

CHAPTER IV

Development of PPV/Zeolite Composites for CO Sensor

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The effect of zeolite type on the electrical sensitivity to carbon monoxide (CO) of poly(*p*-phenylene vinylene) or (PPV)/zeolite composites were investigated. Zeolite 13X, Ferrierite, and ZSM5(Si/Al =23, 80), all having the exchanged Na⁺, were dry mixed with sulfuric acid doped PPV and compressed to form doped PPV/Zeolite pellet composites. For the effect of zeolite type, the highest electrical conductivity sensitivity is obtained with the doped PPV/Na⁺-ZSM5(Si/Al = 23); it is slightly higher than those of the doped PPV/Na⁺-ZSM5(Si/Al = 80), of the doped PPV/Na⁺-13X, and of the doped PPV/Na⁺-ferrierite. The electrical sensitivity values obtained are equal to 1.48, 1.17, 1.02, and 0.91, corresponding to the sodium ion-exchange levels of 28, 17, 100 ,and 17 %, respectively. It appears that a zeolite with more Na⁺ ions located in a channel structure type zeolite can trap more CO molecules through the electrostatic interaction giving the higher sensitivity. The difference in the interaction between CO molecules and the sensing material on the electrical sensitivity has been investigated by using doped PPV/cation exchanged ZSM5 (Si/Al = 23) zeolites (Na⁺ and Cu⁺) as a model though the IR and TPD measurements. The electrical sensitivity of dPPV/Cu⁺-ZSM5 system shows the negative value, -0.154 , while the Na⁺ system give a positive sensitivity of 1.48. Fourier Transform IR spectra of carbon monoxide absorbed at room temperature on doped PPV, Na⁺-ZSM5 , Cu⁺-ZSM5, doped PPV/Na⁺-ZSM5, and doped PPV/Cu⁺-ZSM5 show that the interaction modifies C-O stretching frequency from that of the free molecule (143 cm⁻¹) to higher values. The frequency shifts occur at 2164 and 2172 cm⁻¹ for PPV

and Na-ZSM5, respectively. For the copper ion-exchanged ZSM-5 and CO system, the IR bands appear at 2340 and 2364 cm^{-1} . Corresponding to these data, TPD also gives spectra obtained after room-temperature adsorption of CO on Na^+ - and Cu^+ -ZSM5(Si/Al = 23). The temperature of the maximum desorption rate of CO on the two adsorbents are significantly different; for Na^+ -ZSM5(Si/Al = 23) it is observed at 116 °C, while on Cu^+ -ZSM 5(Si/Al = 23) it is at 222 °C. This result demonstrates that Cu^+ -ZSM5(Si/Al = 23) adsorb CO significantly stronger than Na^+ -ZSM5(Si/Al = 23). The strong adsorption observed for the copper ion-exchange ZSM5 sample than sodium ion-exchange arises from the interaction between the copper ion and the CO molecule. The dry mixing composite systems demonstrate a combination between characteristic peaks of its sensing materials; 2160 and 2172 cm^{-1} for doped PPV/Na-ZSM5 ; 2160, 2340, and 2364 cm^{-1} for doped PPV/Cu-ZSM5. The new IR shift peaks cannot be observed. Because of the dry mixing composites, only the physical contact between polymer and zeolite clusters exist. This fact is interpreted in terms of the difference in the nature of bonding between the electrostatic force for sodium ion-exchange ZSM5 and doped PPV with CO molecules and the covalent nature for the copper in-exchanged ZSM5 with CO molecules.

Introduction

Energy from fossil fuels are associated with the production of toxic by-products such as CO, NO_x, and hydrocarbon. A significant part of CO and NO_x emission originate from motor vehicles. The interaction of CO and NO_x with sunlight tends to produce O₃ and because of its strongly oxidizing behavior it is believed to be harmful to plants and to the respiratory system of human beings.^{1,2}

Conducting polymers such as poly(*p*-phenylene vinylene) (PPV) can serve as an active sensing material in devices because PPV possesses good optical and electrical properties, and it can be synthesized by a relative simple technique.³⁻¹⁴ To obtain an analyte-specific material the sensors should have very narrow chemical specificity with high sensitivity towards polar chemicals. A zeolite is chosen as a selective microporous adsorbent to be introduced into a polymer matrix in order to increase sensitivity towards CO.

Carbon monoxide is a widely used as a probe molecule in surface chemistry to titrate the number and the strength of acidic sites by comparing shift and intensity of the vibrational mode of adsorbed CO to gas-phase molecules. CO molecules interact with Lewis acid centers when exposed to a surface of cations of metal oxides, halides, and with cations of metal-exchange zeolites. The interaction of CO with the surface of ionic oxides and halides has been extensively investigated theoretically.¹⁵⁻¹⁹ These results provide a solid basic for the understanding of the bond nature of the probe molecule to the acid sites and of the origin of the CO frequency shift. The interaction of CO with a transition metal cation implies the donation of electronic charge from the 5σ orbital of CO to a d orbital of the metal in synergy with a back-donation from the metal to the empty antibonding $2\pi^*$ orbital of CO. In the case of cations without d orbitals in their valence shell no such "chemical" bonding can occur and the interaction is essentially mediated by electrostatics.²⁰⁻²³

In the past, several studies have been devoted to the interaction of CO with metal-exchange zeolites by using Fourier transform infrared technique.²⁴⁻³³ In this work, we make an attempt to systematically investigate the interaction between CO with poly(*p*-phenylene vinylene), Na⁺-exchanged zeolite, Cu⁺-exchange zeolite, and the poly(*p*-phenylene vinylene)/zeolite composites toward sensor applications .

Experiment Section

α,α' - Dichloro-*p*-xylene (Aldrich) and Tetrahydrothiophene (Aldrich) was used to synthesize PPV monomers. Analytical grade methanol (Merck) was used as solvent. Sodium hydroxide (Merck) and hydrochloric acid (Merck) were used as a basic and acid reagent, respectively. Sulfuric acid (Merck) was used as an oxidant. Sodium chloride (Merck) and copper(II) chloride (Merck) were used as ion-exchanged agents. Zeolite: Na-13X (Aldrich), NH₄-ZSM5 (Si/Al =23,80) (Zeolyst), NH₄-ferrierite (Zeolyst) were used as the adsorbents. All chemicals were used without further purification. Carbon monoxide (CO, TIG) was used as the target gas. Nitrogen (N₂, TIG) was used as the surface cleaning gas.

A FT-IR spectrometer (Bruker, model FRA 106/S) with resolution of 4 cm^{-1} and number of scans of 20 was used to characterize functional groups and the frequency changes of the samples. A thermogravimetric analyzer (Dupont, model TGA 2950) with a heating rate $10\text{ }^{\circ}\text{C}/\text{min}$ under N_2 atmosphere was used to characterize the PPV precursor, PPV and the doped PPV. An X-ray diffractometer (Rigaku, model D/MAX-2000) was used to determine the degrees of crystallinity of PPV and the doped PPV, and the crystal order of the zeolites. A scanning electron microscope (SEM, JEOL, model JSM-5200) was used to study the morphology of PPV, the doped PPV, the zeolites, and the PPV/Zeolite composites with the magnifications of 1500 and 5000 at 15 kV. The BET (Sorptomatic-1990) was used to measure the pore sizes and the surface areas of the zeolites. An X-ray fluorescence (Bruker, model SRS 3400) was used to measure the Cu^+ and Na^+ exchange capacities of the zeolites. An electron spin resonance (ESR) spectrometer (Varian E-109) was used to observe an oxidation state of copper. The TPD method was applied to the analysis of the CO adsorbed species on $\text{Na}^+\text{ZSM5}$ and $\text{Cu}^+\text{ZSM5}$ samples by using He as the carrier gas at the rate of $60\text{ cm}^3\text{ min}^{-1}$, and the heating rate $5\text{ K}\cdot\text{min}^{-1}$. A custom made two-point probe with linear geometric array was used to measure the specific conductivity of each sample.

Poly(*p*-phenylene vinylene) used in this experiment was synthesized by the sulfonium precursor route². Synthesis of the *p*-xylene-bis(tetrahydrothiophenium chloride) monomer was achieved by reacting α,α' -dichloro-*p*-xylene at a concentration of 0.75 M with excess tetrahydrothiophene at $50\text{ }^{\circ}\text{C}$ in methanol: water (80:20) solution for 24 h. This monomer was purified in the reaction solution, followed by precipitating the product in cold acetone ($0\text{ }^{\circ}\text{C}$), filtration, and vacuum drying. The precursor sulfonium polyelectrolyte, poly(*p*-xylene-bis(tetrahydrothiophenium chloride)), was prepared in an aqueous solution by the base induced polymerization of an appropriate *bis*-sulfonium monomer. The reaction was usually carried out at low temperatures in fairly dilute monomer solutions and in equimolar base to monomer ratios in order to suppress the premature formation of unsaturated polymer segments by thermal or base induced elimination of solubilizing side chains. 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 and the sodium and chloride ions. Poly(p-phenylene vinylene) was essentially obtained by heating poly(p-xylene-bis(tetrahydrothiophenium chloride)) under vacuum at 180 °C for 6h.

Zeolite Na⁺-13X, NH₄⁺-ZSM5 (Si/Al =23,80), and NH₄⁺-ferrierite were calcined at 473 K for 2 hours prior to their use. Na⁺ contained zeolites, ZSM5(Si/Al = 23,80) and ferrierite, were prepared by immersing 1 g of zeolite powder in 100 ml of 0.3M NaCl for 12 hours at room temperature. The precipitate was then filtered, washed doubly with hot water, and then dried at 353 K for 2 hours. Cu⁺ ion-exchanged zeolite was obtained by stirring the zeolite sample in 0.3M CuCl₂ solution at room temperature for 12 hours and activated under vacuum at 573 K for 2 hours.^{6,7} PPV/zeolite composites were prepared by dry mixing PPV particles with the zeolites at volume ratios equal to 10.⁸ The composites were compressed into a disc form by using a hydraulic press at pressure equal to 6 ton and the conductivity values were measured by using the two- point probe technique.

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 ± 5 °C during the experiment. The procedure was as follows. Initially, the steady state electrical conductivity of sample in air was measured and then both chambers were evacuated until the sample conductivity decreased to a nearly constant value; presumably the moisture content was reduced to its minimum value. Then N₂ at 1 atm and 30 ± 2 °C was injected into the working

chamber and the electrical conductivity value was recorded. The procedure of evacuation and N₂ injection was repeated again and again until the steady state conductivity in N₂ ($\sigma_{N_2, \text{before-expose}}$) was close to the electrical conductivity value in vacuum. Then N₂ was then evacuated from the working chamber. CO 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 a source meter (Keithley, model 6517A) connected to a PC. After the steady state conductivity value was obtained and recorded, CO was evacuated. N₂ was injected into the working chamber until its pressure reached 1 atm., The conductivity after exposing CO was recorded ($\sigma_{N_2, \text{after-expose}}$). The electrical conductivity response, $\Delta\sigma$, to CO was calculated from the equation: $\Delta\sigma = \sigma_{CO} - \sigma_{N_2, \text{before-expose}}$ where σ_{CO} is the steady state electrical conductivity value (S/cm). A small difference of few percents was observed between $\sigma_{N_2, \text{after-expose}}$ and $\sigma_{N_2, \text{before-expose}}$.

The sample for IR measurements was prepared as a self supporting wafer and was placed in a cell capable of sample treatment at room temperature with gas in situ. The procedure allows IR spectra to be measured during adsorption process of the probe molecule. The spectra were recorded at room temperature on a spectrophotometer (Bruker, model FRA 106/S) with a resolution of 4 cm⁻¹. The spectrum of adsorbed species was obtained by subtracting a spectrum of the gas-phase CO from the background one.

Results and Discussion

Characterization of Poly(p-phenylene vinylene).

PPV Precursor, PPV and sulfuric acid doped PPV were examined by FTIR spectroscopy. For PPV precursor, the presence of the absorption band near 960 cm⁻¹, resulting from C-H out-of-plane bending, is a characteristic of the trans configuration of the vinylene group.³³ The absorption band around 3022 cm⁻¹ is due to the trans vinylene C-H stretching mode. The absorption band around 550 cm⁻¹ is attributed to the phenylene out-of-plane ring-bending. The bands at 830 cm⁻¹ and 1511 cm⁻¹ can

be assigned to the para-phenylene ring C-H out-of-plane bending and the C-C ring stretching, respectively. The bands at 2872 and 2960 cm^{-1} can be attributed to the CH_3 symmetric and CH_3 asymmetric deformation.³³ After the heat treatment under vacuum, the intensities of these two bands decreased. The intensity of the absorption band near 3022 cm^{-1} increases due to the elimination of the tetrahydrothiopenyl group and HCl. The absence of the C-S linkage peak at 632 cm^{-1} from tetrahydrothiophene indicates the full conversion of the precursor after pyrolysis.³⁴ Upon oxidation of PPV, the infrared spectrum shows new bands at 1550, 1485, 1316, 1280, 1150 and 876 cm^{-1} . The emergence of these new bands in the spectra is related to the formation of the quinoid structures.³⁴ The quinoid structure is a result of a symmetry breaking of the polymeric chain. Although formation of the quinoid structure is evident for the doping agent used, some bands connected with benzoid structure (undoped PPV) survive after doping the polymer. Therefore, even for extensive oxidation, only a partial oxidation of the polymer takes place and two structures coexist.

The thermal behavior of the polymers were investigated by using the TGA technique. There are three transitions for the PPV precursor around 80-150 °C, 150-230 °C and 520-580 °C. The first one is due to the removal of the solvent from the polymer. The second transition, around 150-230 °C, is related to the elimination reaction, yielding tetrahydrothiophene and HCl, which converts the PPV precursor to PPV. The third transition is attributed to the degradation reaction of the main chain.³³ After pyrolysis PPV precursor under vacuum for 6 h, it has two transitions. The weight loss around 50-80°C is due to the removal of the physically absorbed water. The transition temperature occurring around 450-580 °C can be attributed to the decomposition of polymer.⁸ Therefore, The TGA results also confirm that tetrahydrothiophene and HCl were eliminated from PPV precursor after the thermal treatment. The thermal behavior of sulfuric acid doped PPV shows three weight loss. The weight loss around 50-105 °C is attributed to the diffusion of physisorbed water. The second step, 50-250 °C, is due to the loss of counterion which is from the dopant. The last step, 600-680 °C, is related to the degradation of polymer.³³ The TGA results of PPV and doped PPV show that doped PPV has higher thermal stability,

because after doping the degradation temperature of sulfuric acid doped PPV is higher than that of pristine PPV.

From XRD patterns, the interplanar spacing between aromatic group can be identified with the peak at 24.38 Å for PPV. After chemically oxidized with H₂SO₄, the doped PPV possesses peaks at 20.58 Å and 24.28 Å, which can be related to the layer of the dopant and polymer chain, respectively. The doping process does not disrupt the original orientation of the PPV crystallites and the crystalline phase obtained with the dopant.³⁵ Based on this evidence, an electrically conductive phase consisting of layers of polymers separated by a layer of the chemical dopant can be proposed. The particle size analysis gives the particle diameters of PPV and doped PPV of about 52.97 and 62.72 μm, respectively. The standard deviations are 6.97 and 0.84, respectively. This is due to the introduction of charges upon doping, inducing PPV particles to agglomerate on the micro scale from electrostatic interaction. The apparent densities of PPV and doped PPV are about 0.840 g/cm³ with a standard deviation of 0.13 and 0.09, respectively.

Characterization of Zeolite.

The XRD pattern of zeolites: 13X, ZSM5 (Si/Al = 23, 80), and ferrierrite covering angles between $2\theta = 5-90^\circ$ were obtained. The major peaks of zeolites are consistent with those previously published work.³⁶ The BET specific surface area of 13X, ZSM5 (Si/Al = 23, 80), and ferrierrite are about 631, 309, 386, and 224 m²/g, respectively. The pore sizes of 13X, ZSM5s (Si/Al = 23, 80), and ferrierrite were analyzed by using the N₂ adsorption and found to be 8.07, 6.06, 5.92, and 6.15 Å, respectively. The apparent densities of 13X, ZSM5s (Si/Al = 23, 80), and ferrierrite are about 1.95 ± 0.04 , 1.94 ± 0.01 , 1.76 ± 0.08 , and 1.92 ± 0.01 g/cm³, respectively.

Ion-Exchange of Zeolites

The ion-exchanged levels of sodium-exchanged zeolites ZSM5 (Si/Al = 23, 80) and ferrierrite were calculated by taking the Na/Al ratio from XRF results for a theoretical one Al atom to one Na atom $[(\text{Na}/\text{Al}) \times 100 = \% \text{Na exchange}]$.⁶ The Na ion-exchange levels of ZSM5 (Si/Al = 23, 80) and ferrierrite are equal to 28, 17, and 17 %, respectively. In the case of copper-exchanged zeolite ZSM5-23, the theoretical copper-exchange results from two Al atoms for every one Cu²⁺ atom $[2(\text{Cu}/\text{Al}) \times$

100 = %Cu exchange].³⁷ The %Cu exchange of ZSM5-23 is about 44%. The elemental analysis results are summarized in Table 2.

Conductivity measurement

Electrical Conductivity: Steady State Sensitivity to CO. The electrical response ($\Delta\sigma = \sigma_{CO} - \sigma_{N_2 \text{ before-expose}}$ [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 N₂ at 1 atm and 30 ± 2 °C. Due to appreciable differences in initial conductivity between various composites, the sensitivity (sensitivity = $\Delta\sigma/\sigma_{N_2}$) is defined as the electrical conductivity response divided by the electrical conductivity when exposed to pure N₂.

The positive increment of the sensitivity upon exposed to CO can be traced back to the doped PPV-CO interaction mechanism as proposed in our work, and shown here in Table 1. CO molecules act as a secondary dopant, a substance which is subsequently applied to the primary-doped polymer, where charge transfer complex is formed between the polymer and the secondary dopant. This results in a greater number of charges along the polymer backbone and a corresponding larger sensitivity. Temporal response time (t_r) is defined as the duration between the starting time of CO exposure to the time at which the conductivity value reaches its steady state.

TABLE 1: The observed Sensitivity and temporal response for CO Adsorbed on PPV and doped PPV samples

Sample	The sensitivity ($\Delta\sigma/\sigma_{N_2}$)	the temporal response (t_r ,min)
PPV	6.01E-02	10.26
doped PPV	5.44E-01	146

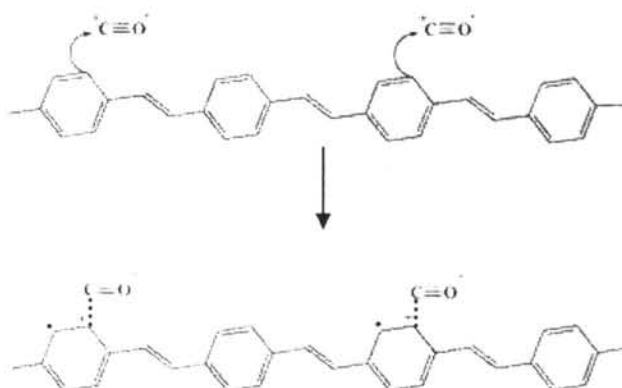


Figure 1. Propose mechanism of the CO-PPV interaction.

Effect of Zeolite Type on Electrical Sensitivity. Three types of zeolite with different pore sizes and Si/Al ratio were used to investigate the effect of zeolite type on the electrical response to CO. Table 2 shows that the sensitivity of doped PPV/ Na^+ -ZSM5(Si/Al = 23), 1.48, is slightly higher than doped PPV/ Na^+ -13X, which is 1.02, and the doped PPV/ Na^+ -ferrierite, which is 0.91,. All composites have larger sensitivity values than that of the pristine PPV, which is $6.01\text{E-}2$, and doped PPV, which is $5.44\text{E-}01$. The increase in the sensitivity value of PPV/Zeolite composites relative to that of the pristine PPV and doped PPV reflects the fact that CO molecules are adsorbed into the zeolites by the electrostatics. Based on this finding, a larger amounts of CO molecules are available to interact with PPV chains.

TABLE 2: Electrical Sensitivity, Temporal Response, and Ion-Exchange Level of Composite Samples

Sample	the sensitivity ($\Delta\sigma/\sigma_{\text{N}_2}$)	the temporal response (t_r ,min)	ion-exchanged level (%)
dPPV/13X_Na	1.02E+00	42	100
dPPV/fer_Na	9.16E-01	123	17
dPPV/ZSM5(23)_Na	1.48E+00	56	28
dPPV/ZSM5(80)_Na	1.17E+00	153	17
dPPV/ZSM5(23)_Cu	-1.54E-01	24	44

Doped PPV/Na⁺-ZSM(Si/Al =23) with the ion-exchange level equal to 28% has a larger sensitivity than that of doped PPV/Na⁺-13X even though 13X zeolite has a higher amount of Na⁺ than ZSM5(Si/Al = 23). The higher sensitivity of doped PPV/Na-ZSM5(Si/Al = 23) sample may originate from the nature of the structure of the zeolite itself. Na⁺-ZSM5(Si/Al = 23) zeolite has a channel structure whereas Na-13X zeolite has a cage structure. Therefore, Na⁺-ZSM5(Si/Al = 23) would allow CO molecules to pass through easily to interact with the doped PPV chains relative to that of 13X zeolite. Doped PPV/Na⁺-ZSM5(Si/Al = 23) and doped PPV/Na⁺-FER both have a channel structure with the ion-exchanged level equal to 28% and 17%, respectively. The composite with Na⁺-ZSM5(Si/Al = 23) has a higher sensitivity value. This is because Na⁺ plays an important role as an adsorption site of CO molecules. Composite with Na⁺-ZSM5(Si/Al = 23) can trap more CO molecules or allow more CO molecules to interact with PPV. The two types of zeolite with the same structure but different in the number of Si/Al ratio were used to investigate the electrical response to CO. The sensitivity of doped PPV/Na⁺-ZSM5(Si/Al = 23) vs. doped PPV/Na⁺-ZSM5(Si/Al = 80) indicate the same result as the previous case. The sensitivity of doped PPV/Na⁺-ZSM5(Si/Al = 23) is slightly higher than that of doped PPV/Na⁺-ZSM5(Si/Al = 80) which is equal to 1.17 with ion-exchanged level of 17%.

Table 2 shows the temporal response times of the composites studied: the doped PPV/Na⁺-13X, the doped PPV/Na⁺-ZSM5(Si/Al = 23), the doped PPV/Na⁺-FER, and the doped PPV/Na⁺-ZSM5(Si/Al = 80). The temporal induction times are 42, 56, 123, and 153 min, respectively. Therefore, the temporal response time is inversely related to the amount of Na⁺ ion as an approximation. It appears that a zeolite with more Na⁺ ions can trap CO molecules through the electrostatic interaction, and hence the interaction of CO with PPV chains is terminated in a shorter time.

Effect of Cation Type on Electrical Sensitivity. In this study, the effect of cation type has been investigated over ZSM(Si/Al = 23). In order to minimize the impact of cation size to its framework, the Cu⁺ (The radii of cation is equal to 96 picometers)⁴¹, metal cation with *d* orbital, was chosen to compare with Na⁺ (the radii of cation is equal to 95 picometers)⁴¹. The Cu²⁺ ions are 3d⁹ paramagnetic ions and

are easily observed by ESR⁷. Cu^+ ions, on the contrary, are diamagnetic ($3d^{10}$) and therefore are ESR silent.^{6,7,12} The results show that the Cu^{2+} ESR signal of Cu^+ -ZSM5(Si/Al = 23) decreases and the spectral feature changes substantially when a hydrated sample was heated and progressively dehydrated. Therefore, the modification of hydrated system upon dehydrating in vacuo at 573 K undergoes a self-reduction of Cu^{2+} into Cu^+ .

The electrical sensitivity of dPPV/ Cu^+ -ZSM5(Si/Al = 23) system shows the negative value, -0.154, while the Na system give positive effect, 1.48, as demonstrated in Table 2. However, The temporal response of dPPV/ Cu^+ -ZSM5(Si/Al = 23), of 24 min, is twice shorter than that of dPPV/ Na^+ -ZSM5(Si/Al = 23) which is 53 min.

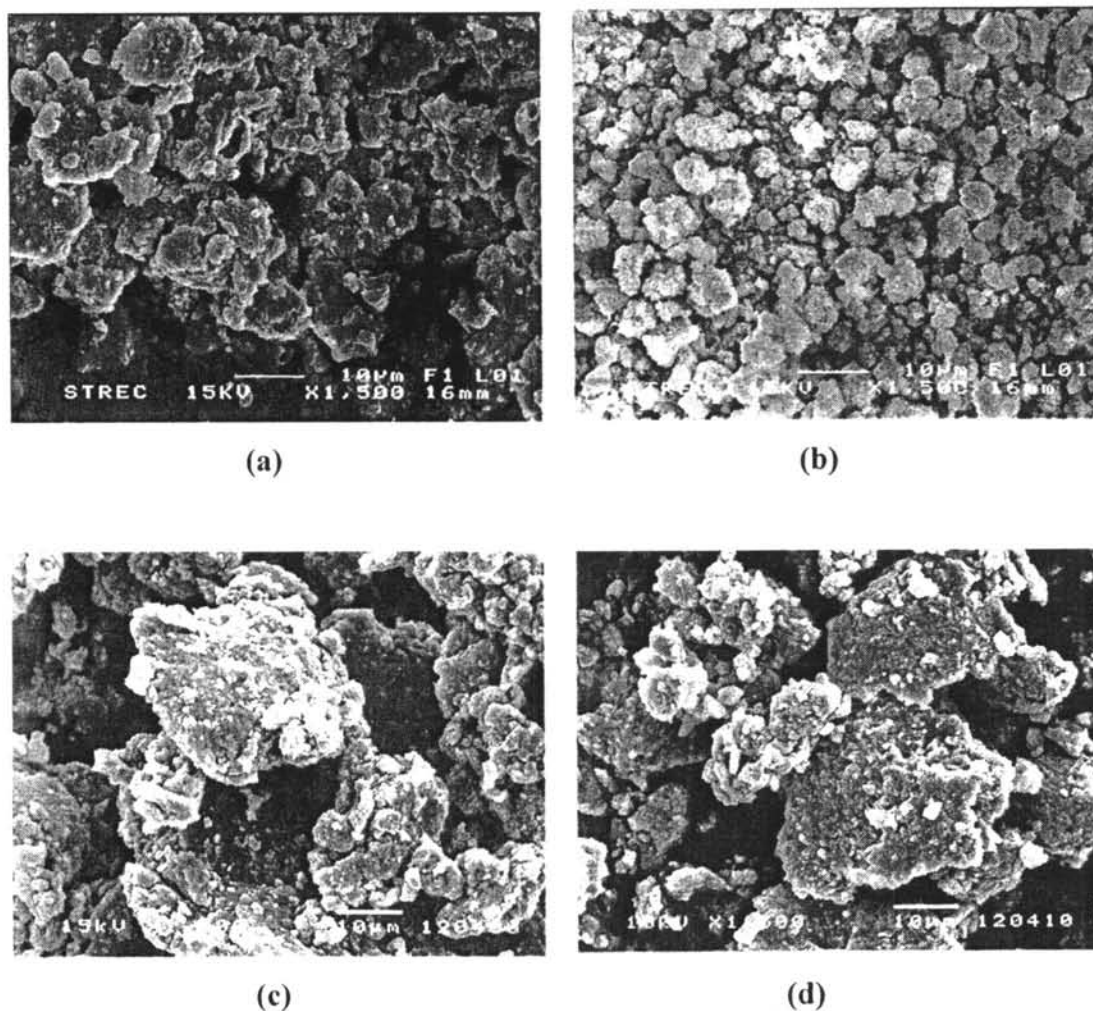


Figure 2. SEM micrographs of powder samples at the magnification 1500 of; (a) doped PPV; (b) NH_4^+ -ZSM5 (Si/Al = 23) before ion exchange; (c) doped PPV/ Na^+ -ZSM5; and (d) doped PPV/ Cu^+ -ZSM5.

To clarify the effect of ion-exchanged types in zeolite on electrical conductivity sensitivity and the temporal response, a comparison of the results has been made by measuring the desorption of CO on Na^+ -ZSM5(Si/Al = 23) and Cu^+ -ZSM5(Si/Al = 23). TPD spectra obtained after room-temperature adsorption of CO on Na^+ - and Cu^+ -ZSM5(Si/Al = 23) are shown in Figure 3. The temperature of the maximum desorption rate of CO on the two adsorbents are significantly different. On Na^+ -ZSM5(Si/Al = 23) it is observed at 116 °C, while on Cu^+ -ZSM5(Si/Al = 23) it is at 222 °C. This result demonstrates that Cu^+ -ZSM5(Si/Al = 23) adsorbed CO

molecules more significantly stronger than Na^+ -ZSM5(Si/Al = 23). The strong adsorption observed for the copper ion-exchanged ZSM5 sample than sodium ion-exchanged arises from the interaction between the copper ion and the CO molecule. Carbon monoxide is a weak Lewis base that interacts with coordinatively unsaturated centers, forming pure σ -complexes (in d^0 systems) and σ,π -complexes (in d^n systems).¹¹ The copper ions in ZSM5 act as the active sites for CO adsorption. In such conditions it is well known that CO forms stable carbonyls with coordinatively unsaturated Cu^+ while it does not coordinated on sodium ion. It can be said that these data clearly confirm the electrical sensitivity and the temporal response results that Cu^+ -ZSM5(Si/Al = 23) is more adsorbable towards CO molecules than Na^+ -ZSM5(Si/Al = 23). Therefore, the lesser amount of CO molecules interact with the doped PPV chains which causes the negative sensitivity and the faster temporal response.

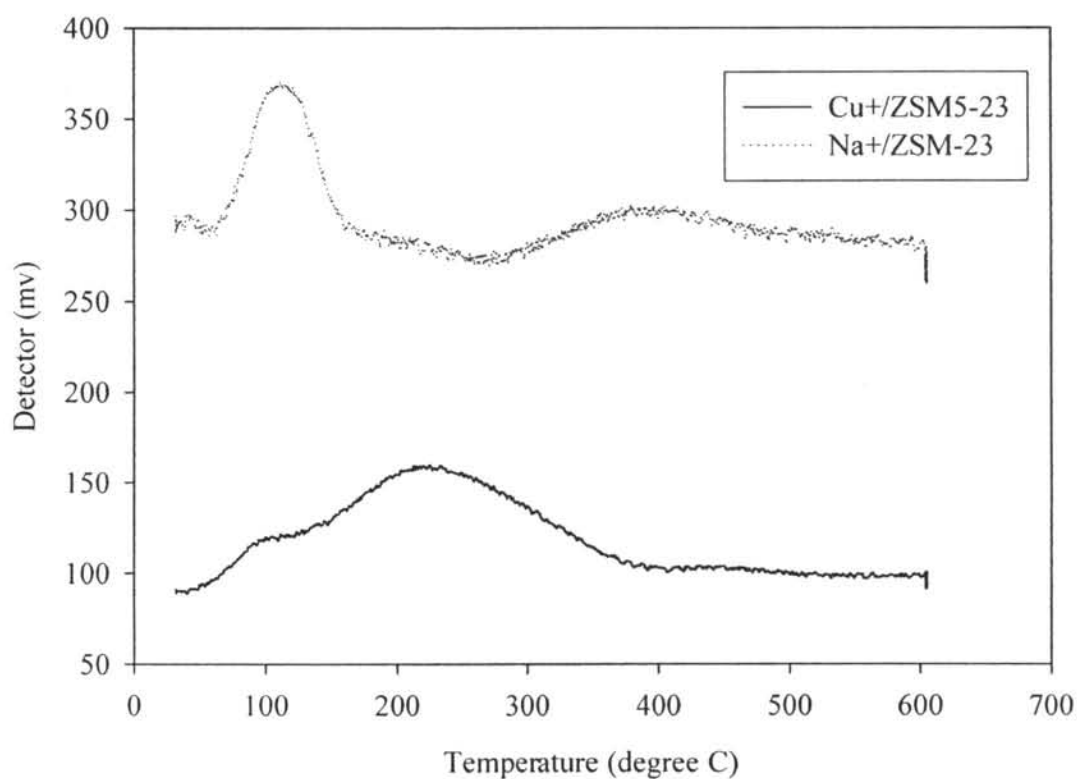


Figure 3. TPD spectra for the Na-ZSM5 and Cu-ZSM5 sample treat sample with CO at 298 K and 1 atm.

FTIR Investigations of Reactions of Adsorbed CO.

The interaction of CO with Na-exchanged zeolite and carbon cation from quinoid structure of doped PPV can be conveniently monitored by means of IR spectroscopy. The IR spectra in the 2000-2300 cm^{-1} region of CO adsorbed at 1 atm ad room temperature on the samples are shown in Figure 4. The vibrational stretching frequency of CO predominately experience a blue shift with respect to the free CO molecule ($\nu = 2143 \text{ cm}^{-1}$) when CO is adsorbed on a cation site. They are all dominated by a strong band in the 2100-2200 cm^{-1} rang.

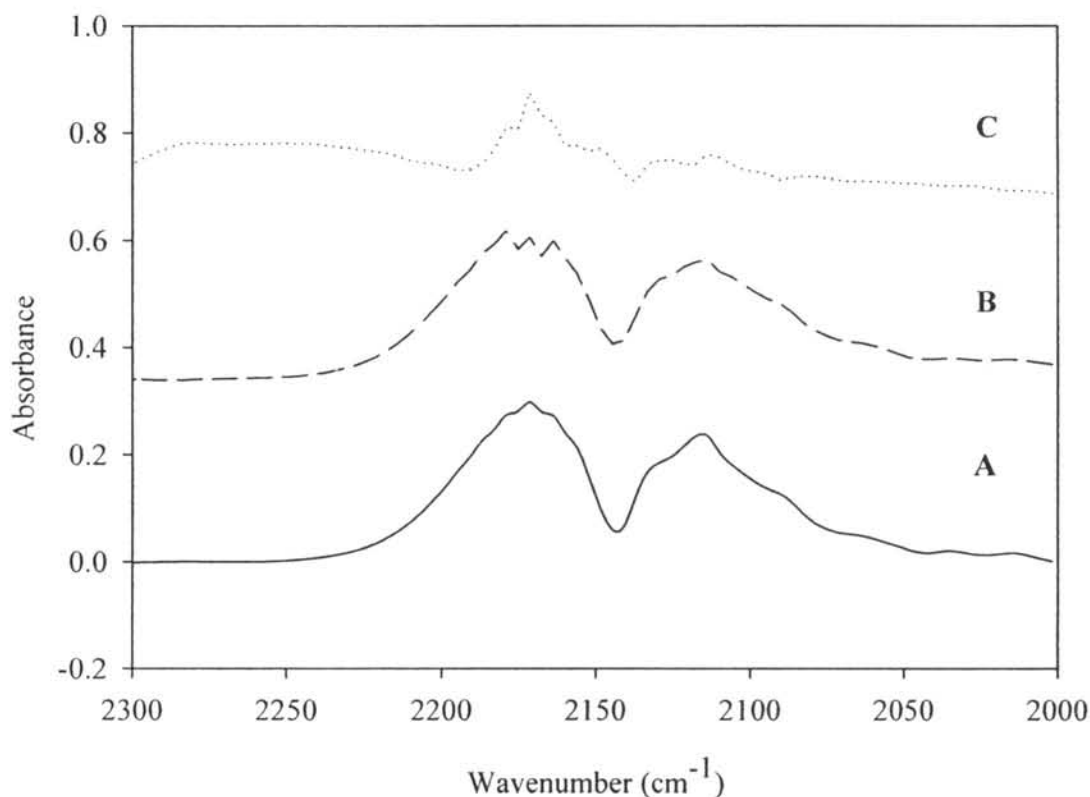


Figure 4. IR spectra of CO (Pressure =1 atm at room temperature) adsorbed on **A** doped PPV; **B** doped PPV/ Na^+ -ZSM5; **C** Na^+ -ZSM5, in which all spectra backgrounds were subtracted.

Band at 2100-2200 cm^{-1} is the most significant feature of the spectra, appears at the following frequency (in cm^{-1} versus the cation). Na^+ from ion-exchanged ZSM5(Si/Al = 23): 2172 and C^+ from the quinoid structure of doped PPV: 2164, as demonstrated in Figure 4. These hysochromic shift can be readily be ascribed to the interaction of CO via the carbon end of its molecule with the positive field set by cations.^{8,10,21}

It has been reported in ref.4 that the prominence of the band, together with the smooth decrease in frequency with increasing cation size. The main IR absorption band in the doped PPV/CO spectrum corresponds to $\text{C}^+ \dots \text{CO}$ adduct and is centered at 2164 cm^{-1} . The smaller value expects for the radii of cations, would seem to lead to a stronger $\text{C}^+ \dots \text{CO}$ interaction and consequently larger CO frequency shift. The observed facts can be explained by assuming that carbon is partially covalently bonded to the backbone of polymer chain. As a consequence, only a part of the C^+ positive charge is available, and the electric field around the carbon cation is consequently reduced thus leading to a smaller polarization of the CO molecules.

The IR absorption for the composite system between doped PPV/ Na^+ -ZSM5(Si/Al = 23) appears the bands at 2172 and 2160 cm^{-1} together with an almost equivalent intensity which results from the sodium and carbon cation site present in the sample and the these nature bond are electrostatic. From the results, we cannot observe any new IR bands. This may originate from the fact that we used the dry mixing composites consisting of only a physical contact between cluster of doped PPV and Na-ZSM5 occur. Therefore, there are no new absorption sites to indicate the new IR frequency shift. However, other significant IR absorptions are also observed. A broad bands around 2110-2130 cm^{-1} arises from the condensation of CO on the absorbate³⁸ or physisorbed CO inside the zeolite structure³⁹ at high CO equilibrium pressure.

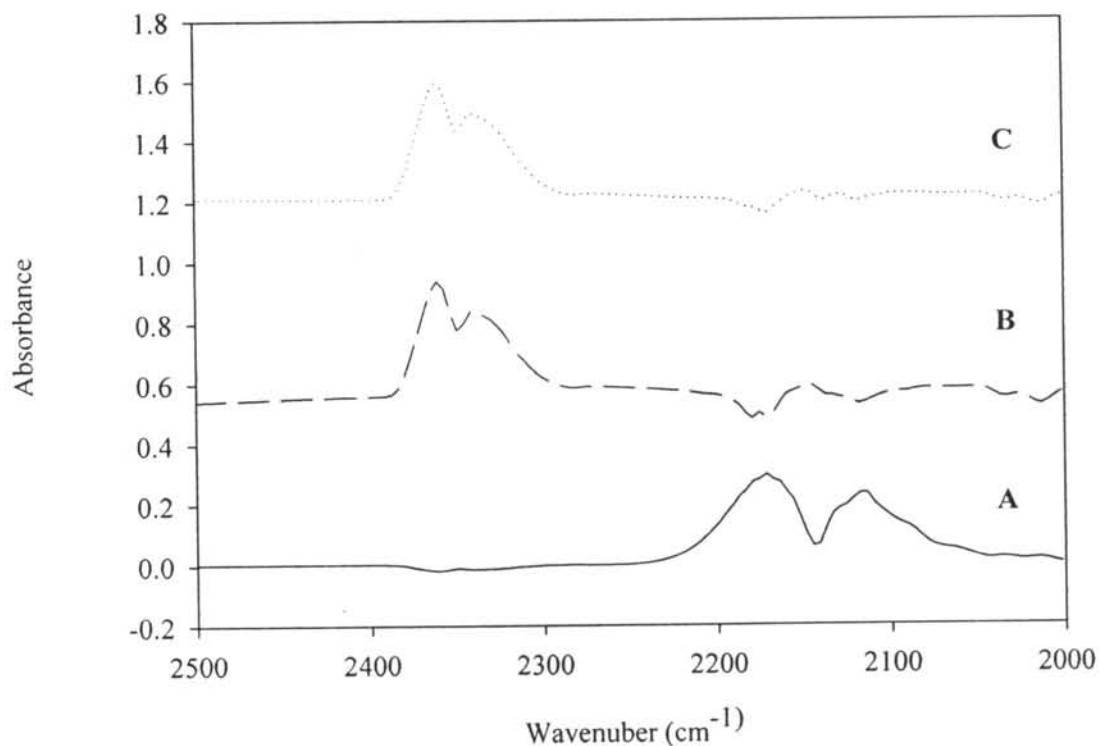


Figure 5. IR spectra of CO (Pressure =1 atm at room temperature) adsorbed on **a)** doped PPV; **b)** doped PPV/Cu-ZSM5; **C** Cu-ZSM5, in which all spectra backgrounds were subtracted.

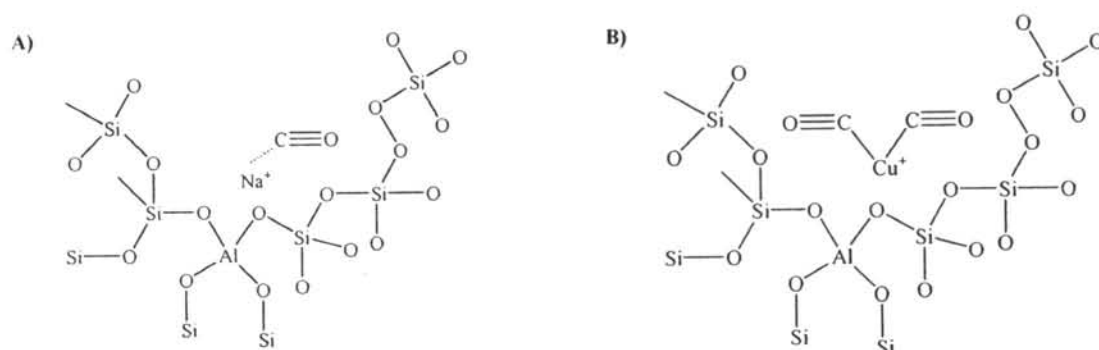


Figure 6. The different adsorption states of carbon monoxide in the ZSM5(Si/Al = 23): a) a proposed mechanism for Na-ZSM5 showing the significant IR frequency at 2,172 cm⁻¹, b) a proposed mechanism for Cu-ZSM5 giving the IR band at 2,340 and 2364, respectively.

Figure 5. shows the IR spectrum of the absorbed CO species on Cu^+ -ZSM5(Si/Al = 23) at 1 atm and at room temperature. CO is absorbed exceptionally strongly on Cu^+ sites, but only weak on Cu^{2+} .^{7,14,15,17} The IR band appears at 2300-2400 cm^{-1} range. The band at 2340 and 2364 cm^{-1} can be assigned to the antisymmetric and symmetric stretching modes of $\text{Cu}^+(\text{CO})_2$, respectively⁴⁰.

It can be expected that the composite between doped PPV/ Cu^+ -ZSM5(Si/Al = 23) affects the nature of CO bond. The result shows that the major peaks appear at 2364 and 2340 cm^{-1} corresponding to the adsorption of CO to Cu^+ . The small peak (the lower the IR intensity) also occurs at 2160 cm^{-1} ; this band is assigned to CO adsorption to carbon cation of quinoid structure of doped PPV. Therefore, The CO molecules are selectively adsorbed on Cu^+ site than C^+ site of the dry mixing composite samples.

Conclusions

The effect of zeolite types and cation exchanged types on the CO interaction with PPV doped with sulfuric acid were investigated. For the effect of zeolite type, the highest electrical conductivity sensitivity is obtained with the doped PPV/ Na^+ -ZSM5(Si/Al = 23) is slightly higher than those doped of the PPV/ Na^+ -ZSM5(Si/Al = 80), of the doped PPV/ Na^+ -13X, and of the doped PPV/ Na^+ -ferrierite. The electrical sensitivity values obtained are equal to 1.48, 1.17, 1.02, and 0.91, corresponding to the sodium ion-exchange levels of 28, 17, 100, and 17 %, respectively. It appears that a zeolite with more Na^+ ions located in a channel structure type zeolite can trap more CO molecules through the electrostatic interaction giving a higher sensitivity. The increase in the sensitivity value of PPV/Zeolite composites relative to that of the pristine PPV and doped PPV reflects the fact that CO molecules adsorb into the zeolites by the electrostatic interaction. Based this assumption, a larger amount of CO molecules are available to interact with PPV chains. The composite of doped PPV/ Na^+ -13X gives the shortest temporal response time, follow by doped PPV/ Na^+ -ZSM5(Si/Al = 23), doped PPV/ Na^+ -FER, and doped PPV/ Na^+ -ZSM5(Si/Al = 80). The temporal response time is inversely related to the amount of Na^+ ion as a first approximation. It appears that a zeolite with more Na^+ ion can trap CO molecules through the electrostatic, and hence the

interaction of CO with PPV chains reached in a shorter time. For the effect of cation exchanged types, we used doped PPV/cation exchanged ZSM5 (Si/Al = 23) zeolites (Na^+ and Cu^+) as a model. The electrical sensitivity of dPPV/ Cu^+ -ZSM5 system shows the negative value, -0.154, while the Na system give a positive sensitivity of 1.48. The IR spectra of the composites modified C-O stretching frequency. The dry mixing composite systems demonstrate a combination between characteristic peaks of its sensing materials; 2160 and 2172 cm^{-1} for doped PPV/Na-ZSM5; 2160, 2340, and 2364 cm^{-1} for doped PPV/ Cu -ZSM5. The new IR shift peaks cannot be observed. Because of the dry mixing composites, only the physical contact between polymer and zeolite clusters exist. The TPD results demonstrate that Cu^+ -ZSM5(Si/Al = 23) adsorbs CO significantly stronger than Na^+ -ZSM5(Si/Al = 23). The strong adsorption observed for the copper ion-exchange ZSM5 sample than sodium ion-exchange arises from the interaction between the copper ion and the CO molecule. This fact is interpreted in terms of the difference in the nature of bonding between the electrostatic force for sodium ion-exchange ZSM5 and doped PPV with CO molecules and the covalent nature for the copper in-exchanged ZSM5 with CO molecules. Therefore, the composite sample of PPV with copper exchanged ZSM5 would allow the lesser amount of CO molecules to interact with the doped PPV chains which causes the negative sensitivity value and the faster temporal response.

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