Effect of copper concentration on ethanol sensing performance of Cu-stilbite thick film sensor

M P Mahabole1,6, M A Lakhane2, K B Naik1, V D Kutte3, A Ghadge4, R S Khairnar1, K A Bogle1 and P B Sabale5
E-mail: mpmsrtmunsp@gmail.com
1Swami Ramanand Teerth Marathwada University, Nanded (MS), India
2St. John College of Engineering and Management, Palghar (MS), India
3Yeshwant Mahavidyalaya, Nanded (MS), India
4NES Science College, Nanded (MS), India
5Deccan College (Deemed University), Pune (MS), India

Abstract: The present study deals with natural stilbite zeolite commonly named as Ca-stilbite. Ion exchange process is carried out for partial exchange of calcium ions by copper ions. Ion exchanged stilbite is characterized by different spectroscopic techniques as XRD, FTIR and EDS techniques. Thick films are deposited on pre-cleaned glass substrates using screen printing technique. The sintered films are finally used for ethanol detecting. The Ca-stilbite zeolite structure is confirmed by the characterization techniques XRD and FTIR. Incorporation of copper ions in stilbite structure can be confirmed by EDS data. The Cu-stilbite films showed good ethanol detectors. The operating temperature, ethanol response, response/recovery nature are observed to be the functions of concentration of copper ions. Higher the copper concentration (0.2M) lower is the operating temperature (90°C) and higher is the ethanol sensitivity (233). It can be concluded that partial replacement of calcium by copper ions in stilbite leads to change in operating temperature and sensitivity.

1. Introduction
Zeolite, one of the pompous classes of porous materials, is a hydrated aluminosilicate crystalline mineral with a typical framework structure containing regular and uniform pores and channels. Natural form of zeolite is the outcome of organic reactions of the volcanic residue and limy water [1-2]. These natural mineral species are categorized based on their crystal composition and framework The facts like excessive availability, large surface area, high thermal & chemical steadiness, extraordinary adsorption capacity, ion exchange capability, easy approachability and cost effectiveness make them versatile materials in terms of industrial and environmental applications [3-5]. Other applications are in agriculture, animal husbandry, construction and especially in sensor field [6-17].

Stilbite, \{(Na\textsubscript{2}Ca\textsubscript{6}) [Al\textsubscript{18}Si\textsubscript{54}O\textsubscript{144}] 60H\textsubscript{2}O, abbreviated as Ca-stilbite\}, is a calcium abundant natural zeolite. Often contain a small amount of sodium in place of calcium with the distinctive framework topology stilbite. Crystal structure of stilbite has a distinctive zeolite openness wherein sizeable ions and molecules can inhabit and can channel freely within the frame. The channels, present within the structure, control the
size of the molecules or ions that can enter/ travel into and out of the crystal structure and act as a chemical sieve. Literature review shows that such a porous material, with its unusual, extraordinary properties has been successfully used in sensor field for the fabrication of low cost and robust ethanol [18-20]. Moreover, the ability to incorporate foreign molecules in the structure results in added on multifarious functionality to the stilbite. Our earlier studies have shown that partial incorporation of magnesium helps to augment stilbite sensor characteristics [21-22]. However, this attribute needs to be further enhanced. Therefore, the main goal of the present work is to develop the sensing element which will comprised of ion exchange form of stilbite for detection of ethanol via adsorption and as a support to improve sensing performance of active sensing material in the form of thick film.

2 Experimental
2.1 Preparation Cu-Stilbite
Naturally occurring Stilbite zeolites (abbreviated as Ca-stilbite), acquired from Pune (Maharashtra), India, are used without further purification. The ion exchange forms of stilbite are obtained by allowing 1 g of stilbite to be in contact with copper nitrate solutions with 0.05, 0.1 and 0.2 molar concentrations in distinct conical flasks. The flasks are kept on mechanical shaker for about 5 hr so as have maximum ion exchange between calcium and copper ions during shaking process, at room temperature and converted into powder by filtering. The obtained raw material (Cu-stilbite) is dried and ready to use further sensing study.

2.2 Preparation of thick film sensor
The thick films are formulated by employing screen printing method [21-23]. The films are designed with the area of substrate (1x2 cm²). The prepared films are ready to use for further studies of ethanol detection followed by drying to remove temporary binders and final annealation of 2 hr at 650 °C in air by using programmable furnace.

2.3 Characterization
Ca-Stilbite and Cu-Stilbite are characterized by XRD technique for crystal structure determination. X-ray diffraction patterns of pure & ion exchanged stilbite are gained by using of Rigaku X-ray diffractometer with specifications CuKα radiation (λ= 0.154056nm) for 2θ range of 5°- 50°. The existence of several functional groups in zeolite is spotted by FTIR spectrophotometer (Shimadzu make) with a scan range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. EDS scales are taken by JEOL–JSM-5 spectrometer.

2.4 Gas Sensing Studies
Gas detecting trials are completed on a nearby assembled sensor unit. The sensor is initially heated at 300 °C and the resistance of sensor is measured in air atmosphere (Rair) as a function of resistance i.e. before the introduction of ethanol in a working chamber. The sensor is then exposed to fixed concentration of ethanol (1000ppm) and resistance of sensor is measured in air + ethanol atmosphere (Rgas) i.e. after exposure to ethanol gas with temperature. The response behavior of sensor films is studied by noting change in resistance of films against ethanol. The sensitivity of the sensor is measured with reference to its base-line resistance in air. The sensor response is defined as S = (Rgas-Rair) x 100/ Rair. Response is plotted against temperature to determine working temperature. The same procedure is repeated for other sensors. The sensors are exposed to air initially & later to ethanol and can recover in air after insertion of the objective gases. The same process is cycled, and the experiment is repeated to test response & recovery behaviour at their respective working temperatures. In other experiment, each sensor is subjected to ethanol vapor with various concentrations and change in resistance and sensitivity are also recorded and plotted as a function of ethanol concentration to investigate active sensor region.

3. Results & discussion
3.1 Characterization
3.1.1 XRD analysis
Ca-stilbite and Cu-stilbite sample materials structures are finalized by XRD study. Figure 1 shows the XRD profile of Ca-stilbite sample. The profile shows the presence of peaks at 20 values of 9.7° (100 % intensity), 21.88°(45% intensity), 29.38°(20% intensity) and 32.24°. These peaks, corresponding to (020), (041), (060), and (260) planes, match to Ca-stilbite structure. The results match with the standard data and the
literature [20-22]. Since the doping level is very small, the XRD profile for Cu-stilbite (0.2M) does not show any variation in stilbite structure.

Figure 1(a-b). XRD patterns revealing typical XRD peaks for pure and ion exchanged zeolites; a) Stilbite, b) Cu-Stilbite

3.1.2 FTIR analysis
FTIR spectral study was done at room temperature in the wave number range 4000–400 cm⁻¹. Figure 2 presents standard FTIR spectra of Ca-stilbite and Cu-stilbite (0.2 M). The presence of absorption bands relating to structure sensitive and insensitive linkages for standard zeolite data are retrieved in both the samples. At 3599 cm⁻¹ one broad peak is observed which corresponds to hydroxyl group. In addition, the shoulder peaks at 3275, 2924 and 2854 cm⁻¹ are also anticipated to the hydroxyl group. The band of 1639 cm⁻¹ is assigned to the H₂O molecule bending mode. In Ca-stilbite, the asymmetric stretching mode of T-O is noticed at 1149 cm⁻¹. At 435 cm⁻¹, one peak is spotted expected to the bending motion of T-O. The characteristic peak of double ring is appeared at 559 cm⁻¹. The external linkages asymmetric and symmetric stretching movements recognized at 1033 and 705 cm⁻¹ respectively [20-22]. The FTIR spectra

Figure 2 (a-b). FTIR of the pure and Cu-doped stilbite revealing unique functional groups corresponding to zeolite structure; a) Ca-Stilbite, b) Cu-Stilbite

of both the samples look to be very identical. It reveals no change in Ca-stilbite structure upon partial exchange of Ca²⁺ by Cu²⁺ ions. The results are very consistent with the literature [19-24] and concur with XRD analysis.
3.1.3 SEM/EDS analysis
The SEM micrograph of Stilbite is shown in figure 3(a). The various elements amount in percentage observed in ion exchanged stilbite, procured using energy dispersive spectroscopy (EDS), are tabularized in Table 1.

![Figure 3. EDS spectrum for Cu-Stilbite showing signals for Si, Al, O, Ca, K and Cu elements](image)

Figure 3. EDS spectrum for Cu-Stilbite showing signals for Si, Al, O, Ca, K and Cu elements

| Element | (keV) | mass% | At% |
|---------|------|-------|-----|
| O K     | 0.525| 33.65 | 49.25 |
| Al K    | 1.486| 11.33 | 9.83 |
| Si K    | 1.739| 39.04 | 32.56 |
| K K     | 3.312| 0.21  | 0.12 |
| Ca K    | 3.690| 11.23 | 6.56 |
| Cu K    | 8.040| 4.54  | 1.67 |
| Total   |      | 100   | 100  |

Table 1. Tabulation of Elemental analysis of Cu-Stilbite (0.2M)

The EDS spectrum of Cu-stilbite, figure 3(b), depicts existence of peaks due to aluminum, calcium, potassium, silica, and oxygen. Furthermore, signals due to copper are also observed. This proves the amalgamation of copper ions in stilbite structure during ion exchange process.

3.2 Ethanol sensing characteristics
3.2.1 Sensitivity
The sensitivity towards ethanol exposure of Ca-stilbite and Cu-stilbite (0.05, 0.1, and 0.2 M) sensor films, for varying temperatures at defined ethanol concentration (1000 ppm) is displayed in figure 4 (a–c). All sensors show similar kind of behavior wherein response increases in low temperature region, attains a maximum value at one particular temperature. Further increase in temperature, dropout in response. The temperatures at which sensors exhibit maximum sensitivity, working temperatures, are determined.
Figure 4(a-c). Response as a function of temperature showing repeatability of the sensors for variable copper concentrations.

The behavior of shift in operating temperature and in ethanol detection observed in Cu-stilbite related to the Ca-stilbite is plotted in figure 5. The figure reveals the variation in sensor response for different concentration of Cu ion in stilbite matrix. The Ca-Stilbite thick film indicates highest gas response of 200 at 110°C for ethanol. The ethanol detection is observed to be the maximum (233) for Cu-stilbite sensor film having highest Cu concentration (0.2M) at lowest operating temperature of 90°C as compared to Ca-stilbite. However, lower copper concentrations in Cu-stilbite films (0.05 M and 0.1 M) results in reduction in ethanol response and increase in working temperatures. Thus, it can be rendered that Cu-stilbite (0.2M) sensor film give highest response to ethanol at 90°C.
The stilbite possesses a three-D configuration with two-D channels. The zeolitic water molecules, which inhabit into canals and coops or cavities, are loosely attached to the frame cations. At lesser heat, these water molecules cause barrier for motion of mobile cations. However, elevated temperature effects in the steady desorption zeolitic water resulting in key changes rearrangement of the structure owing to distributed charge balancing cations. These structural changes provide supplementary space for adsorbed molecules to go through the cages and canal. This consequences in increased mobility of charge carriers vital to enhanced conductivity. Consequently, the resistance of sensor by temperature.

At Initial, the ethanol particles get adsorbed on the porosive surface of stilbite upon ethanol exposure. These ethanol molecules engross themselves into the structure next to the water molecules elimination. The hydrogen bonds turn out to be weak and protons participate in conduction mechanism reinforcing high conductivity. As A Result, the sensor resistance of in existence of ethanol vapor is spotted to smaller compared in air atmosphere.

The gas response is primarily concluded by the interactions amongst a target gas and the sensor surface. The enhanced response indicates higher reactivity of gas with sensor surface at that temperature and greater possibilities for adsorption. At other temperatures, the sensor is less sensitive to such surface reactions. Rate of such reaction, surface reactivity, varies with sensor surface. Hence, working temperatures are different for sensors with variable copper concentrations. Therefore, there is change in operating temperature compared to Ca-stilbite.

3.2.2 Response/Recovery

The response of the stilbite-based sensor films towards ethanol as a function of time is displayed in figure 6.
The response raises sharply on the insertion of 1000 ppm ethanol vapors from its original value in air and then drops quickly to get retrieved to its original value after the releasing ethanol vapors. The similar performance is illustrated by Ca-stilbite and Cu-stilbite films, which indicates that all the films are sensitive towards ethanol. The sensor is remarked good in reversibility followed by many cycles of ethanol exposure and regaining to its original state. The response/recovery time of Ca-stilbite sample for ethanol is 300/350 s, while that for Cu-stilbite film (0.2 M), it reduces to 50/50s. The sample with lower copper concentrations (0.05 and 0.1 M) showed higher response (60s) /recovery time (60s) comparing to of Cu-stilbite (0.2M). Thus, the study signifies that Cu-stilbite film (0.2 M) gives instant response to ethanol and also gets recovered faster (50 s) compared with all other sensor films.

3.2.3 Active region

The maximum ethanol concentration acceptance capability of Ca-stilbite and Cu-stilbite films is shown in figure 7. All films exhibit linear response for low concentrations followed by saturation at higher concentrations. The response of a sensor hinge on the interfacing of gas molecules with sensor surface by adsorption phenomena.

When a gas is introduced in a chamber, gas molecules are exposed to surface area offered by sensor matrix. Low concentration leads to a less disposal of gas molecules on the surface and lessened surface reactions. In other words, only few adsorption sites are occupied. As the ethanol concentration goes on increasing, the active sites get occupied resulting in gradual increase in surface reactions. With further increase in concentration of gas molecules, the sensor surface gets saturated because all active sites are already occupied i.e. point of maximum molecular coverage is reached. Hence, the response, which is small in low concentration region, steadily increases leading to linear relationship and get saturated. From this behaviour, the gas upload capacity of a sensor is determined.

![Figure 7. Sensitivity of the pure & doped stilbite sensors with ethanol concentration revealing the gas sensing limit of each sensor](image)

Ca-Stilbite possesses slightly higher ethanol upload capacity (250-2750ppm) than that of Cu-stilbite films. However, Cu-Stilbite films can sense low concentration of ethanol compared with that of Ca-Stilbite. Consequently, Cu-stilbite (0.2 M) thick film substrate can be rendered as a promising agent to detect ethanol gas from a concentration of 250 ppm to 1500 ppm. Table II presents various gas parameters for Cu-stilbite and are compared with Ca-stilbite.
Table 2. Various gas parameters for original & ion exchanged Stilbite

| Sample            | Operating temperature (°C) | Sensitivity (%) | Response/recovery time (sec) | Saturation limit (ppm) |
|-------------------|----------------------------|-----------------|------------------------------|------------------------|
| Cu-Stilbite (0.05M) | 130                        | 100             | 60/60                        | 1500                   |
| Cu-Stilbite (0.1M) | 120                        | 150             | 60/60                        | 1500                   |
| Cu-Stilbite (0.2M) | 90                         | 233             | 50/50                        | 1500                   |
| Ca-Stilbite       | 110                        | 200             | 300/350                      | 2750                   |

3.3 Conclusion
The stilbite structure is confirmed from XRD pattern. Ion exchange process do not effect on stilbite structure. FTIR reveals the functional groups corresponding to stilbite. Both, Ca-stilbite and Cu-stilbite, sensors are ethanol receptive. The sensitivity, working temperature and response/recovery behaviour are the functions copper concentration. Cu-stilbite with highest copper concentration (0.2M) works at the lowest temperature (90°C) compared to other sensors. It also gives prompt response and fast recovery.

4. References

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