Study of vanadium-modified zeolite as Liquid Petroleum Gas (LPG) sensor

A.A. JOSHI¹, A.N. KALYANKAR² and A.L. CHoudhari³

¹Department of Physics, Matoshri Pratishthan’s School of Engineering, Khupsarwadi, At Post Vishnupuri, Nanded - 431 606 (India).
²Department of Physics, B.S. College of Science, Basmatnagar - 431 215 Perbhani (India).
³School of Physical Sciences, S.R.T.M. University, Vishnupuri, Nanded - 431 606 (India).

(Received: August 08, 2009; Accepted: October 15, 2009)

ABSTRACT

Zeolite is a gas sensing material. The micro pores of H-ZSM5 and H-Beta zeolites are modified with the transition metal Vanadium Pentaoxide (V₂O₅) by ion exchange method. The modified samples Vanadium ZSM5 (V-ZSM5) and Vanadium Beta (V-Beta) are characterized by XRD, IR and TG-DTA techniques. Systematic evaluation of gas sensing characteristics of V-ZSM5 and V-Beta zeolite has been carried for LPG gas. The gas sensing properties of these samples are studied in a static gas characterization system. The maximum Percent sensitivity factor of V-ZSM5 and V-Beta obtained for LPG gas are reported. The V-ZSM5 zeolite is found to be more suitable to LPG gas sensing.

Key words: Zeolite, V-ZSM5, V-Beta, LPG gas, sensitivity.

INTRODUCTION

Zeolites are composed of a framework of tetrahedral TO₄ units. (T = Si, Al etc.) The tetrahedral TO₄ units link with each other by sharing Oxygen atoms to form three dimensional crystalline porous skeletons. The T-O-T links results in a variety of rings, which are responsible for zeolite cages and channels of different window size within the framework structure, the Al³⁺ atom at the center of an AlO₄ tetrahedron connects to a neighboring SiO₄ tetrahedron by sharing an oxygen atom, and thus generates a negative framework charge which is balanced by exchangeable cations, such as an alkaline or alkaline earth cations. These cations are loosely bound with structure, and it can be only replaced by other cations¹. The replacement of cations held in the framework structure is possible by ion exchange. The rate and degree of cations exchange depends on the number of the cations in exchange solution, size and charge on cations, temperature of ion exchange treatment, Si/Al ratio, and treatment before zeolite modification, thermal treatment of zeolite before and after exchange.

One of the basic properties of zeolite materials is their intensive interaction with water molecules; hydrated zeolites lose these guest molecules during careful heating without damage of their framework structure. After dehydration a complete re-hydration takes place even under normal atmospheric conditions². This reversible process of adsorption and desorption is the reason for many technical applications³.

Zeolites contain mobile cations which are located in sites, in cavities, on the channels walls and free within the channels, coordinated with water molecules. Since cations are free, they can move to new positions under the influence of an external charge transport. It is dielectric relaxation and conductivity⁴,⁵.
In addition, to the classical applications in sorption\(^6\) and catalysis\(^7,8\) zeolites are also attractive for novel technologies including highly selective separation membranes\(^9\), host-guest systems and chemical sensors\(^10,11\).

**Measurements of gas sensing characteristics**

In the present study, the gas sensing properties of V-ZSM5 and V-Beta zeolites are studied for LPG gas. The gas sensing property is carried out by using static gas characterization system\(^12\). The system consists of glass chamber (Volume 15Lit.) and a heater of nicrome wire (1.5kW, \(R=120\Omega\)). The heater is used to vary the substrate temperature from 60°C to 250°C by changing voltage using varac. The electrical terminals are brought out from the sensor assembly by using insulated feed- through mounted on the stainless steel base plate. The base plate has a gas inlet. The aluminum foil with press contact system is used for external contacts. The spring press contact electrodes are used during the measurements of gas sensing properties. The temperature of the sample was measured by using the temperature indicator with the help of Cr-Al thermocouple. The conductance of the sample is determined by using the half bridge method. The variable DC power supply (0-250V) is used. The resistance of the sample is measured directly by electrometer (Keithely Multimeter). 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 \(V\) to sensor and measuring the voltage drop \(V_s\) across \(R_s\). The conductance \(G\) and the percentage sensitivity factor (SF) are calculated by using the following formula

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

\[
S.F. = \left[\frac{(G_s - G_a)/G_a} \times 100\right] = \left(\frac{\Delta G}{G_a}\right) \times 100
\]

where \(G_s\) and \(G_a\) are the conductance of the sensor in air and gas+air respectively.

**Preparation of a sensor**

The synthesized ZSM-5\(^13\) and Beta\(^14,15\) zeolites was used for the preparation of a sensor. The ZSM5 and Beta was modified with 5Wt% of vanadium pentaoxide \((V_2O_5)\). \(V_2O_5\) was taken in 250ml round bottom flask and 30ml methanol was added. The 10gm of the dried ZSM5 zeolite is added to it. The mixture was stirred using magnetic stirrer for 15 min. and placed under reflux condition at 65°C for 12hrs. The mixture was washed repeatedly, after reaching to room temperature. Then it is dried in oven at 110°C for overnight. The sample is characterized by XRD, IR, and TG-DTA. The modified Vanadium ZSM5 zeolite (V-ZSM5) was mixed with polyvinyl alcohol (PVA) and is pressed to form pellet (diameter 13mm and thickness 1mm) using hydraulic press. The pellet is then fired at 300°C for 4hrs for removing the binder material. Silver paste is coated on the surfaces of the pellet to ensure good electrical contact. V-Beta pellet is similarly prepared. The similar procedure is adopted for vanadium modified Beta (V-Beta) zeolite.

**Characterization**

**X-ray diffraction**

The zeolite sample is characterized by using X-ray diffraction technique (XRD). The XRD pattern was obtained at 30kV and 15mA on Philips, 3710PW/1710) with CuK\(\alpha\) (\(\lambda=0.1546\text{nm}\)) X-ray diffractometer. The zeolite material is scanned in the 2\(\theta\) range of 20° -80°C.

The XRD analysis of the original sample was recorded earlier. After ion exchange, the XRD analysis is repeated for the ion exchanged sample and the XRD analysis is same as that of original sample. This is to confirm the structure of the ion exchanged sample. The d, 2\(\theta\), hkl, intensity values are given in Table 1 for V-ZSM5 zeolite. The procedure has been repeated for V-Beta sample. In this case also the structure is found to stable. The d, 2\(\theta\), hkl, intensity values are given in Table 2 for V-Beta zeolite. Here, again the XRD is repeated to confirm the structure of ion exchange sample. The XRD patterns of these samples are shown in Fig. 1 and Fig. 2.

**Infra red spectroscopy**

IR spectra of V-ZSM5 and V-Beta sample is shown in Fig. 3 and 4. It is recorded by KBr pellet technique in the frequency range 400-4000cm\(^{-1}\) on Perkin Elmer FT-IR spectrophotometer. The IR spectra studies give useful information about the constitution and surface properties of zeolites.\(^16,18\)

Structure sensitive bands are found to change
before structure collapse, where as structure insensitive bands are unaffected.

**V-ZSM5 zeolite**

In the present study the structure insensitive bands asymmetric stretch and symmetric stretch is found to be at 1104 cm\(^{-1}\) and 797 cm\(^{-1}\) respectively for V-ZSM5 zeolite. The structure sensitive band asymmetric stretch is observed at 1228 cm\(^{-1}\). The water bands are present at 3433 cm\(^{-1}\) and 1624 cm\(^{-1}\). The results show that the bands near 547 cm\(^{-1}\) are the characteristics of the presence of double five member ring. The bend around 797 cm\(^{-1}\) is the characteristics of ZSM5 crystalline structure. The IR study on zeolites is to supports the XRD data.

**V-Beta zeolite**

In V-Beta sample the structure insensitive bands, asymmetric stretch and symmetric stretch is observed at 1083 cm\(^{-1}\) and 789 cm\(^{-1}\). The T-O bend is observed at 463 cm\(^{-1}\) for V-Beta zeolite. The structure sensitive, asymmetric is observed at 1223 cm\(^{-1}\). The water bands are found to be at 3383 cm\(^{-1}\) and at 1627 cm\(^{-1}\). The doublet at 566 cm\(^{-1}\) is the characteristics of highly crystalline Beta zeolite.

**TG-DTA**

The TG/DTA curves for V-ZSM5 and V-Beta zeolite are shown in Fig. 5 and Fig. 6. The thermal stability of the V-ZSM5 and Beta material was studied on T.A. instrument (U.S.A.) SDT-2960 with reference material Al\(_2\)O\(_3\) in nitrogen atmosphere. A T.G. curve for V-ZSM5 shows five distinct steps of 0.923 mg weight loss. The first step is of 1.8% weight loss in the temperature range of 300K to 350K. This may be due to dehydration of physically sorbed water in V-ZSM5 zeolite cavities. The endotherm is observed at 355K corresponds to dehydration of water. The other steps of thermo gravimetric curves are 350K to 450K, 450K to 600K, 600K to 900K and 900K to 1200K. The exotherm at 673K corresponds to decomposition of Tetraethyl ammonium (TEA) cations, which are occluded in the zeolite framework. No transformation is observed in the temperature range 900K to 1200K, confirming thermal stability of zeolite framework.
Above this temperature, the structural water is lost from the framework and structure may collapse.

For V-Beta sample the weight loss is observed in three steps. The first step is 10% weight loss and is maximum. This is due to water loss in the temperature range 300K to 450K. The endotherm is observed at 342K corresponds to dehydration of water. Second step is of 4% weight loss. This is due to decomposition in organic template in the temperature range 450K to 640 K. Third step is of 2.7% weight loss and may be due to desorption of organic amines at the acidic centers in the temperature range 640K to 1000K. These results were in agreement with literature. In DTA curve the exotherm is observed at 658K for V-Beta sample, this may be due to oxidative decomposition.
of template, which is occluded in the zeolite framework.

RESULTS AND DISCUSSION

Zeolite as a sensor
Most of the zeolites have excellent chemical and thermal stability; zeolites can be used as a substrate to prepare compounds and devices with desirable fundamental physical and chemical properties. Some nano-sized metal or metal oxide particles have been successfully inserted into the cages and the pores or highly dispersed on the external surface of zeolites.

Some applications of zeolite materials in gas sensors have been developed, which are based on the characteristics mentioned above and there are a) Encapsulating ruthenium complexes inside zeolite super cages as an oxygen sensor. b) Using quartz crystal micro balances for sensing some gases by selective absorption c) Changing the conductivity of zeolites due to the absorbance of some gases for making sensor based on impedance spectroscopy measurements. d) Placing zeolites onto sensors as filter materials for enhancing the selectivity to a certain gaseous molecule e) Forming composites for making sensors. Using these techniques zeolite can be made to work gas sensor27. In the present study the sensitivity factor

![Fig. 3: IR Spectra of V-ZSM5 zeolite](image1)

![Fig. 4: IR Spectra of V-Beta zeolite](image2)
Fig. 5: TGA-DTA curve of V-ZSM5 Zeolite

Fig. 6: TGA-DTA Curve of V-Beta Zeolite
(S.F.) of a material is varied as a function of temperature and gas concentration.

Fig 7 shows the typical variations of the percent sensitivity factor (% S.F.) as a function of operating temperature of a sensor as gas concentration at 1000ppm of LPG gas to V-ZSM5 and V-Beta zeolite. The %S.F. V-ZSM5 zeolite is found to be 81%, 75%, 67%, and 62% at temperatures 110°C, 165°C, 185°C, 210°C respectively. However the maximum %S.F. is 81% at temperature 110°C for V-ZSM5 zeolite, which is an encouraging result. For V-Beta zeolite the %S.F. is found to be 32% at 85°C temperature. The gas sorption in the zeolite micro pores may cause change of the ionic activity of the V+ ions in the zeolite, causing increase in conductivity.

The other part of the study of %S.F. is a variation of gas concentration at fixed maximum sensitivity temperature. This study revealed that a saturation is observed for V-ZSM5 zeolite where as no such saturation is observed in case of V-Beta zeolite. This is shown in Fig. 8. It is observed that maximum % sensitivity Factor is 25% for LPG gas for V-ZSM5 zeolite and it saturates at 2750ppm.

Fig. 7: Percent Sensitivity Factor (S.F.) as a function of temperature

Fig. 8: Percent Sensitivity Factor (S.F.) as a function of gas concentration
Whereas, for V-Beta zeolite the maximum % S.F. is 45%. However no saturation point is obtained till 30000 ppm gas concentration.

**CONCLUSION**

Both the zeolite worked as the gas sensor at low temperature. V-ZSM5 zeolite shows maximum % sensitivity factor at low temperature and it saturate. Whereas V-Beta zeolite has a low % sensitivity factor at low temperature and no saturation is observed till 30000 ppm. Hence, it seems that V-ZSM5 zeolite is more suitable as a gas sensor for LPG gas.

**ACKNOWLEDGEMENTS**

The authors are thankful to Dr. Prof. Ms. R.C. Ayer, Department of Physics, Pune University.

**REFERENCES**

1. D.W. Break, Zeolite Molecular Sieves, Chemistry and use (John Wiley and sons Inc. New York) chapter 7 and 8, (1974).
2. R.S. Zostak, Handbook of molecular Sieves, (Van Nostrand Reinhold, New York)
3. H.Takaba, R.Koshita, K.Mizukani, Y.Oumi, N. Ito, M.Kubo, A.Fahmi, A.Miyamoto, *J. Membrane Sci.* **134**, 127 (1997).
4. D.C. Freeman, D.C. Stamires, *J. Chem. Phys.* **35**, 799 (1961).
5. R.A. Schoonhedyt, J.B. Uytterhoeven, *Clay Miner.* **8**, 71 (1969).
6. I.Gerner, A. Moissette, C. Bremard, *Chem. Com.* 1563-1564 (2000).
7. A. Corma, J. of catalysis, **216**, 298-312 (2002).
8. J. Augaud, D.S. Sarrano, J.M. Escota, G.S. Migual, *J. Anal. Appl. Pyrol.* **73**, 79-87 (2004).
9. X. Xu, W. Yang, J. Liu, L. Lin., N. Stroh, H. Brunner, *Journal of Membrane Science.* **229**, 81-85 (2004).
10. G. Hagen, A. Schulz, M. Knorr and Ralf Moos, *Sensors 2*, 2681-2692 (2007).
11. F. Manea, A. Pop. C. Radovan, Plamen, A. Bebeselea, G. Burlcica S. Picken, J. Schoonman, *Sensors.* **8**, 5806-5819 (2008).
12. S.K. Joshi, C.N.R. Rao, (New materials, Narosa publishing House, T. Tsuruto, S. Nagakura, New Delhi.), 1 (1992).
13. O.G. Somani, A.L. Choudhari, B.S. Rao, S.P. Mirajikar, *Material Chemistry and Physics,* **82**, 538-545 (2003).
14. M.A. Camblor, A. Mifsued, J.P. Rariantz, *Zeolites,* **1**, 202 (1991).
15. M.A. Camblor, J. Perez-Pariente, *Zeolites,* **11**, 792 (1991).
16. S.P. Zhdanov, A. V. Kiselev, V. I. Lygin, and T. I. Titova, *Zh. Fiz. Khim,* **39**, 2554 (1965).
17. E. M. Flanigen, H. Khatami, and H. A. Szymanski, *Adv. Chem. Ser.*, **101**, 201 (1971).
18. P.A. Jacobs, H. K. Beyer, J. Valyon, *Zeolites* **1**, 161 (1981).
19. D.T. S. Kaliaguine, L. Benneviet, *J. Catal.* **157**, 235 (1995).
20. M.S. Joshi, A.L. Choudhari, P. Mohan Rao, and R.G. Kanitkar, *Thermochimica acta,* **64**, 39-45 (1983).
21. J. Perez-Pariente, J. A. Martens, P.A. Jacobs, *Appl. Catal.* **31**, 35 (1987).
22. B.J. Schoeman, E. Babouchkina, S. Mintova, V.P. Valtchev, J. Sterte, *J. Porous Mater.* **13**, 18 (2001).
23. D.M. Bibby, N.B. Milestone, L.P. Aldridge, *Nature,* **285**, 30 (1980).
24. J. Chao, *Proc. Natl. Sci. Counc. RoC,* **3**, 233 (1979).
25. M.R.S. Manton, J.C. Davidtz, *J. Catal.* **60**, 156 (1979).
26. S.J. Kulkarni, H. Hattori, H. Tanbe, *Appl. Catal.* **49**, 27 (1989).
27. K. Sahner, G. Hugen, D. Schnauer, S. Reib, and Moos, *Sensors,* **179**, 2416-2423 (2008).
28. X. Xu, J. Wang, and Y. Long, *Sensors,* **6**, 1751 (2006).