DETECTION OF ETHANOL VAPORS BY ZnO/STILBITE COMPOSITES

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ABSTRACT

This work deals with the detection of ethyl alcohol using the natural stilbite zeolite. Ethanol sensors, which are essential for various industries are fabricated using natural stilbite as a host material and ZnO as the guest material. The composites of ZnO/Stilbite material are prepared by adding ZnO with variable wt% to stilbite via mechanical mixing. The pure and composite stilbite samples are characterized by XRD (X-Ray Diffraction) and FTIR (Fourier Transform Infrared Spectroscopy) techniques. Thick films of ZnO / Stilbite, developed using screen printing technique are employed as ethanol sensors. The XRD profiles confirm the presence of stilbite zeolite and the incorporation of ZnO into the stilbite matrix. Sensing studies show that the ZnO/Stilbite films are sensitive to ethanol. The operating temperature of composite film is found to be a function of ZnO concentration. ZnO with 50% concentration reduces the operating temperature from 111ºC to 75ºC. The composite film with 50% ZnO concentration gives response to ethanol within 120 seconds and can sense ethanol with a minimum concentration of 250 ppm. The study reveals that ZnO/Stilbite composite thick film can be employed as an ethanol sensor which can be operated at lower temperature.

Key Words: Stilbite zeolite, Stilbite/ZnO composite, Ethanol sensor, Thick films, XRD

INTRODUCTION

Environmental pollution has greatly increased during the last few decades due to technological advancement and is becoming one of the global hot issues as it adversely affects on living being. These pollutants are not only undesirable, dangerous but also detrimental to the environment. Their presence, in huge concentration, leads to global warming, acid rain, smog and adversely affect on leaving being. Therefore sensors, capable of detecting hazardous pollutants are essential. In order to safe guard public health, private property, environment and strict regulations governing pollution, sensors have received great attention. For the implementation of regulations to identify and to control the amount of pollutants, there is a need of development of cost effective, innovative, environment friendly sensors capable of working under adverse conditions. Alcohols and hazardous gases are one the pollutants which affect the environment and are the main cause of sick house syndrome due to poor indoor air quality. Presence of alcohols and hazardous gases may lead to allergies, asthma, cancer and emphysema. Hence, the development of sensitive and stable gas sensors to detect such gases and alcohols has acquired a growing importance, owing to their wide range of applications in diverse fields like drug development, clinical diagnosis, agricultural, horticultural and veterinary analysis, pollution and contamination analysis, fermentation control and analysis, analysis of flavors and pheromones, quality and process control, industrial gases and liquids, explosives detection and biochemical defence for military.

Zeolites are crystalline, porous alumino silicate with large structural cavities / cages and definite entry channels. SiO₄ tetrahedron and AlO₄ tetrahedron, which are building units are linked together by sharing oxygen atoms forming an infinite, open, three-dimensional framework structure. A negative framework charge, thus generated is balanced by exchangeable alkali and alkaline earth cations. The large structural cavities and channels contain water molecules, which form hydration spheres around exchangeable cations.

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The zeolites possess attractive adsorption, cation-exchange, dehydration-rehydration and catalytic properties. These properties can be modified by exchanging framework cations without change of crystal structure. The ion exchange capacity, conductivity and the interaction between the zeolite and adsorbed molecules can be greatly changed by changing Si/Al ratio of the zeolite. 

Hence, to meet the demands for sensors capable of detecting major environment pollutants, it is worth to work on zeolite and zeolite based material due to high and selective adsorption properties for particular gas. Stilbite, [(Na₂Ca₈)[Al₁₈Si₅₄O₁₄₄]·6OH₂O, abbreviated as Ca-stilbite] is a common mineral zeolite with the distinctive framework topology STI. It is a calcium rich zeolite usually containing a small amount of sodium in place of calcium. It belongs to heulandites family. Literature survey shows that stilbite single crystals have been utilized as the alcohol sensor by O. Schaf et al. to sense alcohols namely methanol and propanol. They utilized impedence spectroscopy for confirmation of its applicability as an alcohol sensor. 

A detailed study on Ag ion doped stilbite single crystals for detection of gaseous aliphatic components mixed with nitrogen or synthetic air has also been carried out. However, the Ca-stilbite thick films have not been used for ethanol sensing so far. It is reported in the literature that sensor characteristics can be modified by adding metal ions into the sensor matrix. Therefore, this research work deals with the detection of ethanol by stilbite thick film sensors using conductivity measurement approach. In the present communication, we report study on the effect of ZnO metal ions on ethanol sensing behavior of stilbite. The ZnO/stilbite composites are also characterized by XRD. Various ethanol sensing parameters like optimum operating temperature, response/recovery rates and ethanol upload capacities are determined.

MATERIAL AND METHODS

Preparation of ZnO/stilbite thick films

Stilbite zeolites are collected from queries near to Pashan Area, Pune, India. The obtained crystals are converted into powder form and are used without further purification. The stilbite matrix is used as a host matrix while ZnO is introduced into Ca-stilbite to have metal oxide modified zeolite composite. The stilbite/ZnO composite is prepared by mixing appropriate quantities of Ca-stilbite and ZnO (50wt %). These materials/ingredients are thoroughly grinded/dry mixed in an agate mortar with pestle for about 10h. The composite belongs to simple physical mixture type of composite category. The mixture is then admixed with binders namely glass frit, ethyl cellulose and butyl caribol acetate by keeping organic to inorganic ratio 70%. To produce ethanol detector/sensor, a pasty composite of zeolite/ZnO is uniformly coated onto pre-cleaned glass substrate by using screen printing technique. The films are then dried under IR lamp for about 20 min and finally sintered at 650°C for about 2h. These screen printed composite thick films are used as sensors in further study.

Characterization

X-ray diffraction patterns of calcium stilbite and ZnO doped stilbite samples are recorded with the help of Rigaku make X-ray diffractometer using CuKα radiation (λ= 0.154056nm) in 2θ scan range of 5 to 60°. (Fig. 1) XRD analysis

XRD spectrum of stilbite and ZnO composites, using a Cu-Kα radiation source of λ=1.5406Å by Rigaku X-ray diffractometer as shown in Fig. 2(a) to Fig. 2 (d). The spectrum shows that as the percentage of ZnO increases in the stilbite matrix, the ZnO peaks become dominated over the stilbite. The XRD spectrum results of ZnO and stilbite which almost perfectly match with those calculated for ZnO using the standard. (ICSD Card #: 067849). From XRD patterns, it is observed that the inclusion of ZnO in stilbite zeolite structure shows the change in stilbite structure.
Fig. 1: Gas sensor unit employed for carrying out gas sensing studies

Fig. 2 (a): XRD plot for 100% stilbite

Fig. 2 (b): XRD plot for 75% stilbite

Fig. 2 (c): XRD plot for 55% stilbite
Sensor performance characteristics
The sensor performance characteristics of these composites to ethanol are studied using home-made static gas sensor unit. The sensor device is furnished with a heater so that the composite sensor under test placed inside the chamber on the heater, it is heated externally from room temperature to 350°C. The change in electrical resistance of a composite thick film is determined. The gas response (often called as gas sensitivity) defined as \((R_g - Ra)/Ra\) is also determined and is plotted as a function of temperature to determine an optimum operating temperature.\(^{12,13}\) By exposing the composite film to air and air+ethanol vapors (with fixed concentration) alternately, the rates of response and recovery are also determined. The ethanol vapour loading capacity of the film is also determined by keeping the film at an optimum operating temperature and exposing the film to variable ethanol concentration 250 ppm to 2500 ppm. The same procedure is adopted for every film.

RESULTS AND DISCUSSION

Fig. 3 shows the comparative response of Ca-stilbite and ZnO composite stilbite sensor thick films to a fixed known concentration of ethanol for various compositions of ZnO/stilbite as a function of temperature. From the figure, it is observed that 100% Ca-stilbite film gives maximum response to ethanol at 110°C. In case of ZnO/stilbite, the operating temperatures corresponding to maximum response are found to be 95°C, 75°C and 170°C towards ethanol for 75%-stilbite, 50%-stilbite and 25% stilbite percentage respectively. Ca-stilbite gives maximum response to ethanol (200) at operating temperature 110°C but the sensitivity decreases as the number of trials increases, however 50% ZnO/stilbite composite gives consistent response at lower operating temperature (75°C) comparative to all of the concentrations.
Fig. 4 shows the comparative response/recovery behaviors of Ca-stilbite and ZnO/stilbite thick films as a function of time. Though the response of Ca-stilbite to ethanol vapor is high, it takes longer time (~300 sec) to sense ethanol in comparison with ZnO/stilbite which can sense ethanol within ~120 sec. Fig. 5 shows the ethanol uptake capacities of Ca-stilbite and ZnO/ stilbite thick film as a function of concentration. In both the sensor films, alcohol concentrations are varied from 250ppm to their maximum saturation value. Ca-stilbite film can sense 2750 ppm ethanol and after that it saturates and ZnO/stilbite (75% stilbite) composite film can give response to 3750 ppm ethanol followed by saturation. Whereas the ZnO/stilbite for 50% stilbite and 25% stilbite composite films saturates at very lower ethanol concentration at 1750ppm and 560ppm respectively. This shows the higher saturation limit of Ca-stilbite film than that of ZnO/stilbite for ethanol.

**CONCLUSION**

The characteristic of XRD peaks confirm the successful incorporation of ZnO into the stilbite matrix. ZnO/stilbite composite (of 50% stilbite) can sense ethanol at much lower temperatures compared to 100% Ca-stilbite and rest of the ZnO/stilbite composite sensor. ZnO/stilbite composite (of 50% stilbite) gives fast response (~120sec) to ethanol compared to 100% Ca-stilbite and other ZnO/stilbite composites.

**REFERENCES**

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