Effect of Different Variables on the Electrical Conductivity Sensitivity of Synthesized Zeolite/Polymer Composites for Various Gases: A Review

Muzzaffar Ahmad Mir[1*], Rawoof Ahmad Naikoo[1], Samiullah Bhat[1], Radha Tomar[1], Muzzaffar Ahmad Bhat[1], Rayees Ahmad Bhat[2], Pukhrambam Dipak[3] and D. C. Tiwari[3]

[1]*School of Studies in Chemistry, Jiwaji University, Gwalior (M.P.)-474011, India.*
[2]*Department of Chemistry, Science College, Jiwaji University, Gwalior (M.P.)-474009, India.*
[3]*School of Studies in Physics, Jiwaji University, Gwalior (M.P.)-474011, India.*

Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

Article Information

Review Article

ABSTRACT

In this review synthesis of zeolites, cation exchange of zeolites and polymerization of polymers in zeolites to form zeolite/polymer composites is reported. The effect of various variables like zeolite content, temporal response of the zeolite, effect of cation concentration, effect of vapor type, effect of cyclic interval, pore size, zeolite type, Si/Al ratio and type of cation in the zeolite pore on the electrical conductivity sensitivity of zeolite/polymer composites to various gases is reported here. An increase or decrease in the above variables and their effect on the sensitivity of the composites is summarized.

Corresponding author: E-mail: mirmuzafar92@gmail.com;

Keywords: Zeolite; polymer; composite; sensitivity; gas; conductivity etc.

1. INTRODUCTION

The environment is being contaminated by the combustion of petroleum products like diesel, heating oil and various fuels due to which an enormous amount of toxic gases like CO (carbon monoxide) and SO_2 (sulphur dioxide) are released in the atmosphere. These gases have various damaging effects. Carbon monoxide leads to chest pain and causes diminished mental alertness. Due to acid rain the chemical composition of soil gets changed and leads to the loss of minerals. In addition to the above mentioned gases present in the atmosphere, fossil fuels also release toxic byproducts like NO_x (oxides of nitrogen) and hydrocarbons. A significant part of NO_x emissions originate from motor vehicles. The combination of NO_x and CO in presence of sunlight tends to produce O_3, which is harmful to plants and also to human beings. Conducting polymers are one of the most significant materials in chemistry due to their vast applications. Indeed, conducting polymers have been exploited as potential sensing materials because of their good optical and electrical properties. They have been found as pH sensors [1], humidity sensors [2], biosensors [3], ion selective sensors [4], and also gas sensors [5]. Several evidences reveal the sensing properties of polymers such as polyaniline (PANI) [6], poly(thiophene) (PTh) [7] and polypyrrole (PPY) [8]. Poly(p-phenylene) (PPP) possesses the advantages of high stability, ease of synthesis, and high chemical resistance. In addition, it also finds applications in rechargeable batteries and electrodes [9]. PPP shows varied electrical properties under gaseous exposure [10,11]. PPV has been reported to act as a sensor for various gases e.g., (chloroform, ethanol, acetic acid, hexane, ethyl acetate, methanol, toluene, diethyl ether); the range of sensitivity values lies between 10–40% [12]. A sensor should possess high chemical specificity and sensitivity in a narrow range [13,14]. To influence the interaction between conducting polymers and the target gases, zeolite materials have been utilized [15]; because of their porous structure which provides size and shape selective properties to the polymers. A zeolite has been found to act as a selective microporous adsorbent to increase the sensitivity of polymer towards NH_4NO_3 [16-18]. Zeolites can be synthesized with different chemical compositions and distinct framework topologies, and about 170 of such topologies have been reported. Due to their ion-exchange properties, as well as adsorption and reactions of molecules within its cages, zeolites have found use in numerous applications in catalysis and separations. Use of the novel properties of zeolites for sensor applications is of more recent vintage, yet, several recent reviews have summarized the role of zeolites in sensor development. There are several physical and structural features of zeolites that have been exploited for sensing. The versatility of these materials is evident from the fact that the zeolite can be used to improve the performance of an existing sensor, as well as zeolites have been used as the sensing medium [19]. Since, polymers are conductive in nature; so the change in electrical conductivity of zeolite/polymer composites is used in sensing. Change in resistance of the zeolite/polymer composite is also used in sensing. Different elements have different electronegativity and it has its own effect on the electrical conductivity sensitivity of a composite. Hence, ion exchange of zeolites is carried out to study the effect of different ions on the sensitivity of a composite. Zeolite is a microporous, polycrystalline material with a uniform pore size distribution. A lot of work has been carried out on the varied applications of zeolites, and gas adsorption [20]. This property of zeolite is affected by various factors such as pore type, the pore size distribution, the class and the type of cation present in the zeolite and various other factors. In the light of above background, we became interested to summarize various procedures for the synthesis of zeolite/polymer composites and highlight the effect of various parameters like zeolite content, temporal response of the zeolite, vapor concentration, pore size, zeolite type, Si/Al ratio and type of cation in the zeolite pores etc. on the sensitivity of zeolite/polymer composite to various poisonous gases which are environmentally unfriendly.

The gas sensing experiments are carried out in a setup given below. The gas chamber has one temperature controlled heater for quick evaporation of the liquid organic when they are injected into the gas chamber using a micro syringe, a small 12 V DC fan is placed inside the gas chamber for quick circulation and homogeneous spreading of chemical vapors. The chamber is connected to nitrogen gas cylinder to flush out the exposed chemical vapors after sensing. This process is necessary to allow

the sensor to achieve the base line resistance prior to the next vapor exposure for sensing. Petroleum jelly is used to seal the chamber. This type of gas handling system is called as static gas generation system. For ammonia vapor sensing, the sensors are mounted on the sample holder and the electrical connections are taken by using silver paint and is connected to the LCR meter for data acquisition [21].
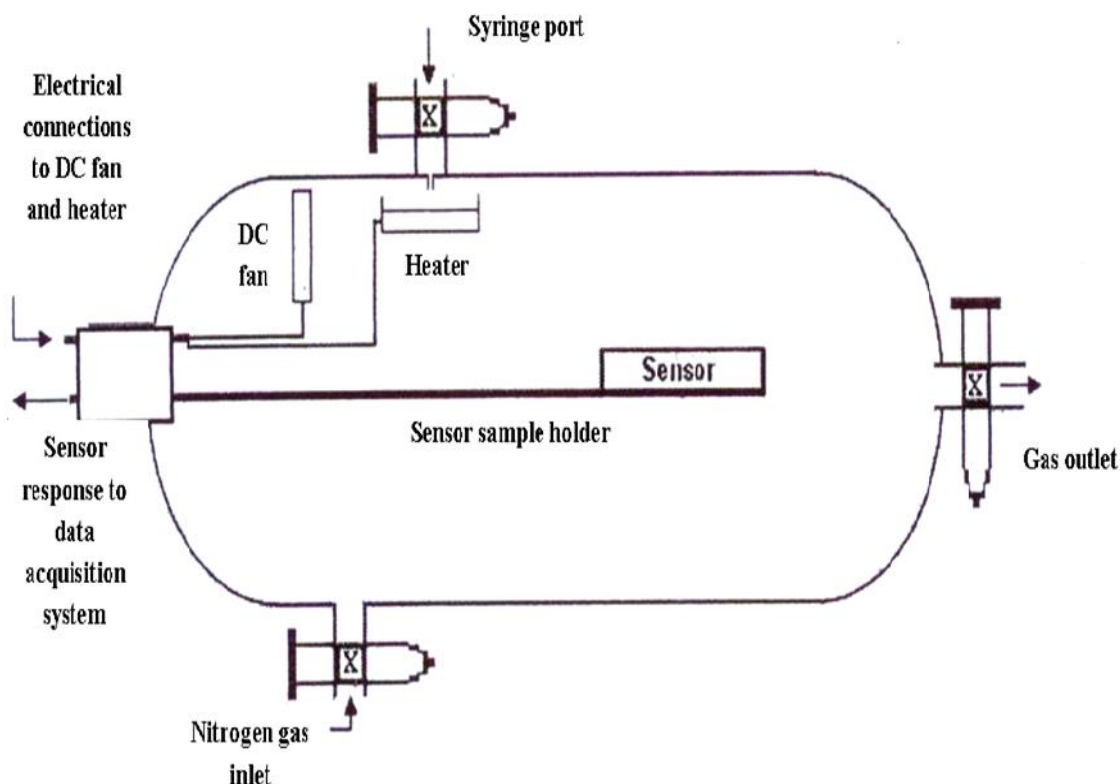
Gas sensing setup [21]

The response of the composite towards the gas (e.g. CO) is determined by the following equation.

$$[\Delta\sigma = \sigma_{CO} - \sigma_{N2}]$$

Where,

$\Delta\sigma$ = The response of the composite towards the gas.
σ_{CO} = Conductivity of the composite in presence of the target gas; CO.
σ_{N2} = Conductivity of the composite in presence of nitrogen.

The sensitivity of the composite is determined by the following equation:

$$[\Delta\sigma/\sigma_{N2}]$$

The gas sensing measurements are performed on the prepared samples/pellets/films at different concentrations of gas vapors by using the above setup.

2. SYNTHESIS OF ZEOLITES

2.1 Synthesis of Zeolite AlMCM41

An aqueous solution of HTAB (Aldrich), a 25% concentrated ammonium solution, and a sodium silicate solution with Na/Si ratio of 0.5 (2.4 wt. % SiO_2, 9.2 wt. % Na_2O, and 88.4 wt. % H_2O) are used to synthesize zeolite AlMCM-41. The mixture is 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 is stirred for 1 h, the mixture is heated to 97°C in an oven for 1 day. During this period, the cap is loosened repeatedly in order to reduce the ammonium pressure. The bottle is then cooled to room temperature, followed by drop wise additions of 30% acetic acid to adjust the solution pH value to 10.2. The bottle is then heated to 97°C again in the oven for 24 h and then cooled to room temperature. Subsequently, 3 mol of NaCl/HTAB and sodium aluminate 0.13 mol silicate are added to the mixture and stirred for 30 min. The reaction mixture is adjusted to a pH value of 10.2 and then heated to 97°C twice more. Finally, the precipitate product is filtered, washed with distilled water and dried at 97°C for 12 h. The dried zeolite AlMCM-41 powder is calcined under an O_2 flow with continuously increasing temperature up to 540°C for 10 h and maintained at that temperature for 10 more hours [22]. The procedure for the synthesis of various types of zeolites can be obtained from **IZA** *(International Zeolite Association).*

2.2 The Cation Exchange of Zeolites

2.2.1 Cation exchange of zeolite Y

Zeolite can be ion exchanged in to different forms by the following procedure. The solution of $MgCl_2$, $CaCal_2$ and KCl at 0.5 M is added in to 5 g of Na-form of the zeolite and stirred at 25°C for 24 h. To synthesize zeolite Y (Si/Al 5.1, 50% mole of Na^+ and 50% mole of Mg^{2+}) or 50 MgNaY, zeolite Y (Si/Al 5.1, 50% mole of Na^+ and 50% mole of Ca^{2+}) or 50CaNaY, zeolite Y (Si/Al 5.1, 80% mole of Na^+ and 30% mole of K^+) or 30 KNaY, zeolite Y (Si/Al 5.1, 50% mole of Na^+ and 50% mole of K^+) or 50 KNaY and zeolite Y (Si/Al 5.1, 80% mole of Na^+ and 20% mole of K^+) or 80KNaY are to be taken. Then zeolite samples are filtered and washed with deionised-water for 5 times [23].

2.2.2 Cation exchange of zeolite L and mordenite

Zeolites L and mordenite can be ion-exchanged with different cations in order to investigate the effects of cation type on the sensitivity of the zeolite/polymer composites. Zeolite L (parent form) is stirred in 1 M solution of NaCl at 80°C for 2 h, at the ratio of 1 g: 70 ml. Zeolite mordenite is stirred in 1 M of LiCl and KCl solutions using the same procedure. This process is repeated many times until each zeolite contained the required amount of cation. After filtering and washing with distilled water for several times, the ion exchanged zeolites are dried and calcined at 500°C for 5 h [24].

3. SYNTHESIS OF POLYMER

3.1 Synthesis of Polyaniline

Chemical polymerization of aniline is carried out in an aqueous acidic solution. 8.09 g of ammonium persulphate is dissolved in 200 ml of deionized water. This solution is added dropwise to a solution of 4 ml aniline dissolved in 200 ml of HCl aqueous solution (1 M), while the reaction mixture is vigorously stirred at -2 to -5°C for a period of 6 hours. The green emeraldine hydrochloride precipitate is collected and washed repeatedly with 80/20 water/methanol solution until the under washing solution became colorless. Washing with methanol solution causes the removal of short low molecular weight chains and therefore improves the mechanical and electrical properties of polymer [25].

3.2 Poly (p-phenylenevinylene) Synthesis and Doping Process

Synthesis of the p-xylene-bis (tetrahydrothiophenium chloride) monomer is achieved by reacting α,α'-dichloro-p-xylene with tetrahydrothiophene. The precursor sulfonium polyelectrolyte is prepared in an aqueous solution by the base induced polymerization of an appropriate bis-sulfonium monomer. The polymerization reaction is terminated by the addition of dilute aqueous hydrochloric acid to the reaction mixture which is then dialyzed against water in order to separate the high molecular weight fraction from the monomeric and oligomeric residues as well as the sodium and chloride ions. Poly(p-phenylenevinylene) (PPV) is obtained by heating pol[(p-xylene-bis(tetrahydro-thiophenium chloride)] under

vacuum at 180°C for 6 hours. 18 M sulfuric acid issued as a dopant solution at the mole ratios between PPV repeating unit per sulfuric acid equal to 1:300. The doping process occurs after adding the dopant solution to a polymeric powder, and it is monitored by observing the color changes of the powder from bright yellow to black [26].

4. SYNTHESIS OF ZEOLITE/POLYMER COMPOSITES

4.1 Synthesis of Polyaniline/Cu^{2+} Zeolite Composite

Prior to composite formation, zeolites Y and 13X are calcined under a N$_2$ flow at 200°C for 2 hrs. Zeolites are converted into Cu^{2+} form by stirring 1 g of zeolite in 200 ml 2.1×10^{-4} M CuCl$_2$ for 12 h at room temperature. The precipitate is then filtered and washed with distilled water and dried at 80°C for 2 hrs in an oven. Polyaniline/zeolite composites are formed by mixing PANI powder with the zeolites. The composites are compressed into pellets by a hydraulic press at a pressure equal to 5 t [27].

4.2 Synthesis of (Doped Polydiphenylamine)/Zeolitey_H$^+$ Composite

The D-PDPA (doped polydiphenylamine) and zeolite Y_H$^+$ powder is ground prior to pellet formation. The powder is then pressed into pellets for measurement of electrical conductivity and sensitivity with a hydraulic press machine (GRASEBY SPECAC) applying a 4-5 ton load. Pellets are prepared in disc form using a 1 cm stainless steel die. The thickness of the pellets can be measured by a digital thickness gauge (PEAACOCK, dial stand type model PDN-20) [28].

4.3 Synthesis of Polythiophene/Zeolite13x Composite

A particular quantity of zeolite 13X powder (1.0 g) in a conical flask containing 25 ml of CHCl$_3$ is sonicated for 15 min. Add a known volume of TP (0.5 g) to it and stir magnetically for 15 min. Thereafter, add a particular quantity of FeCl$_3$ (4.0 g) to this solution at a time under continued stirring for 1 h at room temperature. To stop the polymerization and to remove excess of FeCl$_3$, add 20 ml of acetone. Then filter and wash the mixture with MeOH (10 ml) followed by acetone (5 ml). Finally, dry the black residue at 50°Cunder vacuum for 1 h [29].

4.4 Synthesis of Polyaniline/Polyfuran-13X Composite

A particular quantity of PF-13X composite is taken in a 50 mL conical flask. Add 25 ml 2 (M) HCl solution and a particular volume of PANI monomer. Stir the mixture for 15 min. Thereafter, add a known quantity of PDS and stir for 1 h. Add Excess MeOH. Filter and wash the residues with acetone to remove oligomers of PANI. Finally dry the dark green mass under vacuum at 50°C for 1 h [30].

4.5 Synthesis of Polyfuran/Zeolite LTA Composite

Polyfuran (PFu) is prepared within zeolite LTA by polymerization of furan monomer with FeCl$_3$ in nonaqueous medium. Add 10 mmol furan to the dispersion containing a weighed amount of zeolite in 25 ml of acetonitrile and sonicate for 15 min. The ratio of oxidizing agent to monomer is to be taken as 1.5. Keep the reaction mixture under constant stirring for 24 h. Filter the precipitated mass and wash with acetonitrile and EtOH until the filtrate becomes colorless. Finally, the composite is dried at 50°C for 24 h under vacuum [31].

4.6 Synthesis of Polyaniline/Clinoptilolite Nanocomposite

The aniline monomer is embedded into the clinoptilolite channels and is polymerized using ammonium persulfate as initiator/oxidant. It is proposed that the weakly polar aniline finds it more difficult to penetrate into the clinoptilolite channels than a polar anilinium cation. Hence, a reaction between H$^+$ present in clinoptilolite structure and anilinium cation in solution is carried out. Therefore, clinoptilolite at weight ratios of 0.25, 0.5, 1, 2, 3, 4 and 5% w/w per aniline monomer is mixed in 200 ml of HCl aqueous solution (1 M) already containing 4 ml aniline monomer. Stir the mixture for 48 hours at room temperature. Dissolve 8.09 g of ammonium persulphate in 200 ml of deionized water and add drop wise for a period of 6 hours to the above mixture. Meanwhile the reaction mixture is stirred at -2 to -5°C. Wash the obtained composite repeatedly with 80/20 water/methanol solution unless the under washing solution becomes colorless [25].

5. EFFECT OF VARIOUS VARIABLES ON THE ELECTRICAL CONDUCTIVITY SENSITIVITY OF ZEOLITE/POLYMER COMPOSITES FOR VARIOUS GASES

5.1 Effect of Zeolite Content

The sensitivity of zeolite/polymer composites to various gases increases initially up to certain increase in the zeolite content; above which there is no increase in the sensitivity of the composite. There are several evidences of this fact. The sensitivity of the composites fabricated from zeolite 13X of 3 weight ratios—PANI-10MA/10zeolite13X, PANI-10MA/20zeolite13X, PANI-10MA/40zeolite13X shows a decrease from 1.02 to 0.103 S/cm as the zeolite content is increased from 0 to 40 wt %. A similar trend is observed in the presence of N_2. But they show a reverse trend on exposure to CO. An increase (from 0.157 to 0.950) in the sensitivity of the above composites is found on increasing the zeolite content from 0.004 to 0.138 at 1000 ppm of CO. This increase in the sensitivity of the composites on exposure to CO is because of the fact that CO molecules get adsorbed physically into the zeolite 13X frame work [32]. Hence, as we increase zeolite content more and more zeolite pores/unit surface area are available for CO molecules to interact. The temporal response times of PANI-10MA, PANI-10MA/10Zeolite-13X, PANI-10MA/20 Zeolite-13X and PANI-10MA/40 Zeolite-13X are shown in Table 1. It is observed that the temporal response time varies from 237 to 300 min as we increase zeolite 13X content from 0 to 40%. In composite having high zeolite content, more and more CO molecules get adsorbed and penetrate into the composite and hence they require a long time to interact with polyaniline chains. Hence, the electrical conductivity reaches a steady state value [27].

Similarly P. Phumman et al. [33] reported that the sensitivities of 50:1 D-PPP at 0.625, 1.25 and 5% NH_3 exposure increase from −0.140±0.11 to −0.51±0.02, from −0.16± 0.02 to −0.79±0.01, and from −0.341±0.03 to −0.88±0.01, respectively, as Na-ZSM-5(23) content increases from 0 to 30 wt%. The increase in the sensitivity is because of the fact that as the zeolite content increases more and more NH_3 molecules get a chance to get adsorbed and penetrate into the composite and interact with D-PPP [34]. Further increase in the zeolite content (above 40 wt %) decreases the sensitivity to −0.32±0.13, −0.55±0.01 and −0.73±0.01. This is because increasing zeolite content reduces the no. of active sites present in D-PPP which can interact with NH_3. The effect of zeolite Y-H[+][80] content on the sensitivity of D-PDPA/Y-H[+][80] for halogenated solvents. The composites show a negative response for the solvents [28]. Since, D-PDPA is doped through P- type doping according to the doping theory [35]. Therefore, it receives electrons to fill the hole on its exposure to electron donating solvents. Hence, the mobility of electron along the D-PDPA back bone becomes restricted, resulting in the decrease in electron conductivity. Therefore, the composites show negative sensitivity towards the solvents. Now as the zeolite content (Y-H[+][80]) is increased; the sensitivity increases by one order of magnitude towards DCM and DCE as shown in Fig. 1. At about 30 wt % of zeolite content; the highest sensitivity of the composite is obtained. This is due to the fact that a higher content of zeolite results in greater interaction with the target gas. While there is found no effect of increase in

Table 1. Electrical conductivity, sensitivity and concentration dependence of PANI/Zeolite composites [27]

| Samples	σ_{air} (S/cm)	$\sigma_{N2,final}$ (S/cm)	$\Delta\sigma/\sigma_{N2,final}$		a, b when $\Delta\sigma = a[CO]^b$	t_r (min)
			at [CO] = 1000 ppm	at [CO] = 7.8 ppm		
PANI-10MA	$1.02\pm0.13\times10^{0}$	$2.40\pm0.38\times10^{-1}$	0.158	0.004	3.18×10^{-3}, 0.59	237
PANI-10MA/ 10 Zeolite-13X	$7.83\pm8.1\times10^{-1}$	$7.84\pm8.29\times10^{-2}$	0.810	0.389	2.32×10^{-1}, 0.25	250
PANI-10MA/ 20Zeolite-13X	$6.53\pm0.01\times10^{-1}$	$1.05\pm0.21\times10^{-1}$	0.356	0.011	8.76×10^{-3}, 0.50	285
PANI-10MA/ 40Zeolite-13X	$1.03\pm0.36\times10^{-1}$	$9.85\pm5.30\times10^{-3}$	0.950	0.138	4.15×10^{-2}, 0.42	300
PANI-10MA/ 10Zeolite-Y	$8.82\pm1.33\times10^{-1}$	$1.68\pm0.13\times10^{-1}$	0.431	0.114	6.58×10^{-2}, 0.23	169
PANI-10MA/10 Zeolite-AlMCM41	$1.06\pm0.31\times10^{-0}$	$2.67\pm0.69\times10^{-1}$	0.218	0.017	7.20×10^{-3}, 0.46	365
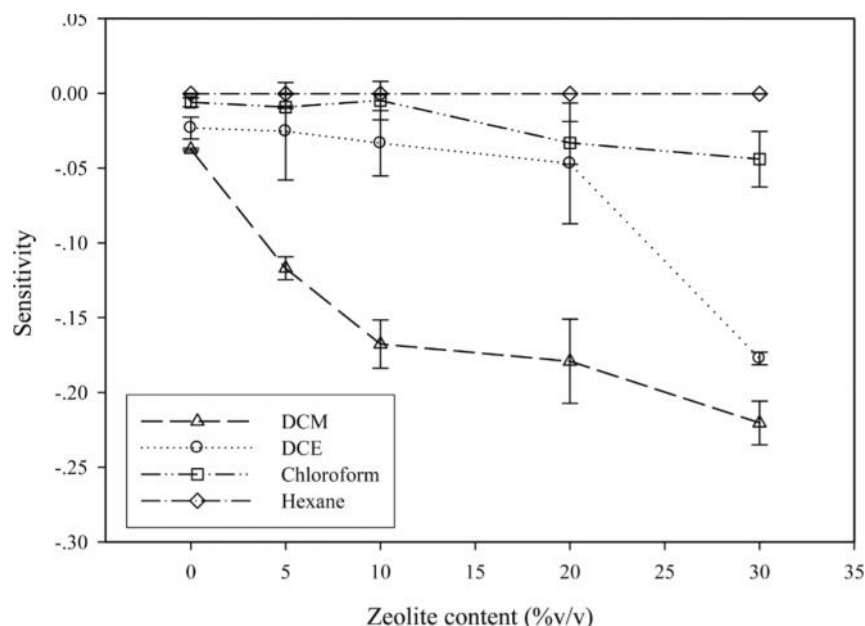
Fig. 1. The sensitivity of D-PDPA/Y_H$^+$[80] at various zeolite concentrations when exposed to halogenated solvents at 27±1°C and 1 atm [28]

zeolite Y-H+[80] content on the sensitivity of the composite towards chloroform because chloroform is having a low dielectric constant [36] and no dipole moment. Furthermore, the composite also shows negative response for hexane as the interaction between these two is a physical absorption. The composite shows a selectivity order towards the solvents, which is given as follows: DCM > DCE > chloroform. Hence, increase in zeolite content increases the sensitivity of D-PDPA [28].

Generally, there occurs an initial increase in the electrical conductivity sensitivity of a zeolite/polymer composite up to certain increase in the zeolite content. This increase is because of the fact that the addition of mesoporous structure (zeolite) in to the composite enhances the interaction of the target gas and the conductive polymer. Hence, a growth in the conductivity is found. But after a certain increase in zeolite content; there is no increase in the conductivity of the composite. The electrical conductivity shows a decrease. This decrease in the electrical conductivity sensitivity after a certain limit is due to the non-availability of active sites present in the composite. Hence, a small interaction occurs and the conductivity shows a decline. The electrical conductivity sensitivity of D-PTh 200:1 at various contents: 0, 20, 30, 40 and 50 wt % is shown here. For zeolite content between 0 and 20 wt %, the electrical conductivity sensitivity

(absolute) increases from $(-2.19\pm0.62)\times10^{-1}$ to $(-4.37\pm0.59)\times10^{-1}$. For zeolite contents between 20 and 50 wt %, the electrical conductivity sensitivity decreases from $(-4.37\pm0.59)\times10^{-1}$ to $(-9.05\pm0.49)\times10^{-2}$ [37]. On adding zeolite 4A to PANI-10MA, the response and sensitivity increases with doping level. The sensitivity values of 0.22, 0.38, 0.40 and 0.52 are obtained for PANI-10MA composites as the zeolite content varies from 0, 10, 20, to 40 wt%, respectively [38]. Hence, there occurs an initial increase in the electrical conductivity sensitivity of a zeolite/polymer composite up to certain increase in the zeolite content. But above a certain limit of zeolite content; there is no increase in the conductivity of the composite due to the non-availability of active sites present in the composite

5.2 Effect of Zeolite Type

Within a first approximation, it can be postulated that zeolites having a higher ion exchange capacity and favorable ion position are found to increase the electronic conductivity sensitivity of the composite to a particular gas. A channel system is more interactive in enhancing the sensitivity than a cage system. The sensitivity of zeolites Y, 13X and AlMCM41 having a pore size of 7A°, 10A°, 36A° and cation exchange capacities of 0.161, 0.086, 0.044 mol/g against CO respectively are summarized here [27] and are

shown in Table 1. These zeolites were utilized to fabricate composites with PANI by 10% weights of the zeolite. On exposing the composites to N_2 the conductivity decreases. While as in presence of CO exposure conductivity increases and sensitivity values of 0.431, 0.809, and 0.253 are obtained at 1000 ppm of CO concentration for the composites with zeolites Y, 13X and AlMCM41 respectively as shown in Table 1. A similar result is obtained at 7.8 ppm of CO concentration. Hence, PANI-10MA/10 Zeolite-13X shows highest sensitivity while as PANI-10MA/10 Zeolite AlMCM41 shows lowest sensitivity. Even if zeolite Y and 13X have comparable pore size of 10A° and 7A°, yet they differ in their sensitivities. This is due to their different ion exchange capacities of 0.086 (zeolite Y) and 0.161 (zeolite13X) mol/g. Due to higher amount of Cu^{2+} in zeolite Y, there is a small space available for CO molecules. Therefore a small interaction occurs. Further, there is a favorable location of Cu^{2+} ions in zeolite 13X, which enhances the interaction and hence increase the sensitivity [32]. The smallest sensitivity of PANI-10MA/10-AlMCM41 (0.044 mol/g) is because of small amount of Cu^{2+} ions available for interaction in its pore and excessively large pore size (36A°) which allows the CO molecules to enter and leave easily. Also sensitivity vs. [CO] of the composites: PANI-10MA, PANI-10MA/10Zeolite-Y, PANI-10MA/10Zeolite-13X, and PANI-10MA/10-AlMCM41 at1 atm. and at 30°C were studied. PANI-10MA/10Zeolite-13X is the highest sensitive to CO at all concentrations studied from 7.8–1000 ppm. While as pristine PANI-10MA is the lowest sensitive in the same concentration range. The temporal response times of 169, 250, and 365 min were obtained for the composites: PANI-10MA/10Zeolite-Y, PANI-10MA/10Zeolite-13X and PANI-10MA/10Zeolite-AlMCM41 respectively, having the Cu^{2+} exchange capacities of 0.161, 0.086 and 0.044 mol/g, respectively. Thus, it can be assumed that, the temporal response time is inversely related to the Cu^{2+} exchange capacity. This also supports the fact that a zeolite with more Cu^{2+} ions can trap and interact with CO molecules more effectively through the dipole–dipole interaction giving rise to a shorter response time [27] as shown in Table 1.

A similar result was obtained by K. Thuwachaowsoan et al. [37]. They obtained a negative response and sensitivity of Pth 200:1 against H_2. On introducing zeolite L, MOR and BETA (20% v/v) into Pth 200:1 the conductivity values obtained for H_2 are $(-1.62\pm0.49)\times10^{-8}$, $(-2.66\pm0.14)\times10^{-6}$ and $(-3.82\pm3.72)\times10^{-4}$ S/cm, having the sensitivity values of $(-7.66\pm1.33)\times10^{-2}$, $(-4.37\pm0.59)\times10^{-1}$ and $(-7.32\pm0.47)\times10^{-1}$, respectively. Hence, the highest response and sensitivity to H_2 is shown by Pth 200:1 /BETA 20. The Si/Al ratio of the zeolite L, MOR and BETA is 6, 17.7 and 41 respectively. They possess K^+, Na^+ and H^+ respectively in their pores. The decrease in the electrical conductivity is due to higher Al content. Since zeolite L possess higher Al content and therefore highest cation content. H_2 molecules get adsorbed to K^+ present in the zeolite and have a small interaction with the polymer molecules. This leads to decrease in the sensitivity [37]. The above fact is evident from the sensitivity values of D- PPV/Na^+-ZSM5(Si/Al=23), D-PPV/Na^+-13X and PPV/Na^+-Ferrierite to CO having different pore sizes and Si/Al ratio. In comparison to the pristine PPV and D-PPV the composites show a higher value of sensitivity which is 1.48, 1.02 and 0.91 respectively. As a result of the increase in the sensitivity of the composites in comparison to the pristine PPV and D-PPV, it is clear that CO molecules have certain interactions with PPV. The difference in the sensitivity between PPV/Na^+-13X and PPV/Na^+-ZSM5(Si/Al=23) is because of the difference in zeolite structures. A channel system of Na^+-ZSM5 (Si/Al=23) allows more CO molecules to interact with PPV in comparison to cage structure of Na^+-13X [39]. Hence, Zeolites having a higher ion exchange capacity increase the electronic conductivity sensitivity of the composite and zeolites having a favorable ion position inside the pore of zeolite also enhance sensitivity.

5.3 Effect of Si/Al Ratio

In accordance with the zeolite content Si/Al ratio also affects the sensitivity of the zeolite/polymer composite in a similar fashion. A lower Si/Al ratio of composite results in lower sensitivity. On increasing Si/Al ratio of the zeolite/polymer composite; an increase in the electrical conductivity sensitivity is found. The effect of Si/Al ratio varying over (Si/Al = 5.1, 30, 60, 80) for zeolite Y against NH_4NO_3 has been studied. The morphology of different Si/Al ratio zeolites is shown in Figs. 2.(a - d). They all possess nearly the same morphology. Further the different Si/Al ratios of zeolite Y possess nearly same pore size, surface area and densities. There has been found an increase by one order of magnitude in the electrical conductivity sensitivity

of the zeolite Y on exposure to NH_4NO_3 at 377 ppm in comparison to the exposure of N_2 [26].

On increasing the Si/Al ratio, a gradual increase in the electrical conductivity sensitivity occurs. They can enhance the interaction between oxygen on the Si of zeolite and NH_4NO_3 molecules [40,41]. The composite D-PPV/zeolite Y containing highest Si/Al ratio shows the highest sensitivity. Similar is the case for induction time. A composite containing higher Si/Al ratio exhibits longer induction time. Because higher Si/Al ratio corresponds to the zeolite containing higher amount of cations and they undergo a favorable interaction between NH_4NO_3 molecules and the polymer chains [42].

Thongchai N, et al. [39] investigated the sensitivity values of doped PPV/Na$^+$-ZSM5(Si/Al = 23) and that of D-PPV/Na$^+$-ZSM5(Si/Al = 80) to study the effect of Si/Al ratio towards CO. They reported a sensitivity value of 1.48 for D-PPV/Na$^+$-ZSM5 (Si/Al=23) having ion-exchanged level of 28%, and 1.17 for D-PPV/Na$^+$-ZSM5 (Si/Al=80) having ion-exchanged level of 17% as shown in Table 2. Hence, a lower Si/Al ratio of composite results in lower sensitivity. On

increasing the Si/Al ratio of the zeolite/polymer composite an increase in the electrical conductivity sensitivity occurs.

5.4 Effect of Cation Type

To understand the effect of type of cation present in the zeolite/polymer composite on the electrical conductivity sensitivity adsorption of CO on Na$^+$ and Cu$^+$ is described here. Generally, it is observed that CO molecules get adsorbed more strongly on Na$^+$ ions than Cu$^+$ ions. There has been found more strong interaction between CO molecules and Cu$^+$ ions. This is because CO molecules are lewis bases. They interact with Cu$^+$ ions and form coordinate bonds. Hence, Cu$^+$ ions act as active sites in the zeolite for CO adsorption. Therefore it is clear that CO molecules form stable carbonyls with Cu$^+$ and does not interact with Na$^+$ ions. Hence, in such a situation CO molecules get adsorbed on Cu$^+$ ions and do not interact with the polymer chains. Thus, resulting in a weak sensitivity of the composite. This is contrary to Na$^+$ ions, in which the CO molecules do not interact with the cation rather than the polymer chains and hence result in a strong sensitivity. Thongchai N, et al. [39], as
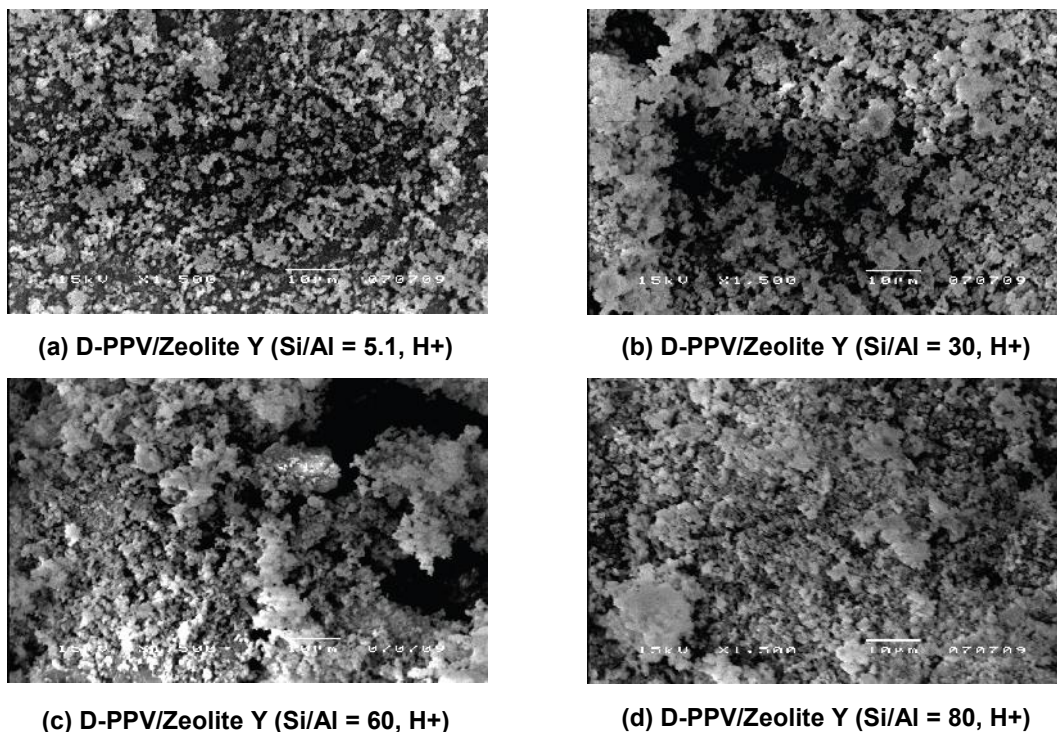

(a) D-PPV/Zeolite Y (Si/Al = 5.1, H+)

(b) D-PPV/Zeolite Y (Si/Al = 30, H+)

(c) D-PPV/Zeolite Y (Si/Al = 60, H+)

(d) D-PPV/Zeolite Y (Si/Al = 80, H+)

Fig. 2. SEM micrographs of the D-PPV/zeolite Y composites having different Si/Al ratios (magnification 1,500, 15 kV) [26]

shown in Table 2, reported positive (1.48) electrical conductivity sensitivity value of D-PPV/Na^+-ZSM5 (Si/Al=23) and a negative value (-0.154) for Cu^+ form of the composite D-PPV/Na^+-ZSM5 (Si/Al=23). This is in support of the above fact. The gas adsorption by the cation present in the zeolite also depends on the electronegativity and ionic radius of the cation [43]. The strong binding between the cation present in the zeolite and the frame work is believed to be due to higher electronegativity [44]. Li, Na and K possesses the electronegativity values of 1.0, 0.9, and 0.9 and ionic radius of 0.60, 0.95 and 1.33A° respectively. Since Li possess higher electronegativity, therefore it causes greater binding of cation and H_2 molecule than Na and K. Furthermore, Li possess shorter radius and there is a small distance between H_2 molecule and Li ion. Hence, the result is a small value of electrical conductivity sensitivity. On the other hand Na possesses low electronegativity and large ionic radius. It leads to lose contact between Na and H_2 molecules. Hence, it gives rise to a strong value of sensitivity. As the gas molecules do not interact with the cation present in the zeolite, and interact with the polymer chains, they show a good conductivity value. The conductivity value of Pth200:1/MOR_Li[90]_20, Pth200:1/MOR_Na[100]_20 and Pth200:1/MOR_K [90]_20 at 20% of zeolite content which is: $(-7.78\pm0.33)\times10^{-2}$, $(-4.37\pm0.59)\times10^{-1}$ and $(-2.20\pm0.12)\times10^{-1}$ S/cm respectively were also studied. The proposed mechanism of the H_2-Pth 200:1 interaction is shown in Fig. 3 [37].
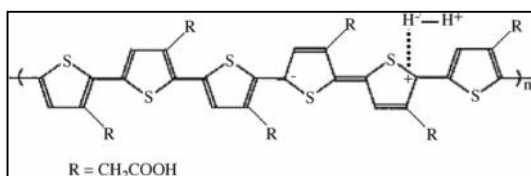

Fig. 3. Proposed mechanism of the H_2-Pth 200:1 interaction [37]

The cation exchange in to Mg^{2+}, Ca^{2+} and K^+ cat 50% mole of Zeolite Y (Si/Al 5.1, Na^+) were studied for the effect of cation type against acetone vapor (3%wt) in N_2. The electrical conductivity sensitivity of $1.97\times10^{-01}\pm5.06\times10^{-03}$, $2.57\times10^{-01}\pm2.40\times10^{-03}$, $2.68\times10^{-01}\pm1.99\times10^{-02}$ and $3.42\times10^{-01}\pm4.67\times10^{-04}$ was obtained for 50MgNaY, 50CaNaY, NaY and 50KNaY respectively. On increasing the cationic radius and decreasing electronegativity (EN); the

electrical conductivity sensitivity was found to increase. Since large cationic radius leads to small electrostatic interaction between the cation and the zeolite. Therefore, the ability of the cation to transfer to another cage and proton mobility increases [27,33,34]. Since K^+ possesses larger cationic radius (1.51°A) than Na^+ (1.16°A), Ca^{2+} (1.14°A) and Mg^{2+} (0.71°A), respectively. Hence, the highest electrical conductivity sensitivity value is shown by 50KNaY than those of NaY, 50CaNaY and MgNaY on exposure to acetone vapor at a concentration of 3 wt % in N_2 [45]. The effect of cation type on the electrical conductivity sensitivity were studied for four cations: Na^+, K^+, NH_4^+ and H^+. The composites were prepared from 50:1 D-PPP and 10% v of ZSM-5 (23) having four different cations Na^+, K^+, NH_4^+, and H^+. The composites are coded as 50:1 D-PPP (90)/NaZ23, 50:1 D-PPP(90)/KZ23, 50:1 D-PPP(90)/NH_4Z23 and 50:1 D-PPP(90)/HZ23, respectively. The electrical conductivity sensitivities obtained for 50:1 D-PPP, 50:1 D-PPP(90)/KZ23, 50:1 D-PPP(90)/NaZ23, 50:1 D-PPP(90)/NH_4Z23 and 50:1 D-PPP(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. As a common cation, Na^+ is used as a basis for the comparison. On replacing the cation by either H^+ or NH_4^+; the sensitivity of composite increases remarkably. This is because of the adsorption of NH_3 onto ZSM-5. The sensitivity of the composites increase in accordance with the acidity of the zeolite. The H-form of ZSM-5 is having the highest acidity, surface area and the pore volume; therefore it provides a more favorable NH_3 adsorption and hence the highest sensitivity is obtained. The sensitivity of NH_4ZSM-5 is close that of H-ZSM-5 as it possesses a lower acidity, surface area and pore volume. It is observed that there is no increase in the sensitivity as the cation is replaced by k^+; instead it decreases the sensitivity slightly. It is because of the fact that NH_3 does not adsorb on K-ZSM-5 due to its lower acidity, surface area, and pore volume. On increasing its content there is no increase in the sensitivity; instead it decreases the number of D-PPP active sites available. Hence, the pure D-PPP possesses more sensitivity than KZSM-5 composite [33]. The effects of cation type were also studied for the response of zeolite Y towards 3 toxic and flammable substances of ketone vapors (acetone, MEK and MIBK). Zeolite Y was ion exchanged in to NaY, 50KNaY, 50MgNaY and 50CaNaY. The highest electrical conductivity sensitivity is shown by 50KNaY. This is due to

Table 2. Electrical conductivity sensitivities, temporal responses, and ion-exchange levels of PPV/Zeolite composites [39]

Sample	The sensitivity ($\Delta\sigma/\sigma_{N2}$) level %	The temporal response (t_r, min)	Ion -exchanged level (%)
D-PPV/13X_Na	1.02E+00	42	100
D-PPV/fer_Na	9.16E-01	123	17
D-PPV/ZSM5(23)Na	1.48E+00	56	28
D-PPV/ZSM5(80)_Na	1.17E+00	153	17
D-PPV/ZSM5(23)_Cu	-1.54E-01	24	44

the electrostatic interaction between the cation and the zeolite framework, which affects the adsorption properties of zeolite. The highest electrical conductivity sensitivity is obtained on exposing samples to acetone, whereas the least value is obtained on exposing the sample to MIBK exposure because of the smaller acetone size [45]. Hence, the effect of the cation depends on adsorption of gas on the metal ion present in zeolite.

5.5 Effect of Cyclic Interval

There will be a difference between the sensitivity of a composite during the first run, 2nd run and so on. The electrical conductivity sensitivity value of 50 KNaY was found to be: $3.42\times10^{-01}\pm4.67\times10^{-04}$, $2.09\times10^{-01}\pm6.27\times10^{-04}$, $1.81\times10^{-01}\pm6.12\times10^{-04}$ and $1.28\times10^{-01}\pm9.12\times10^{-04}$ for the first, 2nd, 3rd and 4th interval respectively. This decreasing trend in the sensitivity after repeating the cyclic after 2 to 4 times is because of the fact that during 1st interval the gas molecules which get adsorbed do not get desorbed quickly i.e. it is not a reversible process. They decrease the no. of active sites. Hence, a decrease in the sensitivity value after repeating the cycle [45]. A similar result is also obtained for NaY, 50CaNaY and 50MgNaY [46-49]. For the effect of cyclic response at the cyclic interval of 1,200 s towards the 3% wt. acetone vapor in N_2 Zeolite Y (Si/Al 5.1, Na^+) was successfully ion exchanged into Mg^{2+}, Ca^{2+} and K^+ cat 50 % mole [45]. The obtained electrical conductivity sensitivity values for 50MgNaY, 50CaNaY, NaY and 50KNaY are: $1.97\times10^{-01}\pm5.06\times10^{-03}$, $2.57\times10^{-01}\pm2.40\times10^{-03}$, $2.68\times10^{-01}\pm1.99\times10^{-02}$ and $3.42\times10^{-01}\pm4.67\times10^{-04}$, respectively for first interval. On increasing the cationic radius and decreasing electronegativity (EN), the electrical conductivity sensitivity was found to increase. Since large cationic radius leads to small electrostatic interaction between the cation and the zeolite. Therefore, the ability of the cation to transfer to another cage and proton mobility

increases [50-53]. Kamonsawas J, et al. [45] studied the effect of cyclic interval of zeolite Y towards 3 different types of ketone vapors (acetone, MEK and MIBK). Zeolite Y was ion exchanged in to ion exchanged at 50% mole: NaY, 50KNaY, 50MgNaY and 50CaNaY for the zeolite Y keeping Si/Al ratio of 5.1. It was observed on behalf of the cyclic interval that the electrical conductivity response decreases as we go on increasing the number of the intervals due to the interaction between the active site and ketone vapors. This decrease in the sensitivity due to repetion of the interval is because the vapors adsorbed in the first interval do not get desorbed simultaneously. Hence, it is an irreversible process. Hence, the sensitivity of the composite will go on decreasing with the cyclic interval.

5.6 The Effect of Cation Concentration

The concentration of a cation present in a zeolite/polymer composite affects the sensitivity based on the electronegativity of the cation present in it. E.g. if the cation present is less electronegative, it will not attract gas molecules more towards itself. Therefore increasing the concentration of a less electronegative cation will lead to more proton mobility and ability to interact with the gas vapor. Hence, increase in the concentration of a less electronegative cation will increase the sensitivity of the composite. But the case is opposite for a more electronegative cation present in the zeolite pore. The electrical conductivity of NaY, 30KNaY, 50KNaY and 80KNaY in the 1st interval response are $2.68\times10^{-01}\pm1.99\times10^{-02}$, $2.78\times10^{-01}\pm4.42\times10^{-03}$, $3.42\times10^{-01}\pm4.67\times10^{-04}$ and $4.26\times10^{-01}\pm1.25\times10^{-04}$ as K^+ concentration in NaY increases from 0, 30, 50 and 80 % mole of K^+, respectively. It is observed that increase in K^+ ion replacing Na^+ in the composite increases the electrical conductivity sensitivity. Since, Na^+ is more electronegative than K^+. On replacing Na^+ with K^+ ion and upon increasing concentration of K^+ will lead to increased proton mobility and a

better interaction of the gas vapor and the composite. Hence, sensitivity increases upon increasing the concentration of K^+ ions [45]. Electronegativity and ionic radius of the cation are the two factors responsible for the adsorption of a gas by the cation present in the zeolite [43]. Higher electronegativity of the cation present in the zeolite leads to strong binding between the cation and the frame work [44]. Li, Na and K possesses the electronegativity of 1.0, 0.9, and 0.9 and ionic radius of 0.60, 0.95, 1.33 A° respectively. Among these Li is having higher electronegativity and shorter ionic radius; hence it causes greater binding of cation and H_2 molecule than Na and K. Therefore, it results in a small value of electrical conductivity sensitivity. Thus increase in the concentration of Li will decrease the electrical conductivity sensitivity of the composite. While as Na is having low electronegativity and large ionic radius. It results in a loose contact between Na and H_2 molecules. Hence, a strong value of sensitivity is obtained. The gas molecules do not interact with the cation present in the zeolite, rather they interact with the polymer chains and show a good conductivity value. The above fact is supported by the study carried out by Thuwachaowsoan K, et al. [37]. They reported the conductivity value of Pth_200:1/MOR_Li[90]_20, Pth_200:1/MOR_Na[100]_20 and Pth_200:1/MOR_K[90]_20 at 20% of zeolite content which as: $(-7.78 \pm 0.33) \times 10^{-2}$, $(-4.37 \pm 0.59) \times 10^{-1}$ and $(-2.20 \pm 0.12) \times 10^{-1}$ S/cm respectively. Hence, more electronegative cation attracts gas molecules more towards itself and therefore interaction between gas molecules and the polymer is small. Hence, lower sensitivity results.

5.7 The Effect of Temporal Response

A zeolite having more cu^{2+} ion exchange capacity will have a small temporal response. Therefore a composite from such a zeolite would show a quick or more response to the gas vapors. The effect of temporal response on the sensitivity of composites: PANI-10MA/10Zeolite-Y, PANI-10MA/10Zeolite-13X and PANI-10MA/10Zeolite-AlMCM41 were studied. They obtained a temporal response of 169, 250, and 365 min with Cu^{2+} exchange capacity of 0.161, 0.086 and 0.044 mol/g, respectively as shown in Table 1. From this study it is clear that the response time of the composites is inversely proportional to the Cu^{2+} ion exchange capacity. Hence, it can be concluded that a zeolite with more Cu^{2+} ion exchange capacity interacts more with gas

vapors and results in a short temporal response time [27]. The induction time of D-PDPA when exposed to DCM, DCE, and chloroform was 13.50±2.12, 8.56±1.25, 15.00±1.41 min, respectively. Also, D-PDPA/30% Y_H$^+$[80] composite was studied [28]. The induction time obtained in this case was 18.50±0.71 min for DCM, 17.65±0.43 min for DCE, 15.95±1.34 min for chloroform respectively. From this study, it is inferred that the induction time of D-PDPA is smaller than the composite. This makes us clear that the presence of a microporous structure (zeolite) makes available more active sites for the gas molecules to adsorb. On exposing D-PDPA to DCM, DCE and chloroform, a reduction of 9.50±4.86, 6.35±1.57, and 13.75±7.84 min, respectively is obtained in the induction time. The composites of poly (3-thiophene acetic acid) (Pth) and zeolite L, Mordernite and BETA were studied against H_2. A large induction time for 200:1/BETA 20 in comparison to the polymer and other composites was obtained [37]. Hence, it can be concluded that the presence of zeolite provides more reactive sites for the gas (H_2) molecules. Thongchai N, et al. [39] reported the temporal response times of doped PPV/Na$^+$-13X, doped PPV/Na$^+$-ZSM5(Si/Al = 23), doped PPV/Na$^+$-FER, and doped PPV/Na$^+$ZSM5(Si/Al = 80) as shown in Table 2. The temporal induction times are 42, 56, 123, and 153 min, respectively. Thus, it seems that the temporal response time is inversely related to the amount of Na$^+$ ion. Hence, a zeolite with more Na$^+$ ions can make CO molecules to get absorbed faster through the electrostatic interaction, and hence the interaction of CO with PPV chains results in a shorter time. Hence, a zeolite with more Cu^{2+} ion exchange capacity interacts more with gas vapors through dipole-dipole interaction and results in a short temporal response time.

5.8 Effect of Pore Size

Zeolites are having a void range of pore sizes. They include the small sized pores of 0.3 A° to very large pore size ≈ 36 A°. This has its effect on the sensitivity of a composite. A zeolite of comparable pore size is observed to be highly sensitive. While as zeolites having excessively large pore size are less sensitive. The excessively large pore allows the gas molecules to enter and leave with the same ease. So, there occurs a small interaction and hence a lower sensitivity. The electrical conductivity sensitivity obtained for the composites with zeolite Y, 13X and AlMCM41 at 1000 ppm of CO concentration is: 0.431, 0.809, and 0.253 respectively. These

zeolites are having a pore size of 7A°, 10A° and 36A° with corresponding cation exchange capacity of 0.161, 0.086 and 0.044 mol/g respectively. The composites were fabricated between PANI-10 MA/10Zeolite13X, PANI-10MA/10ZeoliteY and PANI-10MA/10zeolite AlMCM41. From the study the highest sensitive composite was found to be PANI-10 MA/10Zeolite13X and PANI-10MA/10zeolite AlMCM41 to be the least sensitive. Although zeolite 13X and Y are having comparable pore sizes; 7A° and 10 A° respectively, they have different ion exchange capacities of 0.161 and 0.086 mol/g respectively. Zeolite Y contains highest amount of Cu^{2+} which may reduce the remaining volume available for CO molecules to penetrate into the cavity of the pore. Also the Cu^{2+} locations offer a favorable interaction with CO molecules [32]. The least sensitivity of PANI-10MA/10 zeolite AlMCM41 among the three is because of its excessive large pore size (36A°) and small amount of Cu^{2+} (0.044 mol/g). The excessive large pore allows CO molecules to leave and enter with the same ease. The sensitivity of PANI-10 MA/10 Zeolite 13X is large than PANI-10 MA/10 Zeolite Y because of large free pore volume which is available to interact with CO molecules. Hence, for comparable pore sizes the sensitivity of the composite is high while as for excessive large pore sizes the sizes the sensitivity is small as the gas molecules enter and leave with small interaction [27]. Hence, a zeolite of comparable pore size is highly sensitive. While as zeolites having excessively large pore size are less sensitive.

5.9 Effect of Vapor Type

The effect of vapor type on the zeolite/polymer composite can be expressed in terms of the electrophonic and nucleophilic nature of the target gas. Electrophilic gas molecules withdraw electrons from the polymer chains; resulting in increase in the electrical conductivity of p –type doped polymer which possess polarons and bipolarons. On the other hand; a nucleophilic gas molecule gives electrons to the polymer chains. Hence, there occurs a decrease in the no. of charge carriers, polarons and bipolarons, and hence the decrease in electrical conductivity. Phumman P, et al. [33] studied the effect of vapor type in terms of three vapors CO, H_2, and 10% NH_3 for D-PPP. On exposing the sample of D-PPP to CO a small positive response with a sensitivity of 2.1×10^{-2} is obtained. Since, CO molecules are electrophilic in nature; they are expected to withdraw electrons from D-PPP.

Therefore, the p-type doped conductive polymer possessing polarons and bipolarons cause an increase in electrical conductivity [54,55]. The CO- D-PPP interaction is observed to be weak with much lower sensitivity. Hence, it can be concluded that there is no interaction between D-PPP and CO; if there is any interaction it seems to be very weak. The effect of ammonia gas on the electrical property of a conducting polymer was also studied by Yamamoto and Gu. The electrical conductivity of the PPP film was found to be increased by several orders of magnitude on NH_3 exposure. There was relatively a fast change in electrical conductivity and was reversible. On reducing the partial pressure of NH_3; the electrical conductivity of the PPP film was found to decrease in the same pattern. On exposing the PPP films to diethyl amine and triethylamine, similar results were obtained [34]. The electrical conductivity sensitivity of D-PPP(60)/NaZ23 on exposure to 5% v of NH_3 at 28±1°C and at 1 atm was studied. The observations are plotted in Fig. 4(a) which shows the specific electrical conductivity of D-PPP (60)/NaZ23 vs. time (min). It is clear from the figure that the specific electrical conductivity of D-PPP (60)/NaZ23 shows an initial increase and reaches a maximum value of 0.235 S/cm after a NH_3 exposure time of 2.90 min, after which it shows a decrease and attains a steady state value of 0.03 S/cm and the NH_3 exposure time reaches to 30 min. Now on exposing the composite to N_2 there is a difference observed in the specific electrical conductivity as shown in Fig. 4(b). It is observed that the specific electrical conductivity first increases from a value of 0.01 S/cm to a steady state value of 0.03 S/cm after the N_2 exposure time of 56 min.

Since D-PPP is a *p*-type doped conductive polymer and NH_3 is a strong nucleophilic gas, when D-PPP is exposed to an electron rich molecule such as NH_3, an electron transfer occurs [56], NH_3 will give electrons to D-PPP resulting in a decrease in the no. of charge carriers, polarons and bipolarons, and hence the decrease in electrical conductivity. Therefore, the negative response is expected and observed [33]. The sensitivity of D-PDPA/30%Y-H+[80] for the effect of DCM and DCE vapors at various vapor concentrations was studied. On exposing the composite to DCM, the sensitivity increases from $(-1.23\pm0.004)\times10^{-2}$ to $(-3.47\pm1.64)\times10^{-1}$ as the vapor concentration is increased from 7,696 ppm to 153,914 ppm, respectively while as on exposing the composite to DCE the sensitivity increases from $(-1.09\pm0.96)\times10^{-1}$ to (-1.77 ± 0.04)

×10^{−1} as the vapor concentration increased from 1,015 ppm to 20,299 ppm, respectively. Fig. 5. shows The sensitivity of D-PDPA/30%Y_H[+][80] toward DCM and DCE at different concentrations at 27±1°C and 1 atm [28].

Now on exposing the composite simultaneously to both DCM and DCE, a linear relationship between the sensitivity and vapor concentration is obtained. A similar result is also obtained by Jaing L, et al. [57] who studied the 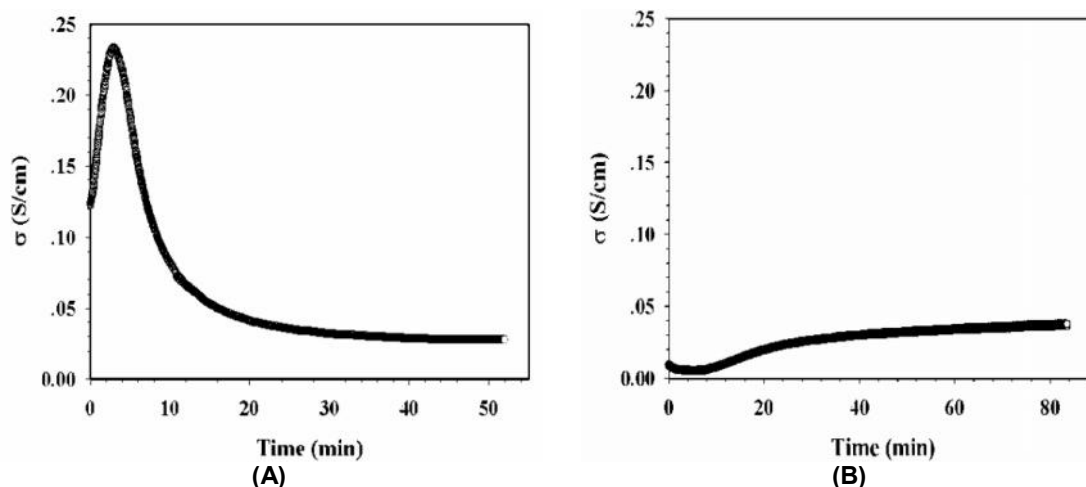composites of polypyrrole and poly vinyl alcohol for methanol vapors. A linear relationship is obtained between sensitivity and gas concentration (gas concentration range of 50-1059 ppm). The proposed mechanism of adsorbed DCM, and DCE on D-PDPA/30% Y_H[+][80] is shown in Fig. 6. Electrophilic gas molecules withdraw electrons from the polymer chains; resulting in increase in the electrical conductivity. On the other hand; a nucleophilic gas molecule gives electrons to the polymer chains resulting in decrease in electrical conductivity.

(A) **(B)**

Fig. 4.The specific conductivity of D-PPP(60)/NaZ23 *vs.* time: (a) when exposed to 5%v NH$_3$; (b) after evacuating 5%v NH$_3$ and exposure to N$_2$, at 28±1°C and at 1 atm [33]
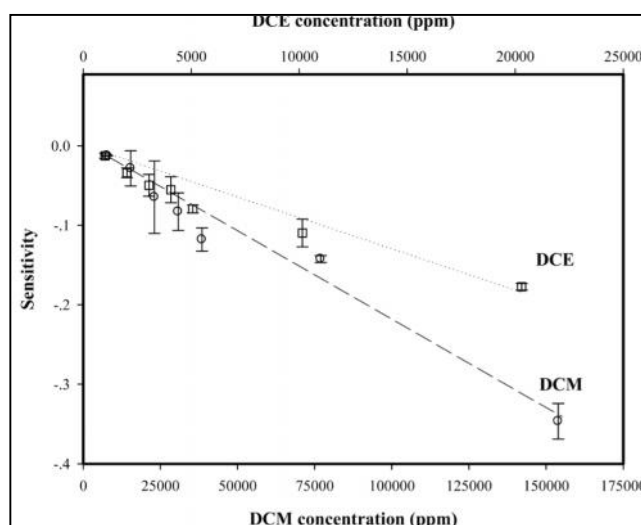

Fig. 5. The sensitivity of D-PDPA/30%Y_H[+][80] toward DCM and DCE at different concentrations at 27±1°C and 1 atm[28]
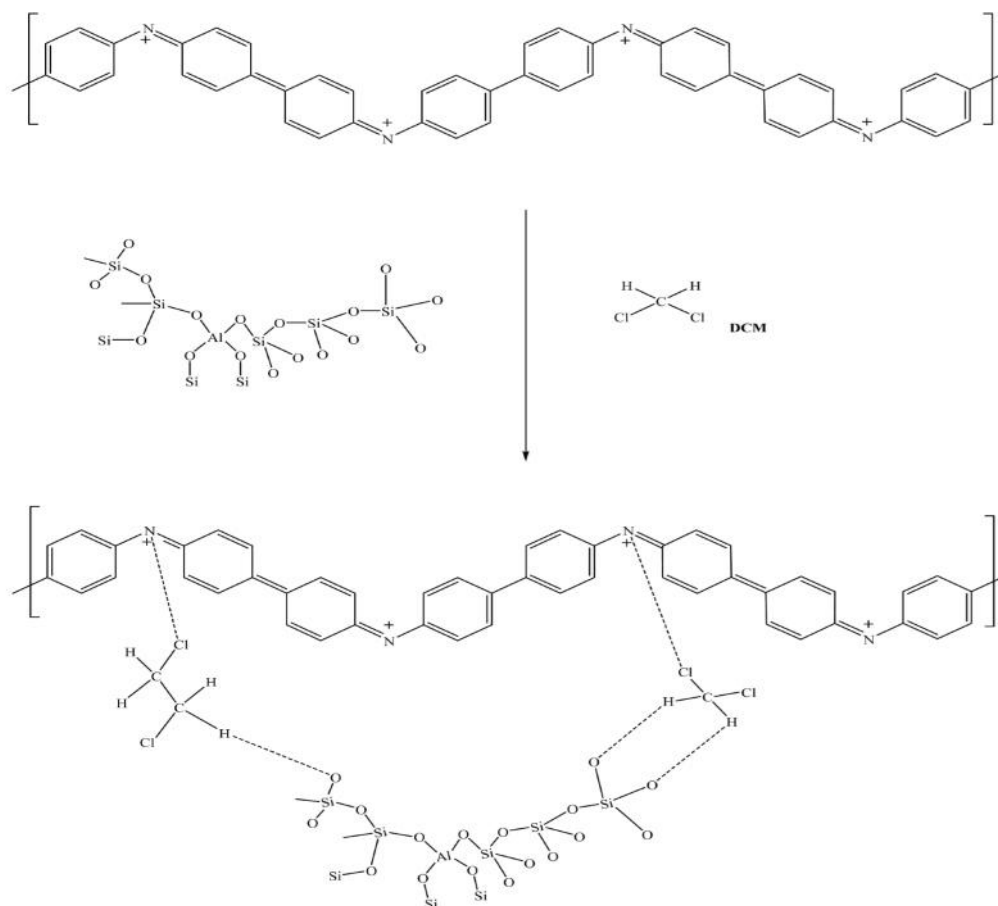
Fig. 6. Proposed mechanism of adsorbed DCM, and DCE on D-PDPA/30% Y_H+[80][28]

6. CONCLUSION

Since, there are two types of procedures for the synthesis of composites; one is the dry mixing of zeolite and polymer powder by a hydraulic press and other is the polymerization of the monomer of a polymer in the zeolite frame work and then pressing the powder into pellets. Among these two the second one is best for the synthesis of composites. In this method the monomer of the polymer fits itself inside the pore of the zeolite and under goes polymerization.

There occurs an initial increase in the electrical conductivity sensitivity of a zeolite/polymer composite up to certain increase in the zeolite content. This increase is because of the fact that the addition of zeolite in to the composite increases interaction of the target gas and the conductive polymer. But above certain zeolite content; there is no increase in the conductivity of the composite. The electrical conductivity decreases. This is due to the non-availability of active sites present in the composite. Zeolites having a higher ion exchange capacity increase the electronic conductivity sensitivity of the composite. Zeolites having a favorable ion position inside the pore of zeolite also enhance sensitivity. A channel system is more interactive in enhancing sensitivity than a cage system. Even if zeolite Y and 13X have comparable pore size of 10A° and 7A°, yet they differ in their sensitivities. This is due to their different ion exchange capacities of 0.086 (zeolite Y) and 0.161 (zeolite13X) mol/g. Due to higher amount of Cu^{2+} in zeolite Y, there is a small space available for CO molecules. Therefore a small interaction occurs. Further, there is a favorable location of Cu^{2+} ions in zeolite 13X, which enhances the interaction and hence increase the sensitivity.

A lower Si/Al ratio of composite results in lower sensitivity. On increasing the Si/Al ratio of the zeolite/polymer composite; an increase in the electrical conductivity sensitivity occurs. CO

molecules get adsorbed more strongly on Na^+ ions than Cu^+ ions. There occurs a more strong interaction between CO molecules and Cu^+ ions. Hence, Cu^+ ions act as active sites in the zeolite for CO adsorption. CO molecules get adsorbed on Cu^+ ions and do not interact with the polymer chains. Thus, a weak sensitivity of the composite results. This is contrary to Na^+ ions, in which the CO molecules do not interact with the cation rather than the polymer chains and hence result in a strong sensitivity. There will be a difference between the sensitivity of a composite during the first run, 2nd run and so on. This decrease in the sensitivity is because the vapors adsorbed in the first interval do not get desorbed simultaneously. Hence, it is an irreversible process. Less electronegative cation will not attract gas molecules more towards itself. Therefore, increasing the concentration of a less electronegative cation will lead to more proton mobility and ability to interact with the gas vapor. But the case is opposite for a more electronegative cation present in the zeolite pore.

A zeolite having more cu^{2+} ion exchange capacity will have a small temporal response. Therefore such a composite would show a quick response to the gas vapors. A zeolite of comparable pore size is highly sensitive. While as zeolites having excessively large pore size are less sensitive. The excessively large pore allows the gas molecules to enter and leave with the same ease. So, there occurs a small interaction and hence a lower sensitivity. Electrophilic gas molecules withdraw electrons from the polymer chains; resulting in increase in the electrical conductivity. On the other hand; a nucleophilic gas molecule gives electrons to the polymer chains. Hence, there occurs a decrease in the no. of charge carriers, polarons and bipolarons, and a decrease in electrical conductivity occurs.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

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

2. Nohria R, Khillan RK, Su Y, Dikshit R, Lvov Y, Varahramyan K. Humidity sensor based on ultrathin polyaniline film deposited using layer-by-layer nano-assembly. Sens. Actuat. B-Chem. 2006; 114:218–222.

3. Grennan K, Killard AJ, Hanson CJ, Cafolla AA, Smyth MR. Optimisation and characterisation of biosensors based on polyaniline. Talanta. 2006;68:1591–1600.

4. Migdilski J, Blaz T, Lewenstam A. Conducting polymer-based ion-selective electrodes. Anal. Chem. Acta. 1996;322: 141–149.

5. Persaud KC. Polymer in chemical sensing. Materials Today. 2005;8:38–44.

6. Watcharaphalakorn S, Ruangchuay L, Chotpattananont D, Srivat A, Schwank J. Polyaniline/polyimide blends as gas sensors and electrical conductivity response to CO–N_2 mixtures. Polym. Int. 2005;54:1126–1133.

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

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

9. Vamstrom C, Ivaska A. An electrochemical study of poly (paraphenylene) in conductive polymer bilayer electrodes. J. Electroanal. Chem. 1997;421:67-78.

10. Blackwood D, Josowicz M. Work function and spectroscopic studies of interaction between conducting polymers and organic vapors. J. Phys. Chem. 1991;95:493-502.

11. Yoshino K, Gu HB. Effect of ammonium gas on electrical property of conductive polymers. J. Appl. Phys. 1986;25:1064-1068.

12. Cirpan A, Kucukyavuz Z, Kucukyavuz S. Synthesis, characterization and electrical conductivity of poly (paraphenylenevinylene). Turk. J. Polym. 2003;27:135-143.

13. Babudri F, Farinola GM, Giancane S, Naso F, Rella R, Scarpa A, Valli L. Deposition and application in gas sensors of thin films of a bridged chain dialkoxy PPV derivative. Mater. Sci. Eng. C. 2002;22:445-448.

14. Bouchet R, Rosiri S, Vitter G, Siebert E. Solid state hydrogen sensor based on acid doped polybenzimidazole. Sens, Actuat. B. 2001;76:610-616.

15. Soontornworajit B, Wannatong L, Hiamtup P, Niamlang S, hotpattananont D, Sirivat A, Schwank J. Induced interaction between polypyrrole and SO_2 via molecular sieve 13X. Mat. Sci. Eng. B-Solid. 2007;136:78–86.

16. Graham SC, Fung S, Moratti SC, Friend RH. High sensitivity radiation sensing by photo induced doping in PPV derivatives. Synth. Met. 1999;102:1169-1170.

17. Hagen G, Dubbe A, Retting F, Jerger A, Birkhofer T, Muller R, Rlog C, Moos R. Selective impedance based gas sensors for hydrocarbons using ZSM-5 zeolite films with chromium (3) oxide interface. Sens. Actuat. B. 2006;119:441-448.

18. Vilaseca M, Coronas J, Cirera A, Cornet A, Morante RJ, Santamaria J. Gas detection with SnO_2 sensors modified by zeolite films. Sens. Actuat. B. 2007;124:99-110.

19. Yangong Z, Xiaogan Li, Prabir KD. Exploitation of unique properties of zeolites in the development of gas sensors. Sensors. 2012;12:5170-5194.

20. Dryer A. An introduction to zeolite molecular sieve, John Willey& Sons, New York; 1998.

21. Tiwari DC, Sharma R, Vyas KD, Boopathi M, Singh VV, Pandey P. Sens. and Actu. B. 2010;151:256-264.

22. Ryoo R, Ko CH, Howe RF. Chem. Mater. 1997;9:1607.

23. Li X, Dutta PK. Interaction of dimethylmethylphosphonate with zeolite Y: Impedance-based sensor for detecting nerve agent stimulus. J Phys Chem C. 2010;114:7986–7994.

24. Thuwachaowsoan K, Chotpattananont D, Sirivat A, Rujiravanit R, Schwank JW. Electrical conductivity responses and interactions of poly(3-thiopheneacetic acid)/zeolites L, mordenite, beta and H_2. Materials Science and Engineering B. 2007;140:23–30.

25. Olad A, Khatamian M, Naseri B. Preparation of polyaniline nanocomposite with natural clinoptilolite and investigation of its special properties. Int. J. Nanosci. Nanotechnol. 2010;6:43-52.

26. Kamonsawas J, Sirivat A, Niamlang S, Hormnirun P, Prissanaroon OW. Electrical conductivity response of poly (Phenylene-vinylene)/ zeolite composites exposed to ammonium nitrate. Sensors. 2010;10:5590-5603.

27. Densakulprasert N, Ladawan W, Datchanee C, Hiamtup P, Sirivat A, Schwank J. Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. Mater. Sci. Eng. B. 2005;117:276-282.

28. Permpool T, Sirivat A, Aussawasathien D, Wannatong L. Polydiphenylamine/zeolite Y composites and electrical conductivity responses toward halogenated hydrocarbons. Materials Research. 2013; 16(5):1020-1029.

29. Ballav N, Biswas M. A conductive composite of polythiophene with 13X-zeolite. Materials Science and Engineering B. 2006;129:270–272.

30. Sardar PS, Ghosh S, Biswas M, Ballav N. Highly conductive polyfuran-13X zeolite-polyaniline composite. The Society of Polymer Science. Japan. 2008;40:1199–1203.

31. Sen S, Bardakcı B, Yavuz AG, Gok AU. Polyfuran/zeolite LTA composites and adsorption properties. European Polymer Journal. 2008;44:2708–2717.

32. Goursot A, Vasilyev V, Arbuznikov A. Modeling of adsorption properties of zeolites: Correlation with the structure. J. Phys. Chem. B. 1997;101:6420-6428.

33. Phumman P, Niamlang S, Sirivat A. Fabrication of Poly (*p*-Phenylene)/Zeolite composites and their responses towards ammonia. Sensors. 2009;9:8031-8046.

34. Yamamoto K, Gu HB. Effect of ammonium gas on electrical property of conductive polymers. Jpn. J. Appl. Phys. 1986;25:1064-1068.

35. Freund MS, Deore B. Self-doped conducting polymers. Wiley; 2007.

36. Ayad MM, El-Hefnawey G, Torad NL. Quartz crystal microbalance sensor coated with polyaniline emeraldine base for determination of chlorinated aliphatic hydrocarbons. Sensors and Actuators B: Chemical. 2008;134(2):887-94.

37. Thuwachaowsoan K, Chotpattananont D, Sirivat A, Rujiravanit R, Schwank WJ. Electrical conductivity responses and interactions of poly(3-thiopheneacetic acid)/zeolites L, mordenite, beta and H_2. Materials Science and Engineering B. 2007;140:23–30.

38. Chuapradit C, Wannatong LR, Chotpattananont D, Hiamtup P, Sirivat A, Schwank J. Polyaniline/zeolite LTA

composites and electrical conductivity response towards CO. Polymer. 2005;46: 947–953.

39. Thongchai N, Kunanuruksapong R, Niamlang S, Wannatong L, Sirivat A, Wongkasemjit S. Interactions between CO and Poly(*p*-phenylene vinylene) as induced by ion-exchanged zeolites. Materials. 2009;2:2259-2275.

40. Zecchina A, Marchese L, Bordiga S, Paze C, Gianotti E. Vibrational spectroscopy of NH_4^+ ions in zeolitic materials: An IR study, J. Phys. Chem. B. 1997;101:10128-10135.

41. Break DW. Zeolite molecular sieves, Robert E. Krieger Publishing: Malabar, Florida. USA; 1973.

42. Densakulprasert N, Ladawan W, Datchanee C, Hiamtup P, Sirivat A, Schwank J. Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. Mater. Sci. Eng. B. 2005;117:276-282.

43. Benco L, Bucko T, Hafner J, Toulhoat H. A Density functional theory study of molecular and dissociative adsorption of H_2 on active sites in mordenite. J. Phys. Chem. B. 2005;109:22491–22501.

44. Ferrari AM, Neyman KM, RON Sch. CO interaction with alkali metal cations in zeolites: A density functional model cluster study. J. Phys. Chem. B. 1997;101:9292–9298.

45. Kamonsawas J, Sirivat A, Hormnirun P. Poly(p-phenylene vilnylene)/zeolite Y composite as a ketone vapors sensor: effect of alkaline cation. Journal of Polymer Research. 2012;19:1-12.

46. Yimlamai I, Niamlang S, Chanthaanont P, Kunanuruksapong R, Changkhamchom S, Sirivat A. Electrical conductivity response and sensitivity of ZSM-5, Y and mordenite zeolite towards ethanol vapor. Ion. 2011; 17:607–615.

47. Scott MA, Katehleen AC, Dutta PK. Hand book of zeolite science and technology. Marcel Dekker, New York; 2003.

48. Florian J, Kubelkova L. Proton transfer between H-Zeolite and adsorbed acetone or acetonitrile: Quantum chemical and FTIR study. J. Phy. Chem. 1994;98:8734–8741.

49. Panov A, Fripiat J. An infared study of acetone and mesityl oxide adsorption on acid catalyst. Langmuir. 1998;14:3788–3796.

50. Yimlamai I, Niamlang S, Chanthaanont P, Kunanuruksapong R, Changkhamchom S, Sirivat A. Electrical conductivity response and sensitivity of ZSM-5, Y and mordenite zeolite towards ethanol vapor. Ion. 2011;17:607–615.

51. Li X, Dutta PK. Interaction of dimethylmethylphosphonate with zeolite Y: impedance-based sensor for detecting nerve agent stimulus. J Phys Chem C. 2010;114:7986–7994.

52. Soontornworajit B, Wannatong L, Hiamtup P, Niamlang S, Chotpattananont D, Sirivat A, Schwank J. Induced interaction between polypyrrole and SO_2 via molecular sieve 13X. Mater Sci Eng B. 2007;15:78–86.

53. McKeen J, Davis M. Conductivity of Mo- and divalent cation in the Microporous zincosilicate VPI9. J. Phys. Chem C. 2009;113:9870–9877.

54. Chuapradit C, Wannatong L, Chotpattananont D, Sirivat A, Schwank J. Polyaniline/zeolite LTA composites and electrical conductivity. Polymer. 2005;46: 947–953.

55. Densakulprasert N, Wannatong L, Chotpattananont D, Hiamtup P, Sirivat A, Schwank J. Electrical conductivity of polyaniline/zeolite composites and synergetic interaction with CO. Mat. Sci. Eng. B-Solid. 2005;117:276-282.

56. Collins GE, Buckley L. Conductive polymer coated fabrics for chemical sensing. Synth. Metal. 1996;78:93-101.

57. Jiang L, Jun HK, Hoh YS, Lim JO, Lee DD, Huh JS. Sensing characteristics of polypyrrole-poly(vinyl alcohol) methanol sensors prepared by in situ vapor state polymerization. Sensors and Actuators B: Chemical. 2005;105(2):132-7.