CHAPTER IV

Polyaniline/Zeolite Composites as CO/N_2 Sensors

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Abstract

The effects of zeolite content, pore size and ion exchange capacity on sensing CO/N_2 mixtures were investigated. Zeolite Y, 13X, and synthesized AlMCM41, all having the common cation Cu^{2+}, were dry mixed with synthessized maleic acid doped polyaniline to fabricate polyaniline/zeolite pellet composites. The Y, 13X and AlMCM41 zeolite have nominal pore sizes of 7, 10, 36 Å, and the Cu^{2+} exchange capacities of 0.161, 0.087, and 0.044 mol/g, respectively. With an addition of 13X zeolite to prestine polyaniline, the sensitivity to CO/N_2 gas increases with zeolite content. For the effect of zeolite type, the highest sensitivity was obtained with the 13X zeolite , followed by the Y zeolite , and the AlMCM41 zeolite, respectively. Poor sensitivity of zeolite AlMCM41 is probably due to its very large pore size and its lowest Cu^{2+} exchange capacity. Y zeolite and 13X zeolite have comparable pore sizes but the latter has a greater pore free volume and a more favorable location distribution of the Cu^{2+} ions within the pore. The temporal response time increases with the amount of zeolite in the composites but it is inversely related to the amount of ion exchange capacity.

Keywords: Conducting polymer, polyaniline, gas sensor, zeolite Y, Zeolite 13X, AlMCM41

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1. Introduction

Carbon monoxide is a contaminated toxic gas generated in a variety of processes: car exhausts, industrial processes or residential heating. It is a colorless, odorless and tasteless gas which can prevent the proper transportation of oxygen in human blood [1]. Many gas sensing materials have been developed for CO detection; they are required to offer high selectivity, long life times and low manufacturing costs [3]. Conductive polymers have many advantages over conventional metal sensors; they are lighter, less expensive and can be operated at lower applied voltage and temperature [2]. Recently, several conductive polymers have been developed as gas sensing materials [4]

Polyaniline is one of the most promising among conductive polymers because of inexpensive monomer, ease of synthesis, good environmental stability, moderately high value of dc conductivity and excellent chemical stability in conductive form [3]. Its can be prepared by either a chemical or an electrochemical oxidative polymerization. The electrical insulator form of polyaniline is the emeradine base which consists of two amine nitrogen atoms followed by two-imine nitrogen atoms [4]. The polyaniline emeradine base can be converted into the conducting form by two different doping processes: the protonic acid doping and the oxidative doping. Protonic acid doping of emeradine base corresponds to the protonation of the imine nitrogen atoms in which there is no electron exchange [5]. In the oxidative doping, emeradine salt is obtained from leucoemeradine through electron exchanges [5]. There have been several applications of polyaniline as gas and vapor sensor materials including the detection of methanol vapor [5,6], H_2 [7], SO_2 [8], NH_3 [9], CO_2, NO_2 and SO_2 [10]. However, there are some issues remaining for using polyaniline as a gas sensor: the sensitivity, the selectivity to a particular species amongst others, and its temporal response towards a target gas.

Zeolite is a polycrystalline, microporous material with nearly uniform pore size distribution. It has been a subject of many recent theoretical and experimental studies such as a gas adsorption material amongst its several applications [11]. The adsorption force of zeolite depends on the pore type the pore size distribution, location and class of cations. In this work, zeolite Y, 13X and AlMCM41, with pore sizes varying from 7, 10 and 36 Å, were used to fabricate composites with conductive polyaniline in order to study the effect of pore size on gas sensitivity, while all zeolites have the same cation Cu^{2+} within their cavities.

2. Experiment

2.1 Materials

Aniline monomer (Aldrich) was used as the monomer. Analytical grade ammonium peroxydisulfate (Merck) was used as the oxidant. 25% of analytical grade ammonia solution (Merck) was used as the basic reagent. 38% of analytical grade hydrochloric acid (Merck) was used as the acid medium in the polyaniline synthesis process. Maleic acid (98% MA, Fluka) was used as the dopant. Carbon monoxide (CO, TIG) stock of 1000-ppm balance with nitrogen gas N_2 was used as the target gas.

2.2 Instruments

The FT-IR spectrometer (Bruker, model FRA 106/S) with resolution of 4 cm^{-1} and number of scans of 20, an elemental analyzer, a thermogravimetric analyzer (Dupont, model TGA 2950) with a heating rate 10 ^{O}C/min under N_2 atmosphere were used to characterized PANI and doped PANI. An X-ray diffractometer (Rigaku, model D/MAX-2000) was used to determine the degrees of crystallinity of PANI and doped PANI, and the crystal order of AlMCM41. The environmental scanning electron microscope (ESEM, ElectroScan, E3 ESEM) was used to study the morphology of PANI/Zeolite composites with the magnifications of 2000 and 5000 time at 25 kV. BET (Autosorb-1) was used to measure the pore sizes and the surface areas of the zeolites. The X-ray fluorescence (Bruker, model SRS 3400) was used to measure the Cu^{2+} exchange capacities of the zeolites. A custom made four-point probe with linear geometric array was used to measure the specific conductivity of each sample.

2.3 Synthesis of Polyaniline

The polyaniline used in this experiment was synthesized by the oxidative polymerization procedure of MacDiarmid and co-workers [12]. The aniline monomer (Merck) was purified under vacuum at 58 ^{O}C before used. 0.0667 mole ammonium peroxydisulphate ($(NH_4)_2S_2O_8$, Merck) was dropwise added to 0.0825 mole of aniline monomer in 1 M hydrochloric acid. After vigorously stirring at 5-0 ^{O}C for 3 hours, the green emeradine hydrochloride precipitate was collected and washed repeatedly with 80:20 water:methanol solutions until the wash solutions were colorless. This powder was subsequently converted into the emeradine base form by immersing it in 0.1 M aqueous an ammonium hydroxide solution (NH_4OH, Merck) for 3 hours. Further washings by the solutions of 80:20 water:methanol solutions were carried out until the washing solutions were neutral. Polyaniline powder was finally obtained after the filtrate was dried in a vacuum oven at 50 ^{O}C for 48 hours. Emeradine salt was essentially obtained by the maleic acid (MA) doping [4] with the acid dopant to emaraldine base molar ratios (N_A/N_{EB}) equal to 1 and 10.

2.4 Synthesis of AlMCM41

Three types of zeolite, Y, 13X, and AlMCM-41 were used in our study. Zeolite Y and 13X were purchased (Aldrich) whereas AlMCM-41 was synthesized following the method of Ryoo and co-workers [13]. An aqueous solution HTAB (Aldrich),a 25% concentrated ammonium solution, and a sodium silicate solution with Na/Si ratio of 0.5 (2.4wt% SiO_2, 9.2 wt% Na_2O, and 88.4% H_2O) were used to synthesize AlMCM-41. The mixture was added into a polypropylene bottle to obtain HTA-silicate gel with the molar composition of $4SiO_2$: 1HTAB: $1Na_2O$: $0.15(NH_4)_2O$: $200H_2O$. After the gel was stirred for 1 hour, the mixture was heated to 370 K in an oven for 1 day. During this period, the cap was loosened repeatedly in order to reduce the ammonium pressure. The bottle was then cooled to room temperature, followed by drop wise additions 30% acetic acid to adjust the solution pH value to 10.2. The bottle was then heated to 370 K again in the oven for 1 day and then cooled to room temperature. Subsequently, 3 mol of NaCl/HTAB and aluminate 0.13mol/ silicate were added to the mixture and stirred for 30 min. The reaction mixture was adjusted to a pH value of 10.2 and then heated to 370 K twice more. Finally, the precipitate product was filtered, washed with distilled water and dried at 370 K for 12 hours. The dried MCM-41 was calcined under O_2 flow while temperature increasing to 813 K for 10 hours and maintained there for 10 hours.

2.5 Preparation of Polyaniline/Cu^{2+} Zeolite Composites

Zeolite Y and 13X were calcined under a nitrogen flow at 473 K for 2 hours prior to their uses. Cu^{2+} contained zeolites were prepared by immersing 1 g of zeolite powder in 200 ml $2.1x10^{-4}M$ $CuCl_2$ for 12 hours at room temperature. The precipitate was then filtered, washed doubly with hot water and dried at 353 K for 2 hours. Polyanililne/zeolite composites were prepared by dry mixing PANI with the zeolites at weight ratios equal to10, 20, 30 and 40. The composites were compressed into a disc form by using a hydraulic press at pressure equal to 5 ton and the conductivity values were measured by using the four- point probe technique.

2.6 Conductivity Measurement and CO Gas Detection

The specific conductivity σ (S/cm) values of the pellets were obtained by measuring the bulk pellet resistance R (Ω). The relation $\sigma = (1/Rt)(1/K)$ was used to calculate specific conductivity, 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 probe width and the length, respectively. The K value was determined by calibrating the four-point probe with semi-conducting silicon sheets of known resistivity values. Electrical conductivity values of several samples were first measured at various applied dc currents to identify their linear Ohmic regimes.

A custom-built gas detection unit was made consisting of 2 chambers of equal volume: a mixing chamber is connected in series with a working chamber. Temperature and pressure in both chambers were controlled and monitored. The operating temperature was fixed at 30 ± 2 °C during the experiment. In the serial operating temperature was fixed at 30 ± 2 °C during the experiment. In the serial dilution method, CO concentration was successively reduced in half from 1000 to 7.80 ppm. The procedure was as follows. Initially, both chambers were evacuated repeatedly until the sample conductivity decreased to a nearly constant value; presumably the moisture content was reduced to its minimum value. Then N_2 at 1 atm and 30 ± 2 °C was injected into the working chamber and the conductivity value (σ_{N2}, pre-exposed) was recorded. Then N_2 was then evacuated from the working chamber. A 1000 ppm CO/N_2 mixture was injected into the mixing chamber until the pressure reached 2 atm and at 30 °C. Half of the gas mixture was then allowed to escape into the working chamber where now the pressures in both chambers were reduced to 1 atm. The conductivity value was recorded through an A/D board (DT2801, Data Translation Board) connected to a PC. After the steady state conductivity value was obtained and recorded, the gas mixture in the working chamber was evacuated. N_2 was injected into the mixing chamber until its pressure reached 2 atm, and therefore the CO concentration was reduced to 500 ppm. Half of the gas mixture was allowed to escape into the working chamber and the sample conductivity value was recorded as a function of time until a steady state values was obtained. The procedure was repeated again and again until the final CO concentration was 3.90 ppm. The conductivity response, $\Delta\sigma$ to each CO mixture was calculated from the equation: $\Delta\sigma = \sigma_{CO} - \sigma_{N2,final}$ where σ_{CO} is the steady state conductivity value at a particular CO concentration (S/cm), and $\sigma_{N2,final}$ is the steady state conductivity value when the 3.90 ppm CO/N_2 mixture was replaced by pure N_2 at 1 atm and 30 °C, or at other operating temperatures. A small difference of few percents was observed between $\sigma_{N2,preexposed}$ and σ_{N2}, final.

3. Results and Discussion

3.1 Characterization of Polyaniline

The FT-IR spectra of PANI and doped PANI were recorded to identify major absorption peaks found in prestine PANI in previously published work [14]. Absorption peaks found are 1590,1495, 1299, 1163, 827 cm^{-1}, corresponding to the C=N stretching of quinoid ring, the stretching of benzenoid ring, C-N stretching of benzenoid ring, C-H bending of quinoid ring and the out of plan bending of C-H bond in aromatic ring. An absorption peak of the acid dopant, maleic acid, was also found: the absorption peak at 1705 cm^{-1} in PANI-10MA indicates the C=O stretching group of the acid dopant [16].

Percent doping levels of PANI samples were obtained from elemental analysis data. The %C, %H, and %N were used to calculate the amount of residue oxidant whereas the moisture content was obtained from TGA data. The calculated percent doping level of PANI-10MA is 90.5 %.

The crystallinity of PAN-10MA was calculated from X-ray diffraction pattern by using the Gussian equation [17]. The relative sharp peaks representing the crystallinity of PANI-10MA were observed at 2θ equal to 9, 15, 21, 25, 27, and 30°. The crystallinity of PANI-10MA is about 57 %.

The TGA thermogram of PANI-10MA indicates a 3 steps transition: 30-130, 130-300 and 300-645 °C; they are identified as the loss of moisture content, the loss of dopant, and the degradation of PANI chain, respectively [18]. The moisture content in the PANI-10MA composites is approximately 5-6%wt.

3.2 Characterization of AlMCM-41

The XRD pattern of AlMCM41 covering angles between $2\theta = 2\text{-}8^{O}$ was obtained. The major peaks of AlMCM41, consisting of one intense line and two weak lines, can be indexed to the (100), (110), and (300) diffraction lines, the characteristic of the hexagonal structure of MCM41 [13].

The BET specific surface area of AlMCM41 is about 504 m^2/g. The pore size was analyzed by using the N_2 adsorption and found to be about 3 nm. The particle size analysis gives the particle diameter of AlMCM41 of about 18.64 μm and the specific surface area of about 0.572 m^2/g. Table 1 summarizes physical properties and compositions of the zeolites studied.

3.3 Ion-Exchange in Zeolite

The Cu^{2+} exchange capacities of the zeolites were calculated from X-ray fluorescence data. Due to the lowest of Si/Al ratio, the Cu^{2+} exchange of AlMCM41 is lowest compared to those of Y and 13X zeolites. The Cu^{2+} exchange capacities of samples measured are 0.161, 0.086, and 0.044 g/mol for the Y, 13X, and AlMCM41 zeolites, respectively.

3.4 Conductivity Measurement

Electrical Conductivity: Steady State Sensitivity to CO

The electrical response ($\Delta\sigma = \sigma_{CO}-\sigma_{N2}$ [S/cm]) of each sample was calculated by the difference between the saturated conductivity when exposed to CO and the steady state conductivity value when exposed to pure N_2 at 1 atm and $30 \pm 2\ ^0C$. Due to appreciable differences in initial conductivity between various composites, the sensitivity (sensitivity = $\Delta\sigma/\sigma$) is defined as the electrical conductivity response divided by the electrical conductivity when exposed to pure N_2.

Figure 3 shows the electrical response of PANI-10MA/10-13X vs. time upon exposed to 1000 ppm CO/N_2 gas at 30^OC and at 1 atm. The conductivity of sample increases steadily until reaching an equilibrium value. The positive increment of $\Delta\sigma$ upon exposed to CO can be traced back to the PANI-CO interaction mechanism as proposed in our previous work [17], and shown here in Fig. 4.. The negative charge of CO molecule coexists with the negative charge counter ion X^- at the positive charge of PANI chain, $-NH^+-$; interaction occurs at the polaron site. This was verified by observing that for a prestine PANI with a larger number of polaron results in a larger $\Delta\sigma$. Temporal response time (t_r) of PANI and PANI/Zeolite composites is defined as the duration between the starting time of CO exposure to the time at which the conductivity value reaches its steady state.

Effect of Zeolite Content

In order to study the effect of zeolite content, 3 weight ratios of the 13X zeolite was used in making composites with PANI-10MA at 10%wt, 20%wt, and 40%wt. As shown in Fig. 5, the sensitivity generally becomes higher with increasing zeolite content. CO molecules adsorb physically in the 13X zeolite pores by the dipole-dipole interaction between Cu^{2+} and CO molecules ($CO\text{--}Cu^{2+}$). The increase in sensitivity can be related to the increase in the amount of zeolite pores per unit area available to interact.

Table 2 shows the temporal response times of PANI and PANI/Zeolite composites: PANI-10MA, PANI-10MA/10-13X, PANI-10MA/20-13X, and PANI-10MA/40-13X. The temporal response time increases from 237 min to 300 min as 13X zeolite content increases from 0% to 40%. For a composite with a higher zeolite content, more CO molecules can adsorb and diffuse into the composite and thus they required a longer time before the interaction with polyaniline chains completes and the specific electrical conductivity reaches a steady state value.

Effect of Zeolite Type

Three types of zeolite with different pore sizes and cation exchange capacities were used to investigate the effect of zeolite type on the electrical response to CO. Composites PANI-10MA/10-13X, PANI-10MA/10-Y and PANI-10MA/10-AlMCM41 all contained 10% weights of respective zeolites. Figure 6 shows that the sensitivity of PANI-10MA/10-13X is slightly higher than that of PANI-10MA/10-Y, but it is much greater than that of PANI-10MA/10-AlMCM41. All composites have larger sensitivity values than that of the prestine PANI. The increase in sensitivity of PANI/Zeolite composites relative to that of the prestine PANI reflects the fact that

CO molecules adsorb into the zeolites and therefore larger amounts of CO molecules are available to interact with PANI chains.

PANI-10MA/10-13X has a larger sensitivity than that of PANI-10MA/10-Y. 13X zeolite and Y zeolite have comparable pore sizes: 7 and 10 Å, respectively. But they differ in the ion exchange capacities: 0.161 and 0.086 mol/g, respectively. The higher amount of Cu^{2+} in Y zeolite may possibly reduce the free volume available for CO molecules to reside in the cavity. In addition, the locations of Cu^{2+} in 13X zeolite allow a more favorable interaction with CO molecules [18]. This observation is further verified by noting that the temporal response time of PANI-10MA/10-13X is larger than that of PANI10MA/10-Y, as shown in Table 2.

The sensitivity of PANI-10MA/10-AlMCM41 is slightly greater than that of the prestine PANI. This is because AlMCM41 zeolite contains the smallest amount of Cu^{2+} (0.044 mol/g) amongst the three zeoliters, and its excessively large pore size (~36 Å) may have allowed CO molecules to enter and leave with equal eases.

Table 2 shows the temporal response times of the composites studied: PANI-10MA/10-Y, PANI-10MA/10-13X and PANI-10MA/10-AlMCM41. The temporal response times are 170, 250, and 365 min, respectively. The corresponding Cu^{2+} exchange capacities are 0161, 0086 and 0.044 mol/g, respectively. Therefore, within a first approximation, the temporal response time is inversely related to the Cu^{2+} exchange capacity. It appears that a zeolite with more Cu^{2+} ions can trap CO molecules through the dipole-dipole interaction in a shorter time, and hence the interaction with PANI chains is completed in a shorter time.

4. Conclusions

The effects of zeolite content and type on the CO interaction with PANI doped with maleic acid were investigated. For PANI-10MA/-13X, the sensitivity and temporal response time increase with zeolite content, reflecting that a larger total pore volume per unit area is available to allow more CO molecules to interact with PANI chains. For comparable pore sizes, sensitivity of PANI-10MA/10-13X is greater than that of PANI-10MA/10-Y because of a greater pore free volume available and a more favorable distribution of Cu^{2+} ions. The sensitivity of PANI-10MA/10-AlMCM41 is lowest because of it excessively large pore size. The temporal response time varies inversely with the Cu^{2+} exchange capacity.

5. Acknowledgements

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Table 1 Summary of Zeolite Properties

Zeolite	Si/Al ratio	Cu^{2+} exchange (mol/g)	BET		Particle size analysis	
			Pore size (Å)	Surface area (m^2/g)	Particle diameter (μm)	Specific SA. (m^2/g)
Y	2.85	0.161	~7	691	5.00	2.392
13X	1.24	0.086	~10	673	6.71	2.083
AlMCM41	27.91	0.044	~36	504	18.64	0.572

Table 2 The conductivity, sensitivity and concentration dependence of composites

Sample	σ_{air} (S/cm)	$\sigma_{N2,\ final}$ (S/cm)	$\Delta\sigma/\sigma_{N2,\ final}$ at [CO]		a, b $\Delta\sigma = a[CO]^b$	tr (min)
			1000	7		
PANI-10MA	(2.40 ± 0.38) x 10^{-1}	(1.02 ± 0.13) x 10^{0}	0.157	0.004	-2.50, 0.59	237
PANI-10MA/10-13X	(7.84 ± 8.29) x 10^{-2}	(7.83 ± 0.81) x 10^{-1}	0.809	0.151	-1.22, 0.36	250
PANI-10MA/20-13X	(1.05 ± 0.21) x 10^{-1}	(6.53 ± 0.01) x 10^{-1}	0.356	0.011	-2.06, 0.50	285
PANI-10MA/40-13X	(9.85 ± 5.30) x 10^{-3}	(1.03 ± 0.36) x 10^{-1}	0.950	0.138	-1.10, 0.37	300
PANI-10MA/10-Y	(1.68 ± 0.13) x 10^{-1}	(8.82 ± 1.33) x 10^{-1}	0.431	0.114	-1.15, 0.23	169
PANI-10MA/10-AlMCM41	(2.67 ± 0.69) x 10^{-1}	(1.06 ± 0.31) x 10^{0}	0.253	0.022	-2.43, 0.60	365

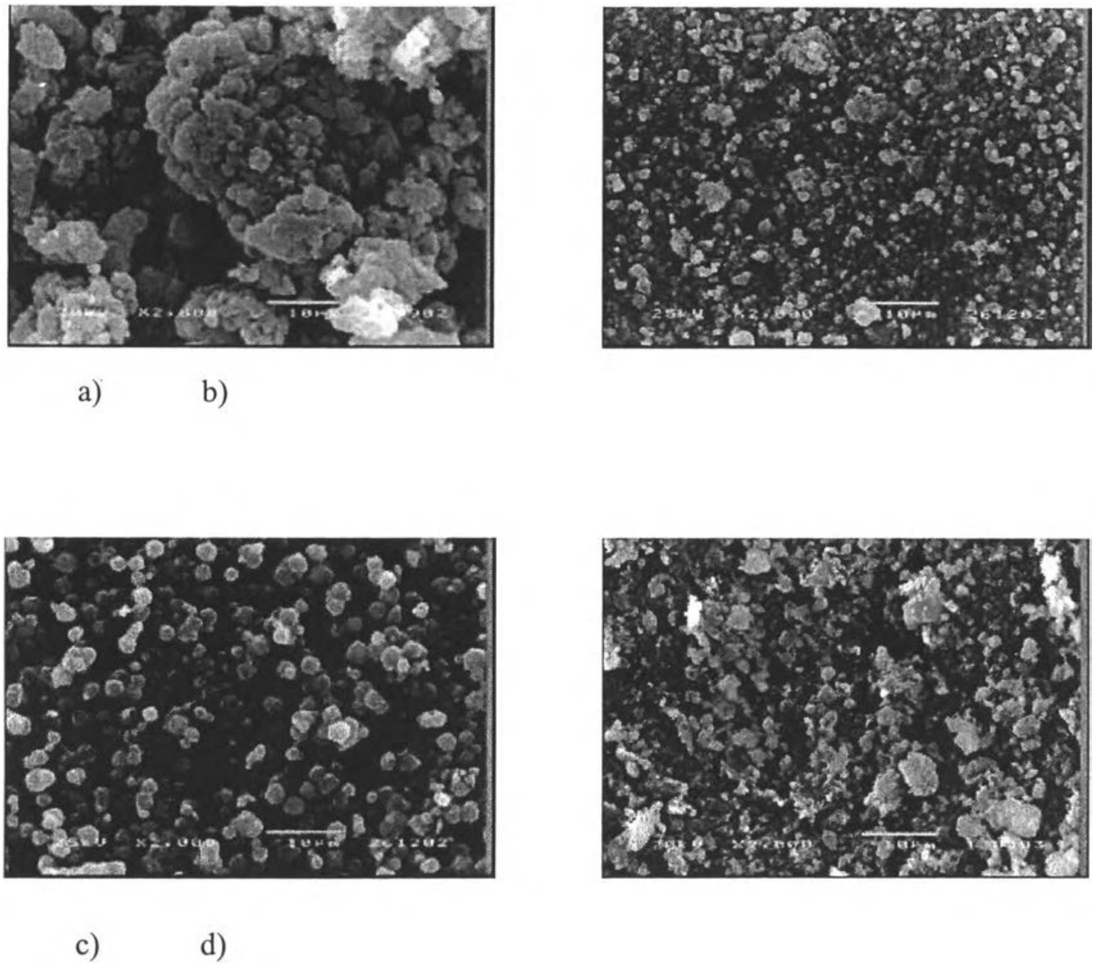
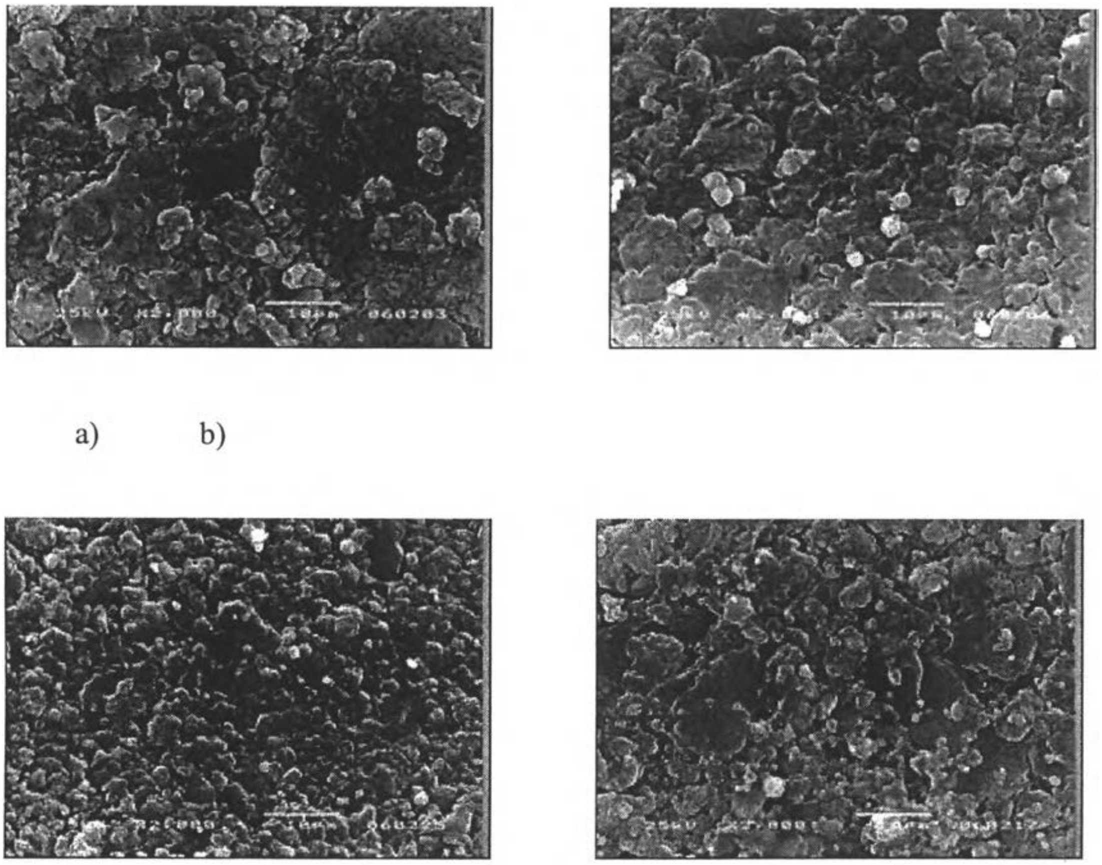


Figure 1 The SEM morphology of powder sample with 25 kV and magnification 2000 of a) PANI-MA, b) Zeolite Y, c) Zeolite 13X, and d) AlMCM41.



a) b)

c) d)

Figure 2 The SEM morphology of pellet sample with 25 kV and magnification 2000 of a) PANI-10MA, b) PANI-10MA/10-Y, c) PANI-10MA/10-13X, and d) PANI-10MA/10-AlMCM41.

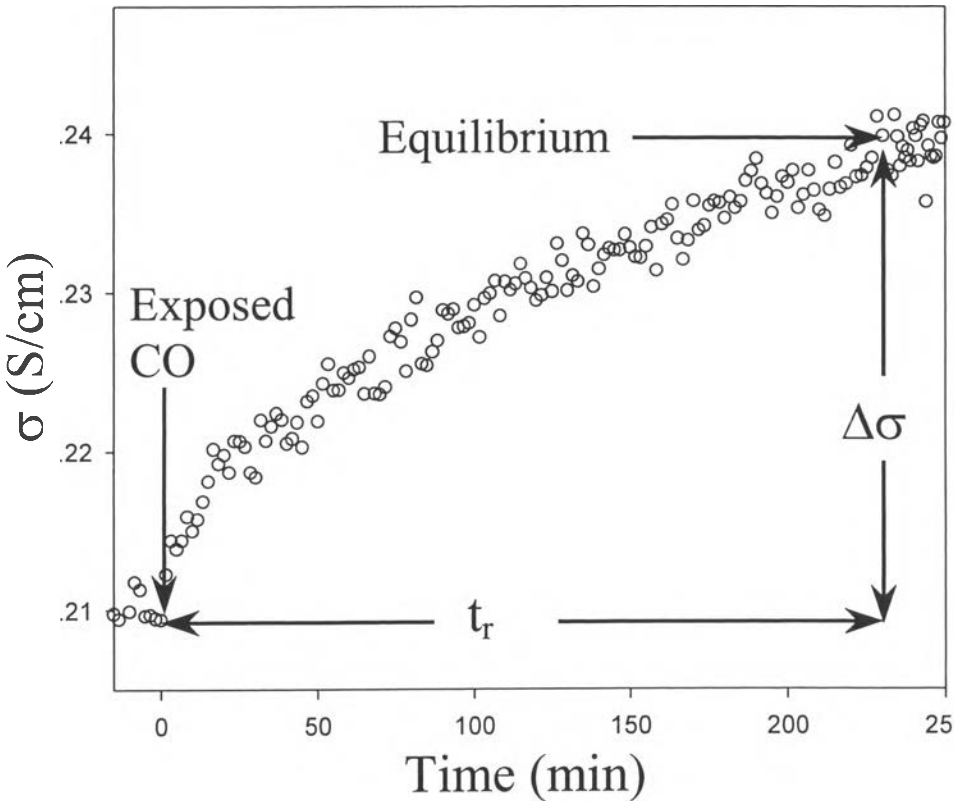


Figure 3 The electrical response of the PANI-10MA to CO at 1000 ppm, at 1 atm humidity 54-67% and temperature 30 ± 2 °C.

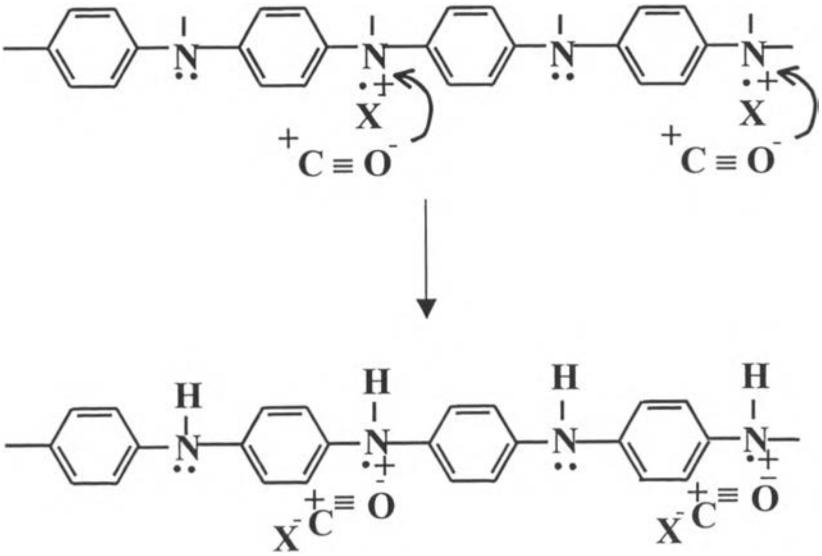


Figure 4 Proposed mechanism of CO-PANI interaction.

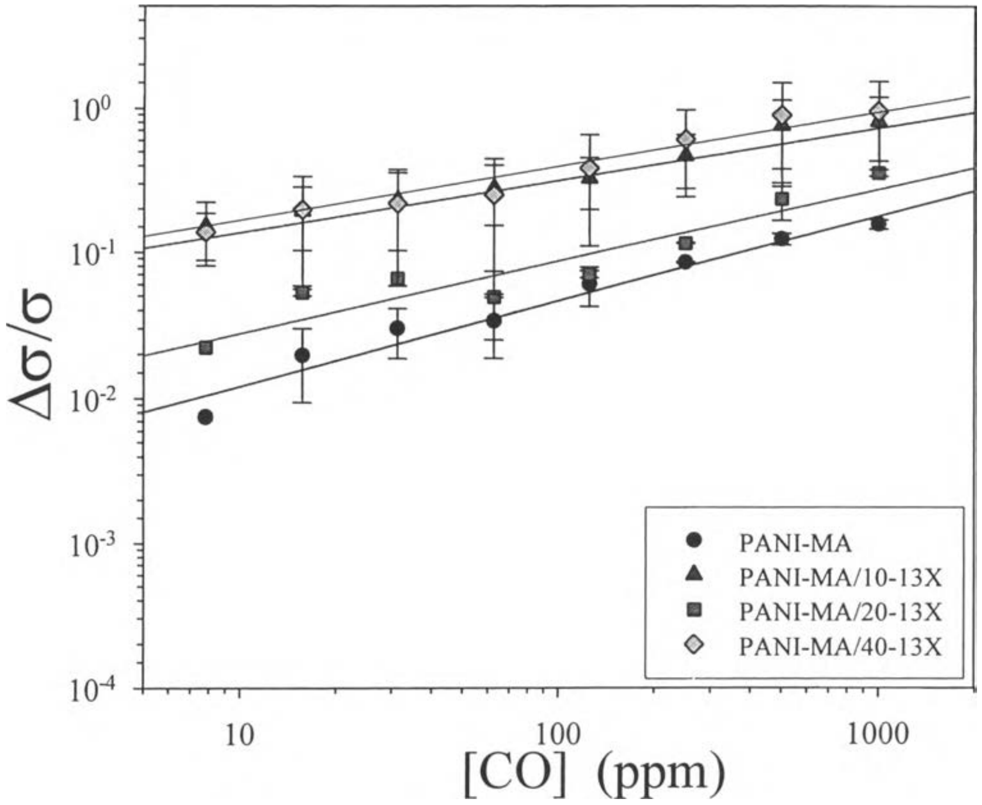


Figure 5 $\Delta\sigma/\sigma$ vs.the [CO] of PANI-MA, PANI-MA/10_13X, PANI-MA/20_13X, and PANI-MA/40_13X at 1 atm, humidity 54-67%, and temperature 30 ± 2 °C.

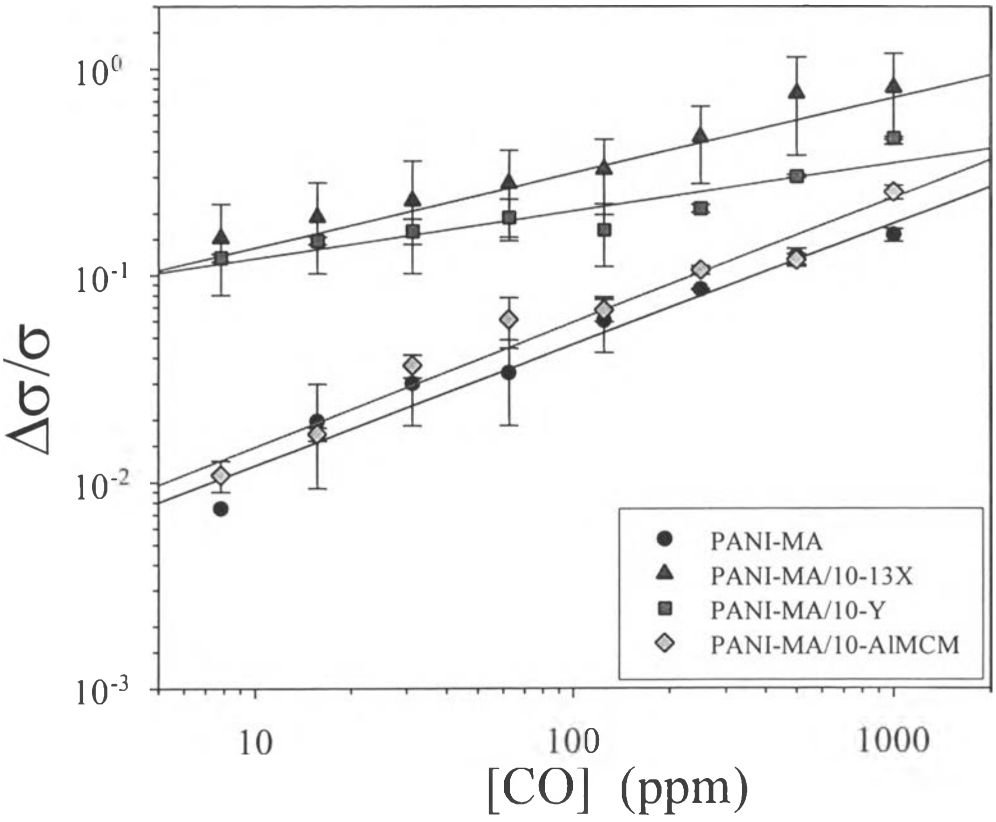


Figure 6 Δσ/σ vs.the [CO] of PANI-MA, PANI-MA/10_13X, PANI-MA/10_Y, and PANI-MA/10_AlMCM41 at 1 atm, humidity 54-67%, and temperature 30 ± 2 °C.

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