Comparative Study of Conductivity based Silver Modified ZSM5 & Beta Zeolites as a LPG and CO₂ Gas Sensor

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Abstract: *Zeolites are the gas sensing materials. The microspores of H-Zeolite Socony Mobil-Five (H-ZSM5) and H-Beta zeolites are modified with metal Silver Nitrate (AgNO₃) by ion exchange method. The modified Silver- ZSM5 (Ag-ZSM5) and Silver-Beta (Ag-Beta) are characterized by X-Ray Diffraction (XRD), Infrared (IR) Spectroscopy, Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis(DTA), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis of X-Ray (EDAX) techniques. Gas sensing characteristics of Ag-ZSM5 and Ag-Beta zeolite have been studied for Liquified Petroleum Gas (LPG) gas and Carbon dioxide (CO₂) gas. The gas sensing properties of Ag-ZSM5 and Ag-Beta zeolite are studied in a static gas characterization system. Adsorption of gas molecules in zeolite changes the ionic activity, which interns changes conductivity. The maximum Percent Sensitivity Factor (PSF) is measured as a function of operating temperature and as a function of gas concentration for LPG and CO₂ gas.*

Keywords: Zeolite, Ion exchange, LPG, EDAX, SEM, PSF

1. Introduction

Zeolites are crystalline micro porous aluminosilicates, composed of corner-sharing AlO_4 and SiO_4 tetrahedra joined into three dimensional frameworks having pores of molecular dimensions. They are a subset of the larger class of molecular sieves. The porous structure consists of cavities, channel and water; also, the cations that counter-balance the negative ions of aluminum sites usually occupy the pore space [1, 2].The presence of aluminum in the silica alumina zeolite framework give rise to anion. These anions attract cations and hence, in the framework cations are present and they are loosely bound with the framework. The replacement of cation held in the framework structure is possible by the other cation. Hence ion exchange is possible. [3] Since cations are free, they can move to new positions under the influence of an external electric field, which causes the electric charge transport. It is conductivity and dielectric relaxation.

Zeolite possesses classical applications like adsorption [4], catalyst [5, 6], and the possibility of zeolite pores to host different ions, atoms, molecules and clusters have opened up numerous opportunities. In last few years, zeolites have been used in the field of novel technologies such as chemical sensors [7, 8, and 9]. As a sensing material, zeolites are very favourable due to its additional high thermal stability and chemical resistance. Zeolite possesses a remarkable property of hydration and dehydration on heating without any major changes in structure. Adsorption of gas molecules in zeolite micropores changes the ionic activity and hence conductivity changes. This property is used as a gas sensor in the present study.

Propane (C_3H_8) is the hazardous gas to be detected due to its flammability. It is a green house gas to be detected and also one of the major constituents of LPG gas. Carbon dioxide (CO_2) is a non –toxic gas, it is one of the important gas to

monitor with respect to "Green House Effect".CO_2 is a good indicator of air quality pollution. So the detection and measurement of presence of CO_2 and LPG gas concentration in the atmospheres of offices and houses are necessary. In the present study zeolite material is used as sensor to sense presence these gases.

2. Materials and Methods

In the present study, the gas sensing properties of Silver-ZSM5 (Ag-ZSM5) and silver-Beta (Ag-Beta) zeolites are studied for LPG and CO_2 gas.
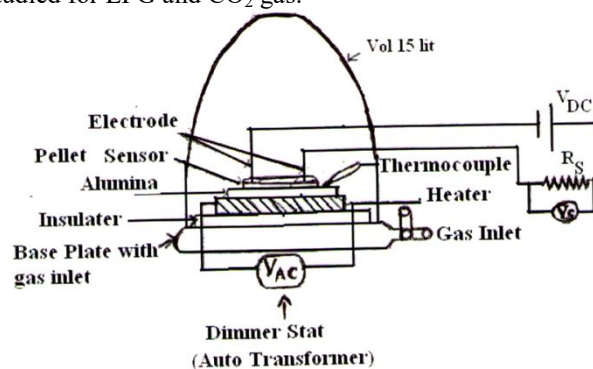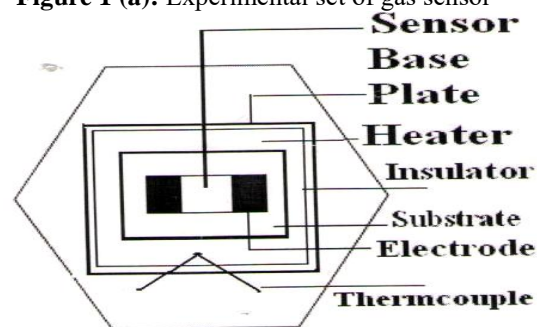

Figure 1 (a): Experimental set of gas sensor

Figure 1 (b): Sensor Assembly

Static Gas Characterization System is used to study gas sensing property which is shown in figure 1(a). A figure 1(b) gives the details of sensor assembly [10]. The system consist of heater of nichrome wire (1.5kW and R=120Ω). It is used to vary the substrate temperature from 345K to 575K with the help of dimmer stat. Temperature of the sample is measured with the help of temperature indicator with Cr-Al thermocouple. The electrical terminals are brought out from the sensor assembly by using insulated bead- through mounted on the stainless steel base plate. The base plate has a gas inlet and on which a glass chamber (Volume ≈15 lit) is mounted. The spring press contact electrodes are used during the measurements of gas sensing properties. Half bridge method is used to determine the conductance of the zeolite sample. The resistance of the sample is measured directly by electrometer (Keithely Multi Meter).The required gas concentration inside the system is achieved by injecting a known volume of the gas in the airtight chamber at ambient conditions. The DC conductance of the sample is obtained by applying the voltage (V) through variable DC power supply (0-250V) to sensor and measuring the voltage drop Vs across Rs. The conductance G and the percentage sensitivity factor (%SF) are calculated by using the following formula.

$$G = \frac{V_s}{[R_s\,(V - V_s)]}$$

$$\% S.F. = \left[\frac{(G_g - G_a)}{G_a}\right] x\,100 = \left(\frac{\Delta G}{G_a}\right) x\,100$$

Where, G_a and G_g are the conductance of the sensor in air and gas + air respectively.

3. Experimental

Sensor materials were prepared by the synthesized ZSM-5[11] and Beta [12] zeolite. The ZSM-5 and Beta was modified with 4g of Silver Nitrate (AgNO$_3$). Silver Nitrate was taken in 250ml round bottom flask and 30ml methanol and 10 gm of dried ZSM-5 zeolite was added. The mixture was stirred using magnetic stirrer for 15 minute for homogenization and placed under reflux condition at 338K for 12 hrs. Further, it was washed repeatedly after reaching to room temperature. Then it is dried in an oven at 383K for overnight. The modified ZSM5 is characterized by XRD, IR, TGA-DTA, SEM and EDAX. The modified silver ZSM5 (Ag-ZSM5) was mixed with polyvinyl alcohol (PVA) as a binder material and is pressed to form pellet (diameter 13mm and thickness 1mm) using hydraulic press. The pellet is then fired at 573K for 4 hrs to drive out the binder material (PVA). Silver paste is coated on the surfaces of the pellet to ensure good electrical contacts. The similar procedure was adopted for the preparation of modified form of Silver-Beta (Ag-Beta) zeolite. For the preparation of Ag-Beta pellet same procedure, as mentioned above, is done. The ion exchanged sample of Ag-Beta is characterized using XRD, IR, TGA-DTA, SEM and EDAX. X-Ray diffractogram (XRD) of the zeolite samples were taken using CuK$_\alpha$ radiation at a scanning speed of 1.2 degree per min. The zeolite material is scanned in the 2θ range of 20^0 to 80^0. The XRD pattern was obtained at 30kV and 15mA on Philips (3710pw/1710) system.

The XRD of synthesized ZSM5 and Beta samples are compared with standard data and are in agreement. The XRD of ion-exchanged samples are similar to that of original samples, indicating that there is no change in crystal structure. The XRD pattern of Ag-ZSM5 zeolite is shown in fig. 2 and of Ag-Beta zeolite in fig.3.
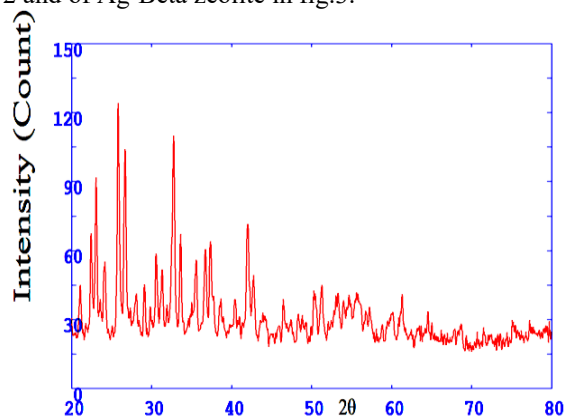

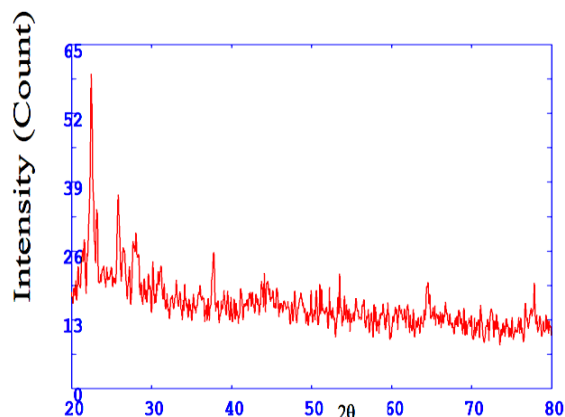**Figure 2:** XRD pattern for Ag-ZSM5 Zeolite

Figure 3: XRD pattern for Ag-Beta Zeolite

Infrared (IR) Spectra of Ag-ZSM5 and Ag-Beta zeolite is recorded on Perkin-Elmer FT-IR spectrophotometer in the frequency range 450-4000cm^{-1} by using KBr pellet technique. This is shown in fig.4 for Ag-ZSM5 zeolite and in fig. 5 for Ag-Beta zeolite.
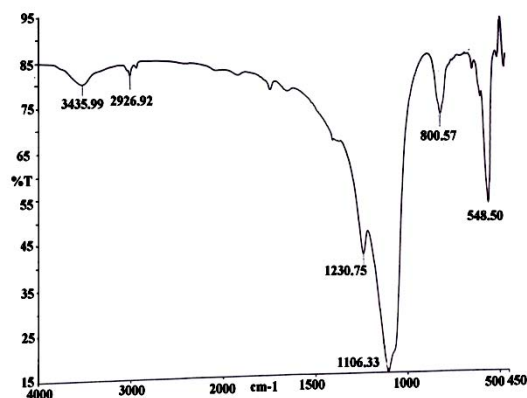

Figure 4: IR Spectra of Ag-ZSM5 zeolite
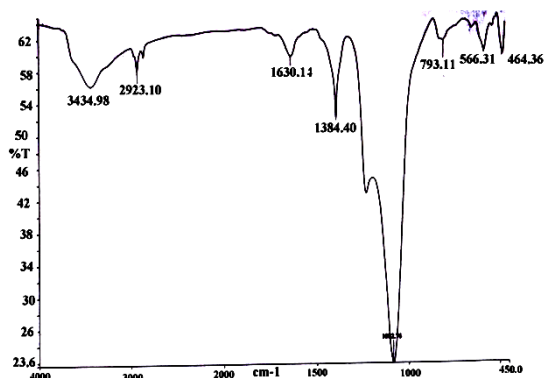
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Figure 5: IR Spectra of Ag-Beta zeolite

In Ag-ZSM5 zeolite the structure insensitive asymmetric stretch and symmetric stretch bands are found to be at 1106 cm^{-1} and 800cm^{-1} respectively. The T-O bend is observed at 460cm^{-1}. The structure sensitive asymmetric stretch band is observed at 1230cm^{-1}. The band near 548 cm^{-1} is the characteristic of the presence of double five member ring [14]. The water bands are present at 3435.9 cm^{-1} and 1650 cm^{-1} [15].

In Ag-Beta zeolite structure insensitive asymmetric stretch band is observed at 1082.7 cm^{-1} and symmetric stretch band is at 793cm^{-1}. The T-O bend is found to be at 464cm^{-1}. The structure sensitive asymmetric stretch band found at 1230 cm^{-1}. The double ring which is the characteristics of highly crystalline Beta zeolite is observed at 566 cm^{-1}. The water bands are observed at 3434 cm^{-1} and 1630 cm^{-1}. These bands are the characteristics of zeolite material.
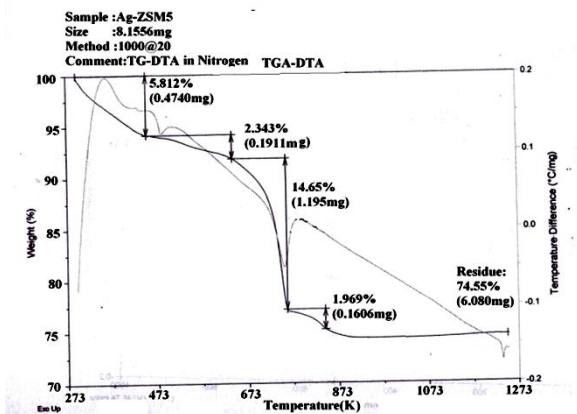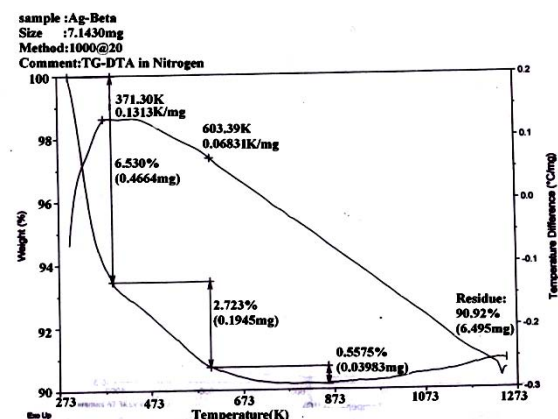

Figure 6: TGA-DTA curve of Ag-ZSM5 Zeolite

Figure 7: TGA-DTA Curve of Ag-Beta Zeolite

The TGA-DTA spectra were studied on T.A. instrument (U.S.A.) SDT-2960 with reference material Al$_2$O$_3$ in nitrogen atmosphere. The TG/DTA curves for Ag-ZSM5 and Ag-Beta zeolite are shown in fig. 6 and fig.7. A TGA curve for Ag-ZSM5 shows four steps of weight loss with total weight loss of 25.45%. In first step the weight loss is of 5.812%, which is in the temperature range of 300K to 450K, and is due to the loss of molecular and adsorbed water [16]. The second step in the temperature range of 450K to 650K, the weight loss of 2.343%, which corresponds to removal of Tetra Ethyl Ammonium Bromide (TEA-Br) and which was used as a structure direacting agent while synthesizing ZSM5 zeolite. The weight loss is highest in third step and it is 14.6%, in the temperature range of 650K to 750K [17]. This weight loss is due to oxidative decomposition of templates and water loss [18]. The weight loss of 1.9% is observed in the temperature range 750K to 850K. It is due to dehydration of sorbed water inside the super cages. Above 850K no weight loss is observed.

The DTA analysis shows two endotherms. These are observed in Ag-ZSM5 zeolite at 437K and at 750K temperature. This indicates that the immobile water in pores is removed at 437K and the physical change is taking place at 750K [19].

Ag-Beta zeolite is potentially the most hydrophilic, was subjected to TG analysis to evaluate the water content [20]. The weight loss is observed in three steps in Ag-Beta zeolite. In first step the weight loss is maximum 6.53% in the temperature range 300K to 400K. This is due dehydration of physically sorbed water in Ag-Beta zeolite cavities [19]. The weight loss is 2.723% is observed in second step in the temperature range of 400K to 600K. This weight loss seems to be due to decomposition of (Tetra Ethyl Ammonium) TEA + ions and mobile water coming out of zeolite cavities [21]. The weight loss of 0.55% is observed in third step, when is in the temperature range 600K to 873K. This is due to decomposition of TEA-Br, a structure directing agent which was used during synthesis. Above 873K no weight loss is observed. In DTA analysis shows, no endotherm is observed in Ag-Beta zeolite, indicating no structural change up to 1200K.

The morphology of the zeolites was investigated using scanning electron microscope, Leo-Leica, Sterioscan model 440, Cambridge (U.K.). Figure 8 shows the microgram of Ag-ZSM5 zeolite, wherein cubic and needle shaped zeolite crystals are observed. These crystals are 3μm in size. Figure 9 shows the microgram of Ag-Beta zeolite. The crystallites are spheroid shaped having crystal size of 3μm.
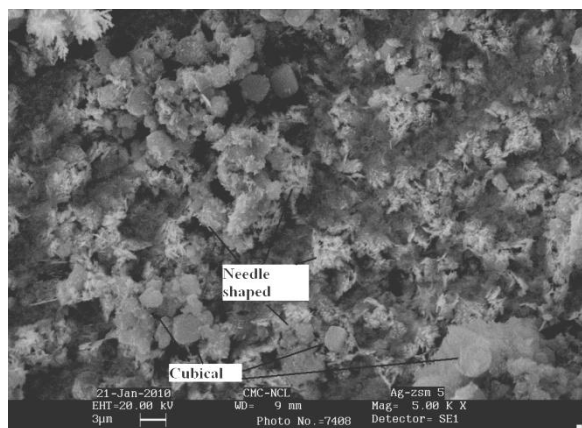
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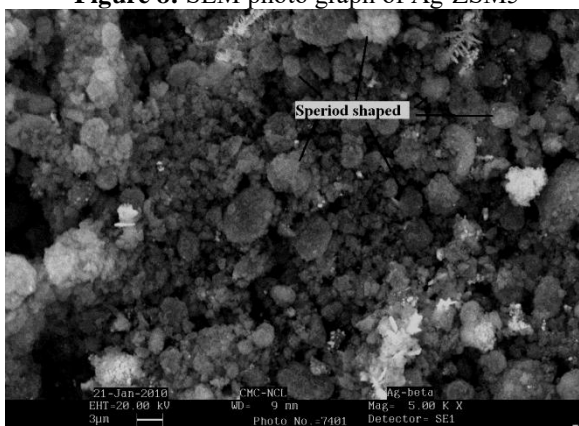**Figure 8:** SEM photo graph of Ag-ZSM5

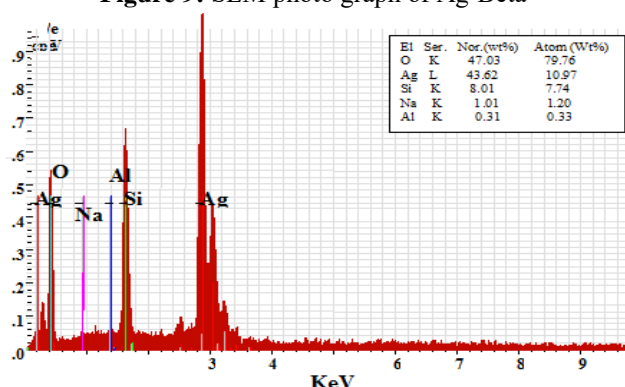**Figure 9:** SEM photo graph of Ag-Beta
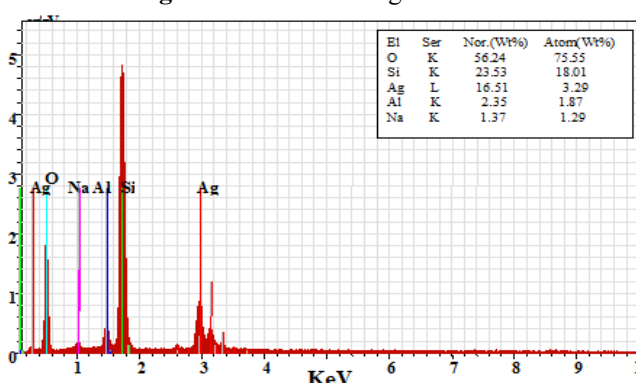

Figure 10: EDAX of Ag-ZSM5

Figure 11: EDAX of Ag-Beta

The elemental analysis is done with the help of EDAX; (Model No. Quanta X-200, Bruker, Germany). The EDAX analysis of Ag-ZSM5 is shown in fig. 10 and of Ag-Beta in fig. 11. The elemental analysis of Ag-ZSM5 and Ag-Beta is given in figure. The elemental analysis indicates that the silver ions are incorporated in Ag-ZSM5 and Ag-Beta

zeolite. The Si/Al ration of Ag-ZSM5 and Ag-Beta is found to be 23 and 9.6 respectively.

4. Result and Discussion

Fig. 12 shows the typical variation of the %sensitivity as a function of operating temperature at 1000 ppm for LPG gas for Ag-ZSM5 and Ag-Beta zeolite. The maximum PSF for Ag-ZSM5 zeolite is found to be 49% at temperature 568K for LPG. Other peaks have been observed at 368K, 433K, 468K but the percent sensitivity factor is less than 49 % (Table1). Several studies have been reported on changes of the complex impedance of zeolite when exposed to hydrocarbons [21, 22]. It was found that conductivity of sensing material increases with increasing hydrocarbon contents [23].Marginal higher temperatures enhance ion mobility in the zeolite lattice leading to a marginal higher value of conductivity. In present study, it is the maximum PSF (71%) at 388K is observed for Ag-Beta zeolite for LPG gas. The pore size of ZSM5 zeolite 5.4 * 5.6 Å and Beta zeolite is 7.6 * 6.4 Å. The molecular diameter of LPG (Propane and Butane) is 4.3 Å. Beta zeolite may be adsorbing more LPG molecules as compare to ZSM5 zeolite. It seems that Ag-Beta zeolite is more suitable material for sensing LPG gas at fairly low temperature.
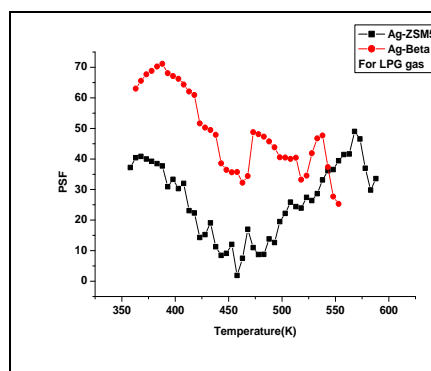

Figure 12: % S. F. as a function of temperature for LPG.
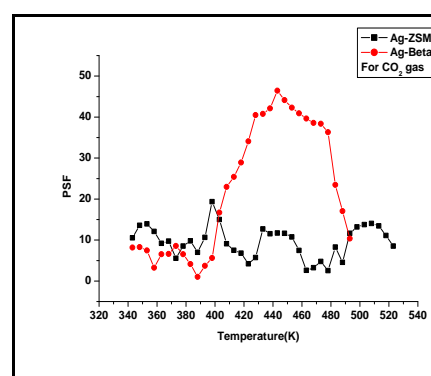
Figure 13: % S. F. as a function of temperature for CO_2 gas

Table 1: Sensor parameter of LPG

Parameters	Samples	
	Ag-ZSM5 (568K)	Ag-Beta (388K)
% S.F.	49 %	71 %
Saturation Point (Gas Concentration)	12,500 ppm	No saturation is observed

Table 2: Sensor parameter of CO_2 gas

Parameters	Samples	
	Ag-ZSM5 (443K)	Ag-Beta (498K)
% S.F.	49 %	19 %
Saturation Point (Gas Concentration)	20,500 ppm	20,500 ppm

Fig. 13 gives presentation of PSF as a function operating temperature for Ag-ZSM5 and Ag-Beta zeolite for CO_2 gas. For Ag-ZSM5 zeolite the maximum PSF observed for CO_2 gas is 49% at temperature 443K. PSF observed for Ag-Beta zeolite for CO_2 gas is 13.5%, 19%, 13% at temperature 348K, 398K, and 433K respectively. The maximum PSF 19% is observed at 398K temperature (Table2). The sensitivity observed may be due to chemical reaction occurring between Ag-CO_2 [24] and thereby an acceptance or release of an electron is possible to produce a change in the conductivity of the zeolite. The variation of PSF as a function of operating temperature study reveals that Ag-Beta zeolite is found to be more sensitive for LPG gas compare to CO_2 gas.
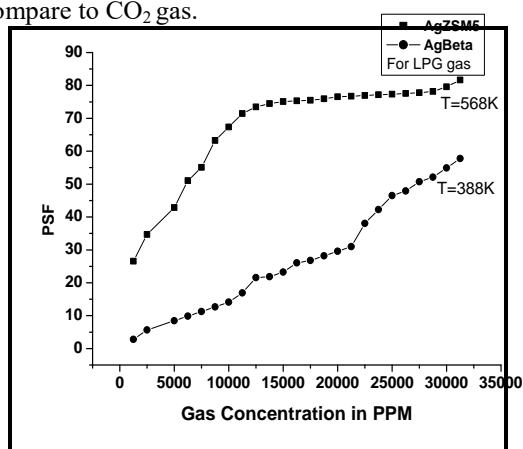

Figure 14: % S. F. as a function of concentration for LPG
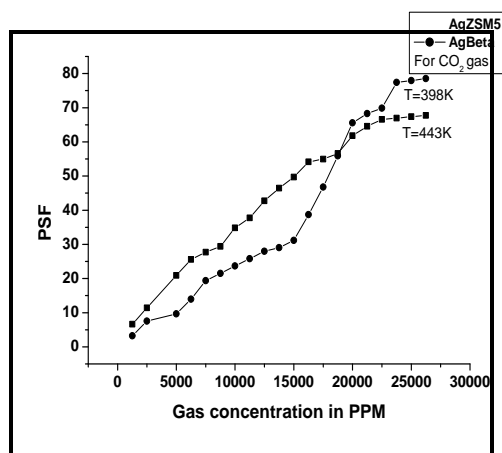

Figure 15: % S. F. as a function of concentration for CO_2

Fig.14 shows variation of PSF as a function of gas concentration of Ag-ZSM5 and Ag-Beta zeolites at temperatures 568K and at 388K respectively for LPG gas. In Ag-ZSM5 the PSF increases with increasing gas concentration up to 12500ppm remains constant thereafter. For Ag-Beta PSF as a function of gas concentration is quasi linear. The PSF increases from 1250ppm to 22500ppm linearly and again from 22500ppm to 32500ppm steeply. PSF as a function of gas concentration for CO_2 gas for Ag-ZSM5 and AG-Beta is shown in fig. 15. The PSF increases with gas concentration up to 20500ppm and remains constant, thereafter for Ag-ZSM5 zeolite. The PSF increases from 1250ppm to 15000ppm slowly and there is rapid increase in PSF between15000ppm to 20500ppm. Above 20500ppm the PSF remains almost constant for Ag-Beta zeolite.

5. Conclusions

PSF as a function of temperature for LPG gas: Ag-Beta zeolite senses the LPG gas at fairly low temperature as compared to Ag-ZSM5 zeolite. The PSF is 71% at 388K for Ag-Beta zeolite. Hence, Ag-Beta zeolite is more suitable for LPG gas.

PSF as a function of gas concentration for LPG gas: Ag-ZSM5 saturates at 12,500ppm gas concentration, whereas such a saturation point is not observed in Ag-Beta zeolite. Hence, in this case no definite conclusion can be drawn.

PSF as a function of temperature for CO_2 gas: Ag-ZSM5 senses the CO_2 gas at 443K with 49PSF. Ag-Beta senses the CO_2 gas at 498K with 19PSF. Hence, Ag-ZSM5 zeolite is suitable to sense the CO_2 gas.

PSF as a function of gas concentration for CO_2 gas: As a function of gas concentration Ag-ZSM5 and Ag-Beta saturates at 20,500ppm. But, Ag-ZSM5 saturates at low temperature. Hence, it is more suitable to sense the CO_2 gas.

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