA, PANI-MA/Zeolite composites are exposed to pure N_2 instead of air, their electrical conductivity values decrease slightly. For examples, it decreases from 3.65 to 2.48 S/cm for PANI-10MA, and from 1.52 to 0.70 S/cm for PANI-10MA/20Zeolite 5A. Electrical conductivity values of other composites under N_2 exposures are tabulated in Table 1. A likely cause for higher values in air is the interaction of O_2 at the active site; it would replaces or coexists along with the negatively charged counter ion X^- at the positively charged $-NH^{\cdot +}-$ or the polaron species. This interaction is reversible within few percents. The other possible cause is the effect of moisture present in air [22,27].

3.3. Electrical conductivity in CO–N_2 mixtures

Next, we investigate the electrical conductivity response of PANI and PANI/Zeolite when exposed to CO at 27–28 °C and at 1 atm. The electrical conductivity response is defined as the difference between the equilibrium conductivity value when exposed to a particular CO concentration and that when exposed to pure N_2 under the same temperature and pressure ($\Delta\sigma \equiv \sigma_{CO} - \sigma_{N2}$). Table 1 lists the electrical conductivity responses of all our composites tested. The responses of PANI-1HCL, PANI-10HCl, PANI-1MA, and PANI-10MA are 0.75, 0.54, 4.91×10^{-3}, and 0.54 S/cm, respectively. The corresponding sensitivity values, defined as the ratio between $\Delta\sigma/\sigma_{N2}$, are 0.28, 0.36, 0.52, and 0.22, respectively. Generally, it appears that the response and sensitivity increase with doping level.

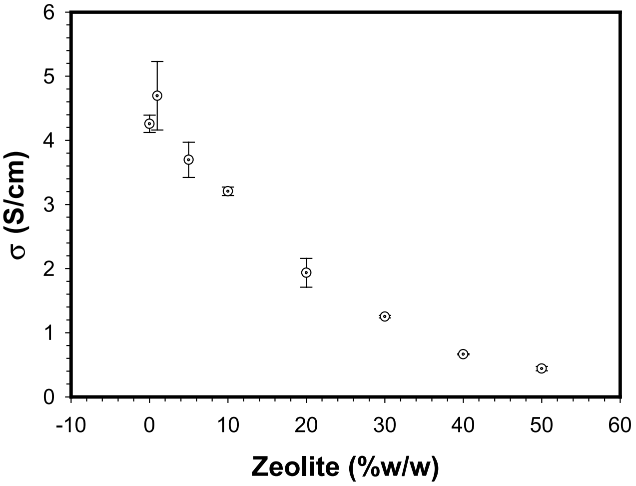

Fig. 2. σ vs. zeolite 4A content by weight of PANI-10MA/Zeolite 4A in air at 1 atm and 27–28 °C.

When zeolite 4A is added, the sensitivity to CO is improved. The sensitivity values are 0.22, 0.38, 0.40 and 0.52 for PANI-10MA composites with zeolite content of 0, 10, 20, and 40%, respectively. Evidently, the zeolite contents are still below the percolation threshold value and we expect that the sensitivity value to diminish beyond that. Thus the addition of a microporous material, such as zeolite A, to a conductive polymer seems to enhance the sensitivity towards CO detection.

At zeolite content fixed at 20% w/w, the sensitivity values towards CO of PANI-10MA/Zeolite 3A, 4A, and 5A are 0.12, 0.40, and 0.67, respectively. Therefore, the larger pore size assists in trapping CO molecules and allowing interaction with the conductive polymer.

The temporal response time is the time required for the electrical conductivity value to rise from its initial value towards the equilibrium value when exposed to CO. Table 1 tabulates the response times, Δt_r, of all our composites investigated. The response time appears to increase with doping level, from 17 to 35 min for PANI-1MA and PANI-10MA. This suggests that a longer response time is required for a highly doped polyaniline and this corresponds to more available attack sites for CO, in our case the palaron species. When zeolite is added, the effect on the response time seems to be small, it varies between 30 and 45 min for the composites investigated.

When CO is replaced with N_2, we find that the electrical conductivity values of all our composites return to the original σ_{N2} within a few percents. Therefore, the responses to CO are reversible. FT-IR spectra of PANI-1HCl and PANI-10HCl before and in situ exposure to 1000 ppm CO/N_2 show no quantitative difference. This suggests that CO molecules do not chemically interact with polyaniline. CO molecules may physically adsorb onto the polyaniline chain and a nearly complete desorption occurs after a vacuum process. XRD diffraction patterns of PANI-HCl and PANI-MA were taken before and after exposure to CO. There is also no discernable difference in the XRD patterns. Thus, there is no macroscopic changes in morphology and charge mobility [28]. Since CO is an electrophillic gas it is likely possible that it withdraws a lone pair electron at the amine nitrogen, resulting in more charge carriers. In addition, CO could interact with PANI by displacing the counter ion at the polaron species, but no change in the number of charge carriers.

Figs. 3(a) and 1(b) show the electrical conductivity responses vs. CO concentration of PANI-10MA, PANI-10MA/10Zeolite 4A, PANI-10MA/20Zeolite 4A, and PANI-10MA/40Zeolite 4A at 1 atm and at 27–28 °C. Evidently, the electrical conductivity response decreases with increasing zeolite content at [CO] between 16 and 1000 ppm, as shown in Fig. 2(a). This may reflect the number of attack sites available. The dependence of $\Delta\sigma$ on [CO] appears to be less than linear; it follows the power law of the form $\Delta\sigma = a[\mathrm{CO}]^b$. Table 1 lists the prefactors a and the scaling exponents b of all our composites investigated. On the other hand, Fig. 3(b) shows that the sensitivity increases with increasing zeolite content. Thus the addition of zeolite 4A promotes CO interaction with polyaniline.

Fig. 4(a) and (b) show the electrical conductivity responses vs. CO concentration of PANI-10MA, PANI-10MA/20Zeolite 3A, PANI-10MA/20Zeolite 4A, and PANI-10MA/20Zeolite 5A at 1 atm and at 27–28 °C. Here, the zeolite content is fixed at 20% w/w. In Fig. 4(a), we find that $\Delta\sigma$ values of PANI-10MA/20Zeolite 3A and PANI-10MA/20Zeolite 4A are less than those of PANI-10MA at [CO] between 16 and 1000 ppm. On the other hand, $\Delta\sigma$ values of PANI-10MA/Zeolite 5A are comparable to those of PANI-10MA. Therefore, the larger pore size is more effective in trapping CO molecules. In Fig. 4(b) the sensitivity values of PANI-10MA and PANI-10MA/20Zeolite 3A are comparable in magnitude, except when [CO] is greater than 100 ppm the sensitivity values of the former become greater. It is pleasing to find that sensitivity values of PANI-10MA/20Zolite 4A and PANI-10MA/20Zeolite 5A are larger than those of PANI-10MA at all CO concentrations; the former composites have greater sensitivity values toward CO relative that of PANI-10MA by nearly an order of magnitude.

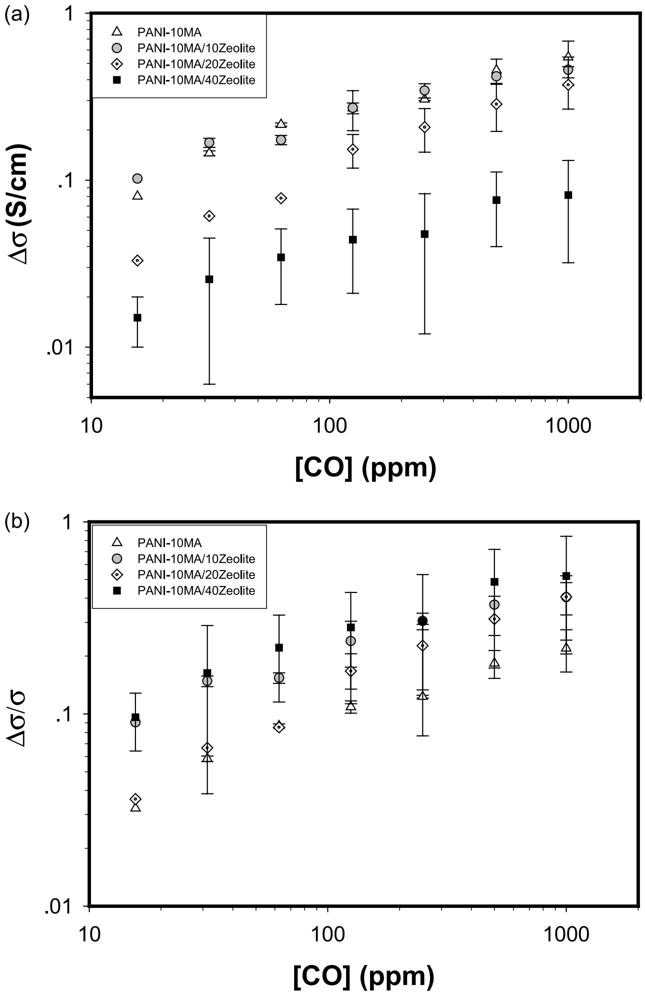

Fig. 3. (a) $\Delta\sigma$ vs. [CO] and (b) $\Delta\sigma/\sigma$ vs. [CO] of PANI-10MA/Zeolite 4A composites at 1 atm and 27–28 °C: PANI-10MA (σ_{N2} 2.48 S/cm); PANI-10MA/10Zeolite (σ_{N2} 1.13 S/cm); PANI10MA/20Zeolite (σ_{N2} 9.15×10^{-1} S/cm); and PANI-10MA/40Zeolite (σ_{N2} 1.56×10^{-1} S/cm).

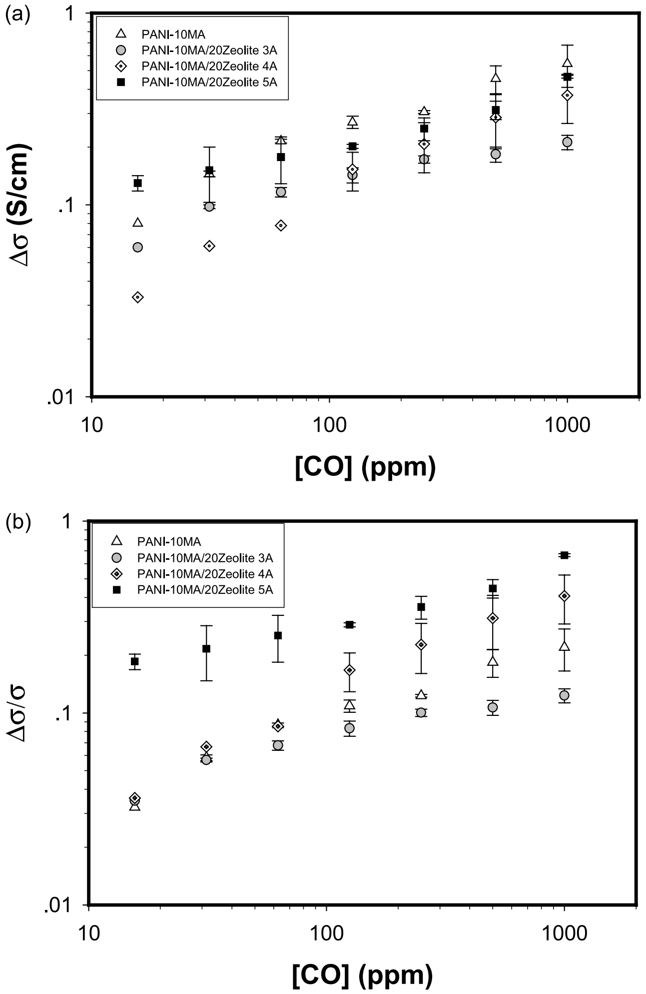

Fig. 4. (a) $\Delta\sigma$ vs. [CO] and (b) $\Delta\sigma/\sigma$ vs.[CO] of PANI-10MA/Zeolite A composites containing 20% w/w zeolite content at 1 atm and 27–28 °C: PANI-10MA (σ_{N2} 2.48 S/cm); PANI-10MA/20Zeolite 3A (σ_{N2} 1.72 S/cm); PANI-10MA/20Zeolite 4A (σ_{N2} 9.15×10^{-1} S/cm); and PANI-10MA/20Zeolite 5A (σ_{N2} 7.01×10^{-1} S/cm).

4. Conclusion

We have investigated the effects of acid dopant type, dopant concentration, zeolite type and zeolite content on electrical conductivity response of polyaniline when exposed to CO under the atmospheric condition. MA dopant is slightly less effective that HCl in promoting the bulk electrical conductivity of polyaniline. The electrical sensitivity of polyaniline towards CO is improved with the addition of zeolite 4A up to 40 w/w; this concentration is still below the percolation threshold which is estimated to be above 50% w/w. At a fixed zeolite content of 20% w/w, zeolite 5A is the most effective in promoting interaction between CO and polyaniline. The interaction is physical and reversible. The CO attack sites are at the amine nitrogen or at the polaron species.

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