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Synthesis and Characterization of Polyaniline-Zeolite Composites and their Response towards Carbon Monoxide

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Abstract

A composite of polyaniline and zeolite erionite were utilized to study the electrical response towards carbon monoxide in terms of effect of various ion exchange forms, vapor concentration, cyclic interval and zeolite content. Among various cation forms Na-form shows highest response because of having least electronegativity and large ionic radius. The response of polyaniline towards CO increases as zeolite is added to it because the gas molecules are provided with large surface area. PANI shows least response towards CO among various ion exchanged composites. The response of composite increases when exposed to CO within four minutes of exposure time and then remains constant. The response of composite decreases by increasing number of cyclic intervals. Also response of the composite towards CO attains a steady state above 50 % zeolite content due to reduction in no. of active sites. The composites were characterized by FTIR, XRD, SEM and TGA techniques

Keywords: ***Carbon monoxide; Polyaniline; Zeolite; Composite; Electrical response***

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Introduction

Energy from fossil fuels produces toxic by-products such as NOx, CO and hydrocarbons. A significant part of CO and NOx emissions originate from motor vehicles also. The interaction of CO and NOx, in presence of sunlight tends to produce O_3 which is having strong oxidizing behavior, is believed to have harmful effects on plants and also on human beings [1,2]. Moreover, toxic air contaminants get accumulated in the body due to long-term exposure and contribute to a wide range of diseases. Carbon monoxide (CO) causes pain in patients having heart problems, nausea, headaches and reduces mental alertness [2]. There has been considerable interest in utilizing conductive polymers in place of metal or metal oxide sensors [3,4]. Conductive polymers are having numerous advantages for sensing replacing metallic or ceramics counter parts: low cost and relatively simple fabrication. Polyaniline (PANI) is often used because of its ease of synthesis and environmental stability [5]. Polyaniline deposited on quartz and an alumina substrate exhibit quick responses on exposing to gases or vapors at room temperature. A simple polyaniline film was used for detecting different vapors such as methanol, ethanol, acetone, and benzene. However, there still remain certain issues in using polyaniline as for gas sensing: the sensitivity and selectivity to a particular species amongst others, and its temporal response towards a target gas.

Zeolites are crystalline mesoporous materials with 3D framework structures capable of forming regular and uniform pores and channels. They are having a wide range of chemical composition and framework which results in a wide variety of materials; in fact there are more than 200 synthetic zeolites known so far [6,7]. Zeolites are having tetrahedral units of T

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(where T is Si, Al but can also be another element e.g. B, Ga, Ge, or P) bonded to oxygen atoms which result in a framework containing cages and channels of different sizes and shapes. The internal microporosity of zeolite provides high surface area and active sites for adsorption. In terms of designing zeolites for specific applications, zeolite crystallization is an important process [8]. In summary, synthesis of materials having large surface area might allow the selective sensing of gases from exhausts. A porous material having open accessible size, high surface area and strong interactions with the analyte would be very important for design of the required material. In this work we studied response of polyaniline-zeolite erionite composites towards carbon monoxide. Also, effect of different ion exchange forms on the response of composite is studied.

Material and Methods

Synthesis of polyaniline

Polyaniline was synthesized by the oxidative polymerization method [9]. The aniline monomer (Merck) was purified under vacuum at 58°C before used. 98.44 ml of ammonium peroxydisulphate in 1 M HCl solution were added drop wise to 7.67 g (0.0825) mol of aniline monomer. After vigorously stirring at 5 to 0°C for 3 h, the green emeraldine hydrochloride precipitate was collected and washed repeatedly with 80:20 water: methanol solutions until under washing solutions were colorless. This powder was subsequently changed into the emeraldine base form by stirring it in 0.1M aqueous ammonium hydroxide solution for 3 h. Further washings by 80: 20 water: methanol solutions were carried out until the under washing solutions were colorless. Polyaniline powder was obtained when filtrate was dried in vacuum oven at 50°C for 48 h. Emeraldine salt was obtained by the acid doping to emaraldine base.

Synthesis of zeolite erionite

Zeolite erionite (Si/Al= 9) was synthesized by mixing 6 g sodium hydroxide and 15 g potassium hydroxide in 25 ml water. To this solution 10 g sodium aluminate were and till clear solution was obtained. After the solution was cooled to room temperature; 11 g tetra methyl ammonium chloride was added drop wise with vigorous stirring. 90 g silica sol were dissolved in 115 ml distilled water and stirred for four hours in a separate beaker. This solution was then transferred to the previous one which resulted in the formation of thick gel. The obtained gel was kept at room temp. for two hours in polypropylene bottle and then placed in a teflon lined autoclave and kept in preheated oven at 175°C for 72 hrs. The autoclave was poured in cold water and the resulting material was washed and centrifuged until $pH \leq 9$ and subsequently dried at 110°C. The obtained sample was grinded into powder and calcined by heating at 540°C for 7 hrs in order to remove water [10].

Ion exchange of Zeolite erionite

Ion exchange of zeolite erionite was carried out by replacing Na ion present in parent zeolite with other metal ions viz: Fe, Cu etc. 5 g of parent zeolite were mixed with 144 ml of 0.0125 M metal nitrate $Fe(NO_3)_3$ and $Cu(NO_3)_2$ and stirred at 353 K for 24 hours. The sample was dried for 12 hours at 393 K and calcined at 723 K for 4 hours to remove nitrate ions from the surface [11].

Conversion of Zeolite erionite in to H-form

Na-form of zeolite erionite (Si/Al=9) can be converted into H-form by taking 9.0 g of synthesized zeolite, 7.230 g of NH_4Cl and added to 13.80 ml of deionized water containing 0.1 M HCl to make pH 4.0. The resulting mixture was stirred at 80°C for 30 minutes. The material was filtered under suction and washed with deionized water. After removal of chlorides, the resulting material, NH_4-zeolite, was placed in an oven at 60°C for 24 hours. The ammonium form of zeolite by calcinations over 60 min at 500°C was converted into H-form.

Preparation of PANI-erionite Composites

Polyaniline-erionite composites were obtained by dry mixing method. Polyaniline and erionite particles, dried previously at 120°C for few hours, were ground by mortar and pestle. Four types of ion exchanged forms of zeolite erionite were used in composite formation: Na, Fe, Cu and H. The percolation threshold for electrical response of zeolite erionite is 50 % w/w of zeolite powder [9].

Formation of PANI-erionite thin Film

0.50 g of polyaniline powder or nanocomposite were dissolved in 20 ml of N-methyl pyrrolidne and stirred magnetically at normal temperature. In order to remove any undissolved particles, the solution was filtered. The thin films of polyaniline and PANI/erionite composites were prepared by casting 50 micro liters of the solution on a glass surface (1 × 1.5 cm) and dried for 48 hours at 50°C [12].

Characterization

A Scanning Electron Microscope (SEM LEO440i-England) was used for examining the surface of Polyaniline/erionite composites. A Fourier Transform Infra-Red spectroscopy (Bruker Tensor, 27-Germany) was utilized for examining the bonding between organic and inorganic phases. An X-Ray diffractometer was carried out to determine the crystallinity of the materials. EDX was used to determine the elemental composition of Polyaniline.

Electrical response to carbon monoxide

flow controllers (Sierra Smart Trak 2), glass sensing chamber, LCR to apply a constant voltage and to measure the resistance. The composite was put in the glass chamber with a diameter of 2.0 inches and a length of about 10.0 inches connected to the LCR via copper wires. In this study, carbon monoxide was used as the target gas. For carrying out the sensing measurements, the target gas was carried by N_2 into the glass chamber through a mixing chamber. The experiment was carried at 28 ± 2°C and 20 % humidity. The humidity was measured by using dew point sensor (Owlstone, Model no. OHG -4, U.K). The stock gas was diluted from higher concentration to required lower concentration (1000 ppm to 5 ppm). Initially both the chambers contain nitrogen till the sample shows a constant electrical resistance. Then the nitrogen was removed from the chamber and 5 ppm of CO/N_2 was injected into the mixing chamber. The concentration of CO was checked by CO detector. Then gas was allowed to enter into the working chamber. After maximum value of resistance was obtained the gas was removed from working chamber and N_2 was injected into working chamber. The response of sensor (R%) is calculated as: $R\% = [(R_g - R_o)/R_o] \times 100$, where, R_o is the baseline resistance in dry nitrogen atmosphere and R_g is the max. resistance during gas exposure. Here, we may take in consideration response of the composite instead of the resistance. The procedure was repeated for various concentrations [13].

Results

Characterization of zeolite/polymer composites

FTIR spectra of PANI/Na-erionite (Si/Al= 9) was taken to analyze the characteristic absorption peaks. The absorption peaks were obtained at 1153, 1296, 1428, 1575, 3216, 818 cm-1 which are due to vibration mode of the quinoid ring, stretching vibration of C-N bond, stretching vibration of the benzenoid ring, the stretching vibration of N-Quinoid ring, N-H bond stretching, C-H bond bending. The typical absorption peaks of the nanocomposite in FTIR spectra furnish valuable information about the presence of PANI in zeolite erionite. The FTIR of PANI show characteristic absorption peaks at 825, 1161, 1297, 1493, 1586 and 3300 cm^{-1}. In the nanocomposite of Polyaniline/zeolite erionite; observed peaks typical of polyaniline were transferred to lower-level wave numbers, indicating an interaction between polymer and the zeolites. Also absorption peaks are obtained in the region 3500-3700 cm^{-1} which suggests bridging between Al-OH-Si (**FIG. 1**) [14].

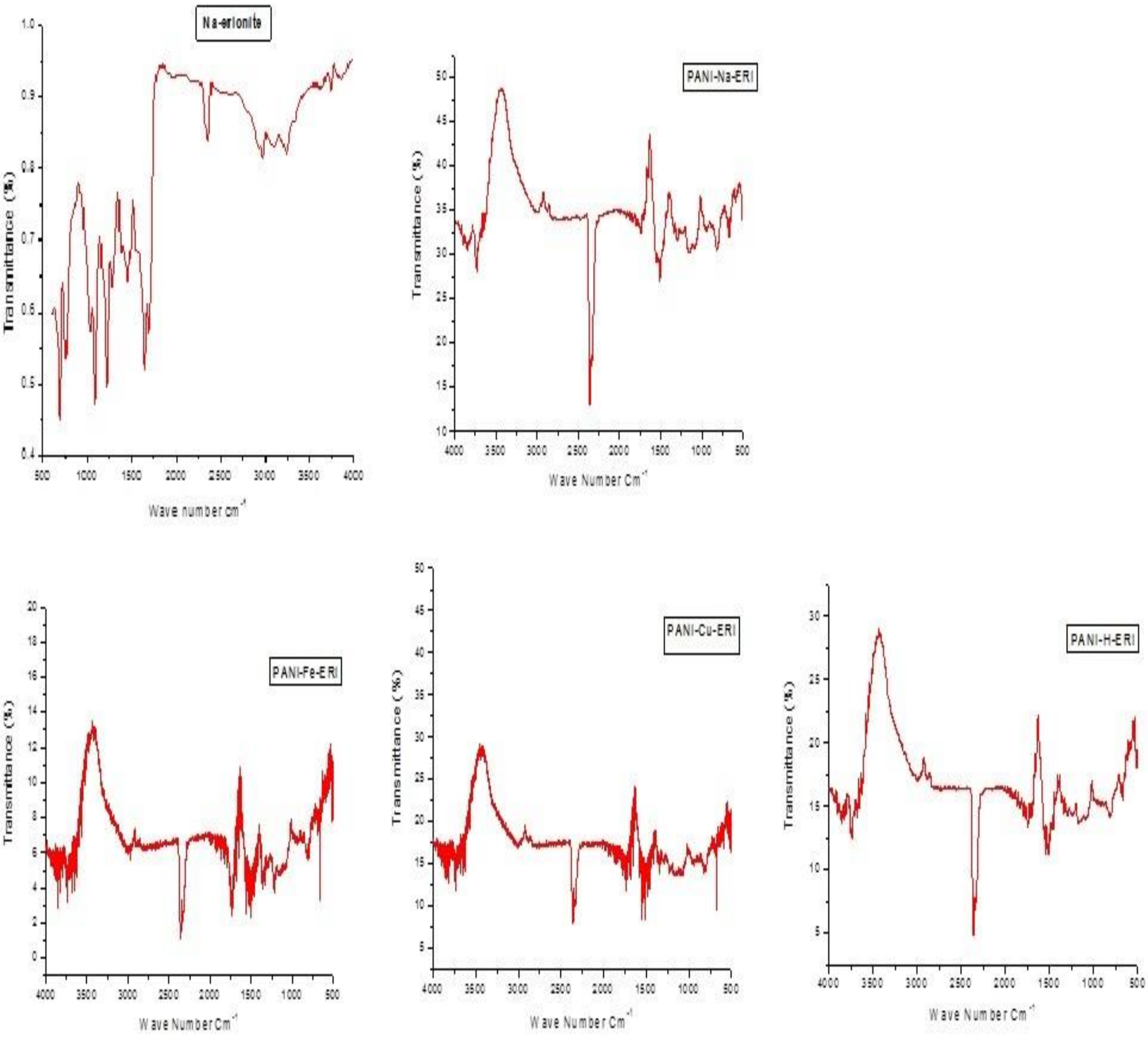

FIG. 1. **FTIR spectra of PANI-erionite Composites.**

X-Ray diffraction technique is used to determine the crystalline phases present in the material and other structural information such as strain, stress and defects (**FIG. 2**).

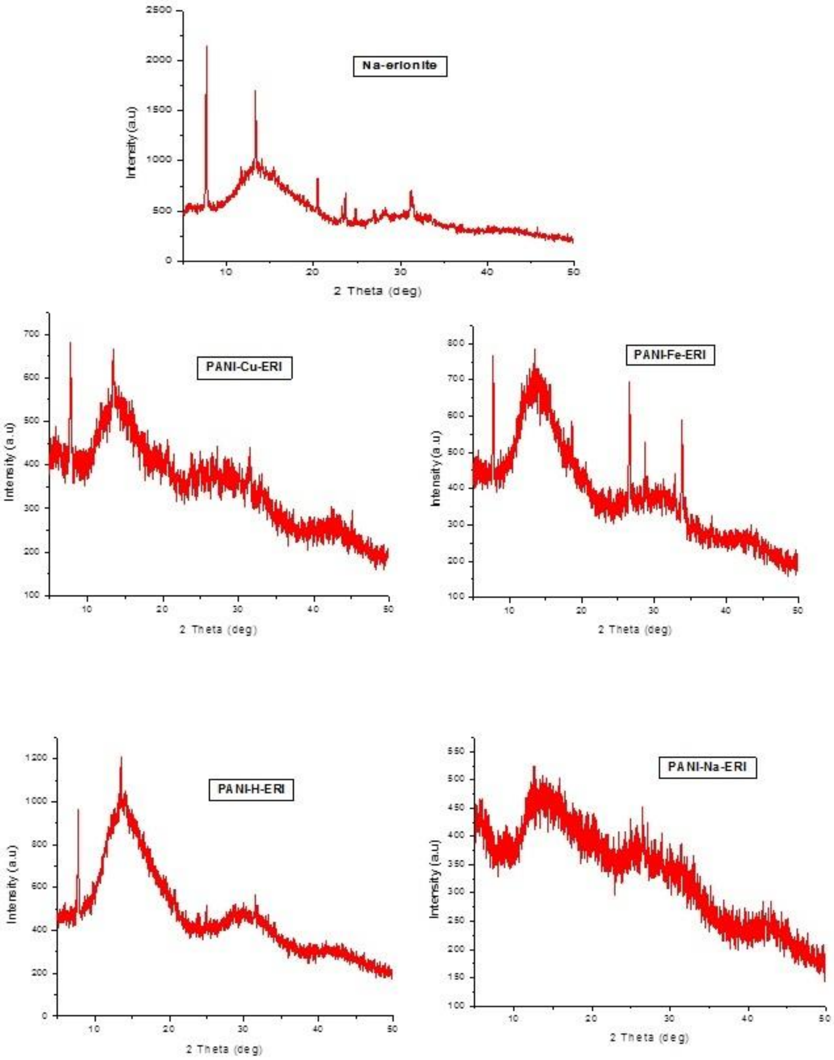

FIG. 2. **XRD spectra of PANI/erionite (Si/Al=9) composites.**

The X-Ray diffraction pattern of polyaniline is amorphous which is due to the coil structure resulting from H-bonding between amine and imine positions. It can be noted that polyaniline has a relatively amorphous structure, but by encapsulation of polyaniline in the zeolite channels the alignment and arrangements of polyaniline chains significantly improves and as a result, the intensity of the peaks related to the nanocomposite increases. Increasing the peak sharpness is directly due to the increasing of the structural order in materials [15]. The characteristic peaks of the nanocomposite were obtained at 2 theta value of 8.5^0 and 14.7^0. The intensity of the peaks has been affected by the amorphous nature of the polyaniline. This confirms the presence of the polymer in the zeolite micropore (**FIG. 3**).

The morphology of surface of zeolite erionite and the nanocomposite was studied by Scanning Electron Microscopy. The SEM images of the zeolite are rod shaped wile as that of composites are quite regular. Also the SEM images show that the diameter of the composite is in the nanometer range (**FIG. 4**).

The unit cell contents of zeolite erionite is $(Na_2,K_2,Ca)_2Al_4Si_{14}O_{36}\cdot 15H_2O$. The elemental composition of zeolite erionite was determined by EDX. Polyaniline possesses the following composition: C, H, N and some residual matter.

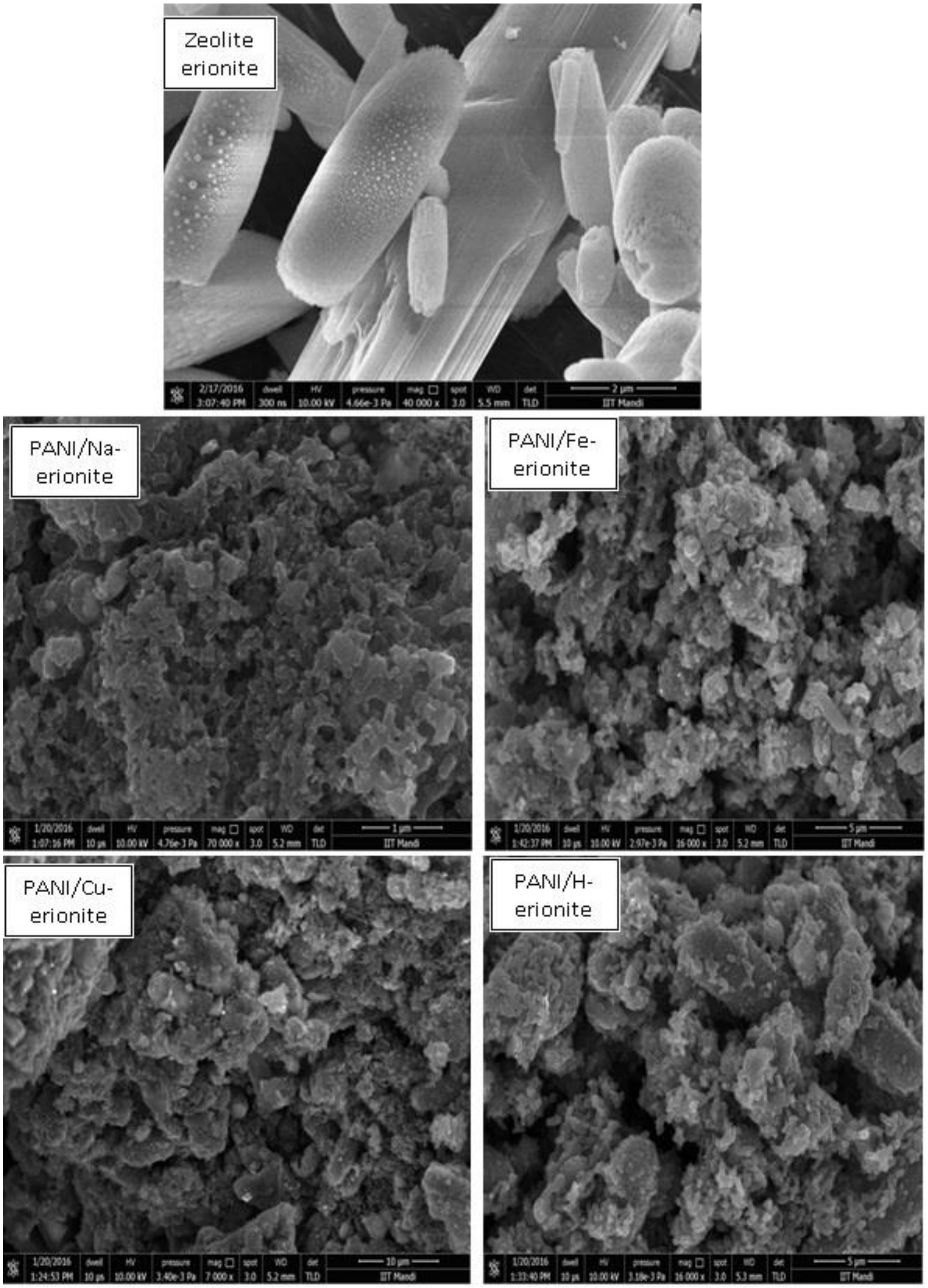

FIG. 3. **XRD spectra of PANI/erionite (Si/Al=9) composites.**

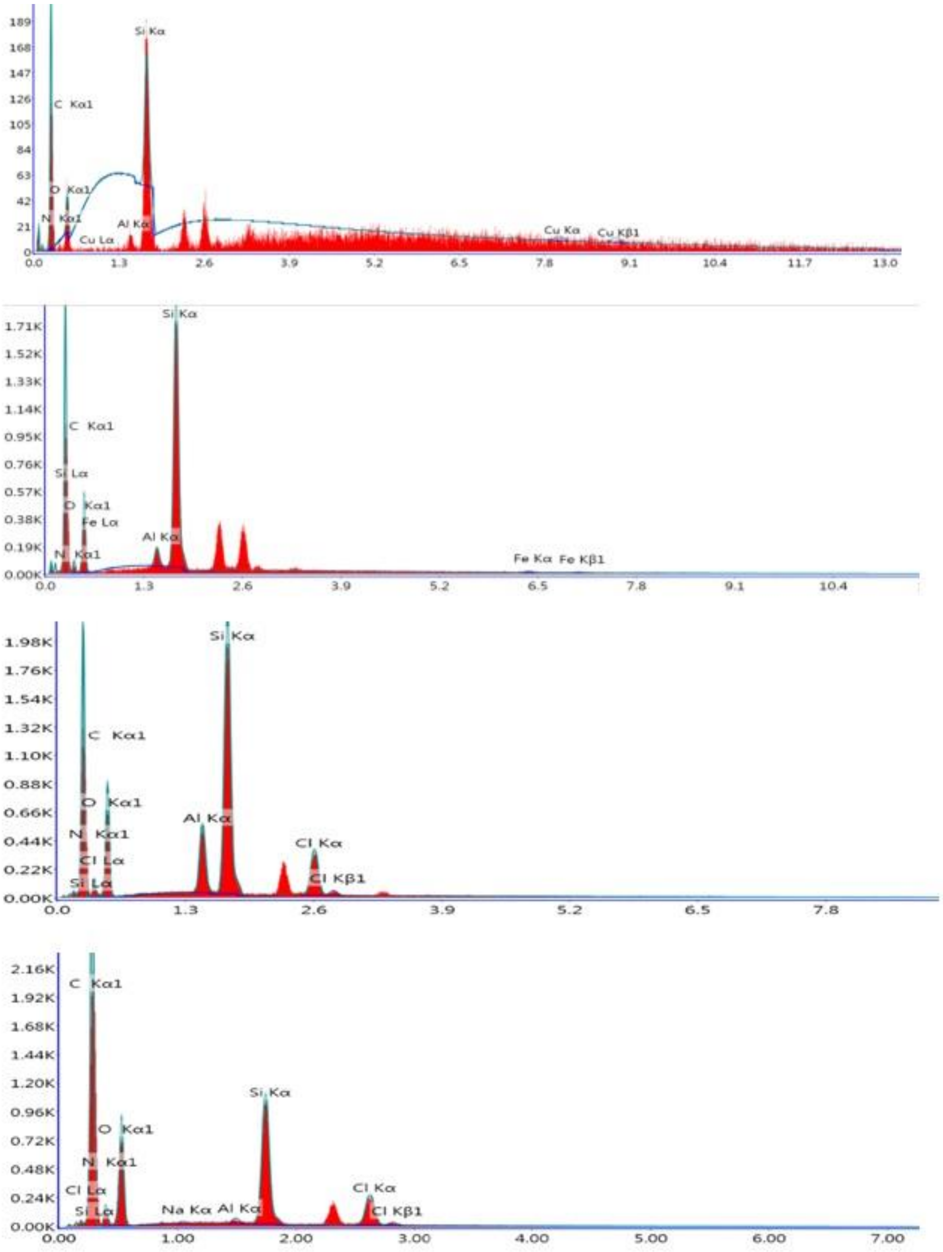

FIG. 4. **DSC-TGA of zeolite–erionite.**

TGA of the nanocomposite was carried out and it shows two steps in weight loss. The first weight loss around 150°C can be assigned to the bound water or oxidant. The second weight loss around 250°C can is due to the degradation of the polymer structure (**FIG. 5**).

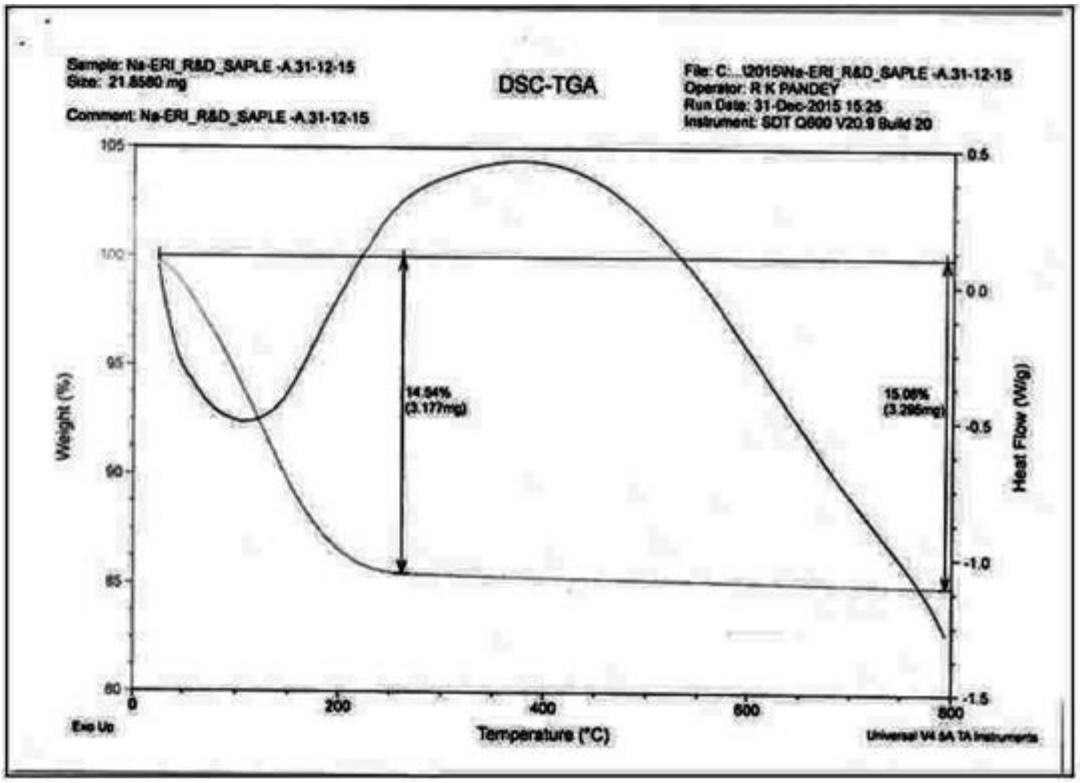

FIG. 5**. DSC-TGA of zeolite –erionite.**

Discussion

PANI-CO interaction (Response of PANI towards CO)

The response of PANI and composites for CO (R% = [(R_g _ R_o)/R_o] ×100) was determined by difference between the saturated value when exposed to CO and the baseline value when exposed to nitrogen at 28 ± 2°C as shown in **FIG. 6.**

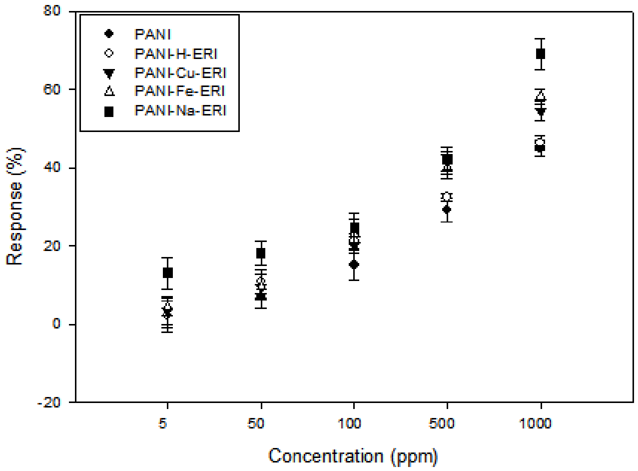

FIG. 6. **Response of PANI and PANI/Zeolite erionite composites towards CO**.

TABLE 1 shows response of polyaniline and composites in presence of CO at 5 ppm and 1000 ppm. When PANI is exposed to CO concentration of 5 ppm; it shows a response of 2.11 %. On increasing the concentration of CO; response of PANI towards CO also increases. It can be noted that as we increase the concentration of CO from 5 ppm to 1000 ppm; response increases from 2.11 to 45 %. This increase in response of PANI towards CO can be attributed to increase in the no. of CO molecules which interact with PANI chains. From TABLE 1; it can be observed that when zeolite is added to PANI response towards CO increases from 45 to 69.11 %. The increase in the response of PANI towards CO on adding zeolite erionite is due to increased surface area of the composite. Since, zeolites are aluminosilicates made of SiO_4 and AlO_4 tetrahedra building blocks which result in a ring structure. They are three-dimensional (3D) frameworks having ordered mesopores and micropores. They have an open porosity that gives rise to an large surface area. Silicon ions are replaced by Aluminum ions and introduce a negative charge into the framework. This charge developed is now to be compensated by an exchangeable cation, such as an alkaline or alkaline-earth cation and, thus, the ion exchange property is provided. Zeolites are having high adsorptive property, high surface area and porosity. Hence, the gas molecules are provided with a large surface area so that they can interact with polymer chains and the response increases.

TABLE 1**. Response and induction time of PANI and PANI/Zeolite erionite composites**

Sample	**Sample Code**	**Electronegativity**	**Ionic radius (pm)**	**Response (%) to CO**		**Induction time (sec)**
				at [CO] = 5 ppm	**at [CO] = 1000 ppm**	
Polyaniline	PANI	--	--	2.11	45	300
PANI-zeolite erionite	PANI-Na-erionite	Na = 0.93	Na = 186	13.11	69.11	260
(Si/Al = 9, Na)						
PANI-zeolite erionite	PANI-Fe-erionite	Fe = 1.83	Fe = 124	4.32	58.11	241
(Si/Al = 9, Fe)						
PANI-zeolite erionite	PANI-Cu-erionite	Cu = 1.9	Cu = 128	3.21	54.46	232
(Si/Al = 9, Cu)						
PANI-zeolite erionite	PANI-H-erionite	H = 2.1	H = 78	2.11	46.33	228
(Si/Al = 9, H)						

Effect of cation type

The effect of cation type on the electrical response of the composite was studied next. For this purpose four ion exchanged forms were selected: Na, Fe, Cu and H. H-form was obtained by calcinating NH_4-form over 60 min at 500 ^{0}C. The Response of PANI and PANI/erionite (Si/Al=9) composites when exposed to 5, 100 and 1000 ppm of CO concentration is shown in fig. 7. It can be observed that response increases with ion exchange of the composite. PANI is having the least response towards CO among various composites. Since, zeolites are well-defined three-dimensional (3D) microporous and mesoporous frameworks connecting channel systems. They have open pores; those result in a large surface area. The purpose of using zeolites in sensors is to make the sensor sensitivitive and selectivitive for adsorption; in addition, thin films assure a fast response time of the sensor. From **FIG. 7** it can be seen that Na-form is having highest response while as H-form is having least response towards CO. The response follows the following order: Na-form > Fe-form > Cu-form > H-form > PANI.

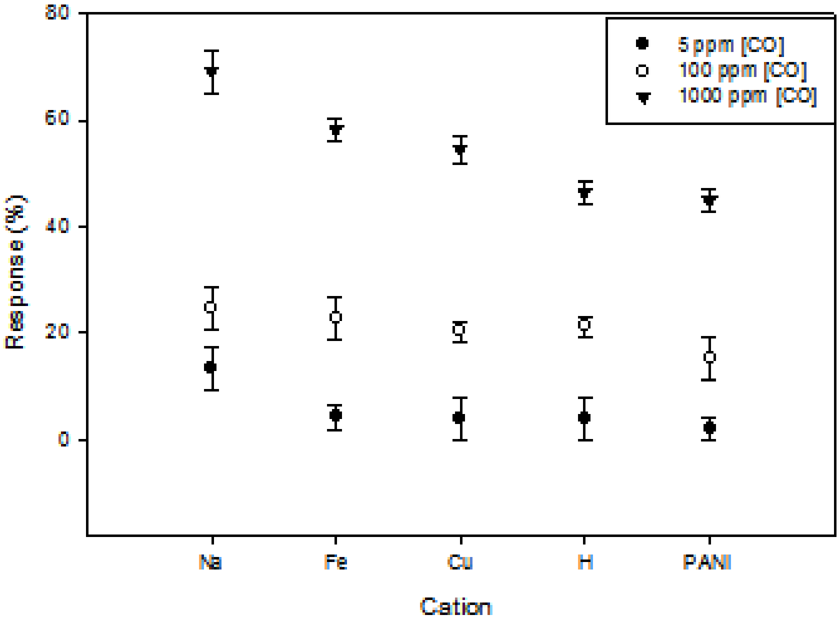

FIG.7. **Response of PANI and PANI/erionite (Si/Al=9) composites of various cation types when exposed to 5, 100 and 1000 ppm of CO concentration**

The electrical response depends upon two factors: electronegativity and ionic radius of the cation. Na- form is having the highest electrical response as Na (EN=0.93) is having lowest value of electronegativity and large ionic radius. We may note that the electronegativity of Na, Fe, Cu and H is 0.93, 1.83, 1.9, 2.1 with corresponding ionic radii 186 pm, 124 pm, 128 pm, 78 pm respectively. Due to small value of electronegativity and high value of ionic radius of Na-form; the gas molecules interact with the polymer chain and not with the ion in zeolite. Hence result in large response. Due to large electronegativity of H-form, the response is small. The gas molecules interact with the ion instead of PANI and resulting in small response. Two factors Electronegativity and ionic radius of cation are responsible for adsorption of gas by cation present in the zeolite [16]. Higher electronegativity of the cation present in zeolite leads to strong binding between cation and frame work [17].

Li, Na and K possesses electronegativity of 1.0, 0.9, and 0.9 and ionic radius of 0.60, 0.95, 1.33 A° respectively. From 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 response. Hence higher concentration of Li gives small value of electrical response from the composite. While as Na is having low electronegativity and more value of ionic radius. This leads to small interaction between Na and H_2 molecules. Hence, a strong value of sensitivity is obtained. The gas molecules do not interact with cation present in the zeolite; rather they interact with polymer and result in large electrical response. The above fact is supported by the study carried out by Thuwachaowsoan, et al. [18]. They reported conductivity value of $(-7.78 \pm 0.33)\times10^{-2}$, $(-4.37 \pm 0.59)\times10^{-1}$ and $(-2.20 \pm 0.12)\times10^{-1}$ S/cm for Pth_200:1/MOR_Li[90]_20, Pth_200:1/MOR_Na[100]_20 and Pth_200:1/MOR_K[90]_20 respectively at 20% zeolite content.

Also the order of response is directly related to surface area of different ion exchanged forms. Na-form might be having highest surface area. Thus CO molecules can penetrate more easily into the Na-form and have a stronger interaction with the polymer. Therefore interaction time of PANI and gas molecules increases. It can be observed that the response of PANI towards CO increased on adding zeolite to it. Since zeolites are composed of well-defined 3-D microporous and mesoporous system. They result in high surface area. Therefore on adding zeolite to PANI, the surface area increases and CO molecules get adsorbed easily and interact with the polymer chains.

Effect of vapor concentration

Next we studied effect of vapor concentration on electrical response of the composite over time. **FIG. 8** shows response of PANI/Na-erionite (Si/Al=9) vs time towards CO at 5, 100 and 1000 ppm. It can be noted that when PANI/Na-erionite (Si/Al=9) was exposed to CO concentration of 5 ppm; response increases from 2.00 to 13.11 % over an exposure time of 4 minutes. Beyond this time the response attains a constant value. Similarly, when PANI/Na-erionite (Si/Al=9) was exposed to CO concentration of 1000 ppm; response increases from 10.11 to 69.11 %. When we increase the concentration of CO; response of composite also increases. At higher concentration more and more CO molecules come in contact with PANI and therefore response increases. However beyond some time response attains a steady state value. This is due to reduction in the no. of active sites on the surface of composite on which gas molecules may get adsorbed.

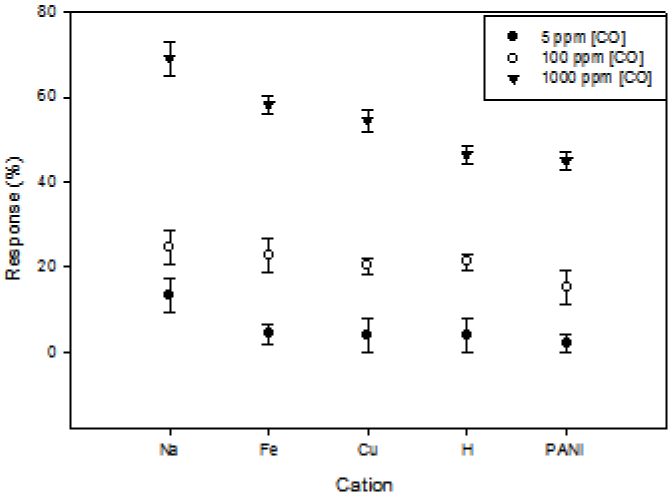

FIG.8. **Response of PANI/Na-erionite (Si/Al=9) vs time towards CO at 5, 100 and 1000 ppm**

The effect of NH_3 concentration on DPPP over time was studied by P. Phumman *et al.* [19]. The specific electrical conductivity of DPPP (60)/NaZ23 vs. time (min) when exposed to 5%v of NH_3 at 28 ± 1°C and at 1 atm showed results shown in **FIG. 9**. Under the exposure to NH_3, the specific electrical conductivity of DPPP (60)/NaZ23 first increases and reaches a maximum value of 0.235 S/cm after an NH_3 exposure time of 2.90 min, then decreases to a steady state value of 0.03 S/cm after the NH_3 exposure time of 30 min.

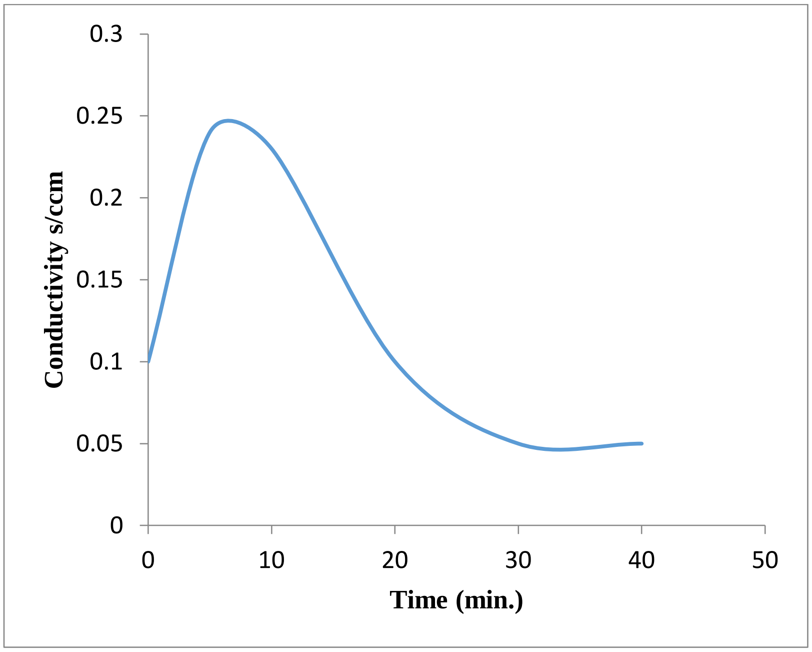

FIG.9**. Effect of NH3 concentration on DPPP vs time [19].**

Effect of cyclic interval

Next we studied the effect of cyclic interval on the electrical response of the composite towards CO as shown in **FIG. 10.** It can be noted that response of the composite decreases with increase in no. of cyclic intervals. The response of PANI-Na-erionite decreases from 69.11 to 60.21 % within four cyclic intervals. This decreasing trend in response after repeating cyclic after 2 to 4 times is because of the fact that during 1st interval gas molecules which aret adsorbed take some time to desorb and hence decrease the no. of active sites. Hence, a decrease in the response occurs after repeating the cycle.

A similar result was also obtained for NaY, 50CaNaY and 50MgNaY [20-23]. For the effect of cyclic response at cyclic interval of 1,200s towards 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. The obtained electrical conductivity sensitivity values for 50MgNaY, 50CaNaY, NaY and 50KNaY are: $1.97 \times 10^{-01} \pm 5.06 \times 10^{-03}$, $2.57 \times 10^{-01} \pm 2.40 \times 10^{-03}$, $2.68 \times 10^{-01} \pm 1.99 \times 10^{-02}$ and $3.42 \times 10^{-01} \pm 4.67 \times 10^{-04}$, respectively for first interval. Kamonsawas, et al. [24] examined the variation of response by repeating the sensing interval of zeolite Y for 3 different types of ketone vapors (acetone, MEK and MIBK). Zeolite Y was ion exchanged at 50% mole: NaY, 50 KNaY, 50 MgNaY and 50CaNaY for the zeolite Y keeping Si/Al ratio of 5.1. It was observed on behalf of cyclic interval that the electrical conductivity response decreases as we go on increasing number of cyclic intervals due to interaction between the active site and ketone vapors. This decrease in the sensitivity due to repetion of cyclic intervals is because the vapors adsorbed in the first interval do not get desorbed simultaneously. Hence, the sensitivity of the composite will go on decreasing with the cyclic interval. However, if the composite is provided with a sufficient time (recovery time) the gas molecules get desorbed from the surface of the composite and there is no loss in the response of the composite.

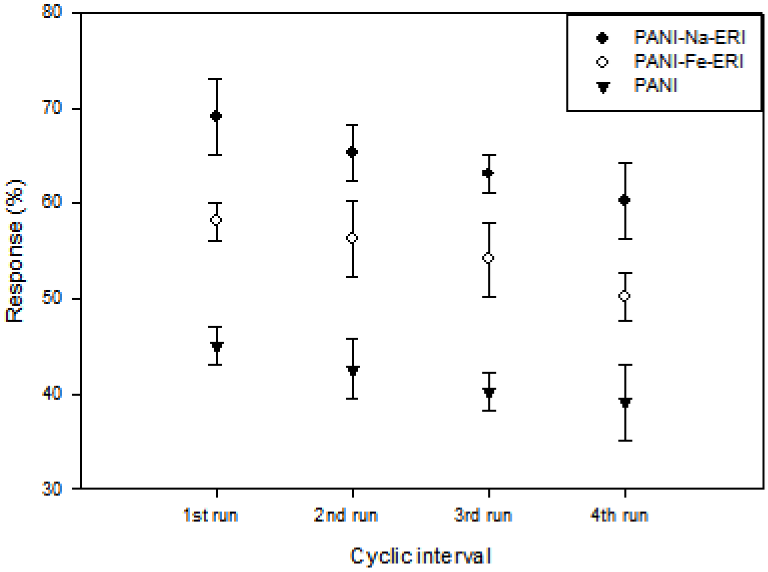

FIG. 10. **Response of PANI, PANI-Fe-erionite and PANI-Na- erionite (Si/Al=9) towards CO at 1000 ppm for various intervals.**

Effect of Zeolite content

The response of the composite towards CO over a range of zeolite content is shown in **FIG.11.** It can be noted that with increase in zeolite content response of the composite increases. The response of Na-form, Fe-form, Cu-form and H-form increases from 11.31 to 69.11, 8.62 to 58.11, 6.41 to 54.46 and 6.40 to 46.33 % as the zeolite content was increased from 10 % to 50 % respectively. This increase in the response of the composite towards CO with increasing zeolite content can be attributed to the greater no. of active sites available for CO molecules on which they can get adsorbed and interact with polymer chains. The response of the composite goes on increasing with increase in zeolite content up to 50 % w/w. above 50 % w/w zeolite content response does not increase and remains constant. This is due to the reduction in the no. of available active sites. Therefore the response attains a steady state above 50 % zeolite content.

When PANI-10MA/10Zeolite-13X, PANI-10MA/20Zeolite-13X, and PANI-10MA/40Zeolite-13X having weight percentages of 10, 20, and 40% correspondingly were exposed to CO at 1000 ppm, the sensitivity increases from 0.157 to 0.950 when zeolite content varies from 0 to 40 wt.%. For CO concentration of 7.8 ppm, the electrical sensitivity increases from 0.004 to 0.138 respectively. Generally, it appears that electrical conductivity sensitivity to CO can be increased by adding zeolite 13X. CO molecules adsorb physically in the 13X zeolite pores. The increase in electrical response obtained on increasing zeolite content is due to the increase in the amount of no. of zeolite pores available per unit surface area to interact. For a composite with higher zeolite content, more CO molecules diffuse inside the composite and thus they require a longer time to complete the interaction with polyaniline chains during which the specific electrical conductivity finally reaches a steady state value [25].

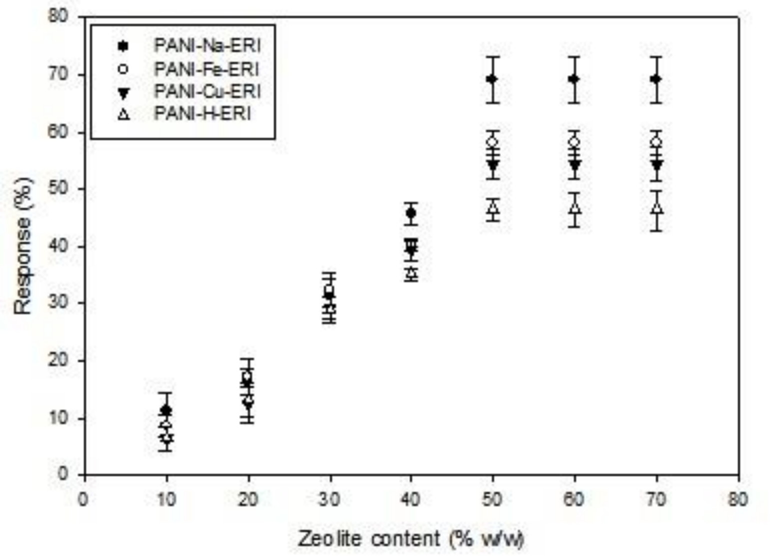

FIG. 11. **Response of PANI-/Na- erionite, PANI-/Fe- erionite, PANI-/Cu- erionite and PANI-H- erionite (Si/Al=9) vs zeolite content towards CO at 1000 ppm.**

Conclusion

We have investigated the effects of CO concentration, ion exchange form and vapor concentration over time, cyclic interval and zeolite content on the electrical response of polyaniline-zeolite erionite composite when exposed to CO under normal atmospheric conditions. The response of composite increases with increase in the CO concentration. Among various ion exchange forms Na-form shows highest response because of small electronegativity and large ionic radius. Due to small electronegativity of Na; CO molecules do not interact with it; instead interact with PANI. Hence the response increases. H-form is slightly less sensitive towards CO due to higher electronegativity. The response of the composite increases with time when exposed to CO but after some time remains constant due to reduction in the no. of active sites. The response of the composite towards CO can be improved with the addition of zeolite erionite up to 50 % (w/w). The response of the composite decreases by repeating the no. of cyclic intervals.

Acknowledgements

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