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Development of Ethanol Sensor using Sodium A Nano Zeolite

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Abstract* – Zeolites have large number applications due to its unique features. The NaA zeolite thick films are prepared by screen printing technique and utilized for sensing of ethanol particularly sensing performance for low concentration in the range of 5 ppm to 100 ppm. The nano sized NaA zeolite powder as well as the thick film sensor substrates are characterized by XRD, TG-DTA, FTIR, and AFM, for their structural identification, thermal behavior, functional group identification, and surface topography respectively. The thick films are found to have maximum sensitivity for ethanol at the temperature of 65°C. The quick response and recovery time for these substrates suggest their potential applications in gas sensing devices.

***Index Terms*– Nano zeolites, Gas sensors, Ethanol sensor, Atomic force microscopy.**

I. INTRODUCTION

Due to industrial and technological developments, many hazardous gases are discharged into air creating pollution and causing environmental threats. Due to stringent regulations governing air pollution, it is much important to develop low-cost gas sensor materials, which can have high sensitivity, fast response and recovery. Most of the sensor work is concentrated on semiconducting oxides like ZnO, SnO_2, TiO_2, CuO, WO_3, and TeO_2 [1]-[5]. There are few reports of gas sensing ability using zeolites. Zeolites are porous materials with various shapes and morphology such as cylindrical, spherical, and slit types having unique properties viz., ion exchange, and reversible water desorption [6-9]. Zeolites have a high surface area, ordered uniform structure, fluid permeability, non toxic, and thermally stable [10]-[12]. Zeolites are composed of a framework of tetrahedral TO_4 building units (T=Si, Al, etc.). Tetrahedral TO_4 units link with each other by sharing oxygen atoms to 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 sizes within the framework structure, the Al^{3+} atom at the centre of an AlO_4 tetrahedron connects to a neighboring SiO_4 tetrahedron by sharing oxygen (o) atom. There is utmost need of new cost effective sensors for fast, continuous, and detection of ethanol vapors with reproducible response characteristics and rapid sensitivity. The literature review reveals that the research work in this field is concentrated on sensor size reduction and quantitative identification of different gas species with desirable sensor parameter like operating temperature, quick response/recovery, good reversibility and low concentration level. Most of the materials used so far to meet these demands belong to three categories like polymers, ceramic and semiconductors [13-15]. Only few sensors can sense ethanol at room temperature and most of the sensors work at high operating temperatures [16-18]. Hence, still there is a need and scope of improving the sensor performance for ethanol vapors. However, detailed examination on sodium A-Zeolite for sensing ethanol vapors have not been reported so far. Hence, the present paper reports the study of the ethanol sensing properties of sodium A-Zeolite matrix and its characterization by XRD, TG/DTA FTIR, and AFM.

II. EXPERIMENTAL METHOD AND MATERIALS

A. Substrate cleaning

To get uniform these micro-slides are used to deposit thick films of sodium A-zeolite by screen printing technique. Commercially available glass micro-slides and alumina micro-slides of dimension 20 mm x 10 mm x 2mm are cleaned in the acetone for 10 min, washed with distilled water for 5 times. These micro-slides are used to deposit thick films by screen printing technique.

B. Material and its characterization.

Synthetic nano sized NaA zeolite powder is supplied by Center for Mechanical Technology and Automation, Department of Mechanical Engineering, University of Aveiro, Portugal, which is converted into thick films by screen printing technique. Sodium A-zeolite (functional materials), glass frit (permanent binder) and the temporary binders like ethyl cellulose and butyl carbitol acetate (BCA) are mixed and pasted on glass/ alumina substrates by keeping inorganic to organic ratio 70:30. The thick films are annealed for 2 hr. at 200ºC in air using programmable furnace, for the proper adhesion of material on the glass/ alumina substrate. The permanent binder provides homogenous binding of material with the substrate [19]. These developed screen printed thick film sensors are used for characterization and sensing ethanol vapors.

X-ray diffraction pattern is recorded with the help of x-ray diffractometer (Rigaku miniflex) by using CuKα radiations of wavelength λ=1.5418 A° in the 2θ range from 20° to 80°. The thermal analysis (TG-DTA) of NaA zeolite powder is carried out in the temperature range of

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40°C-800°C to observe phase change and thermal information of the material. The functional group determination is carried out using shimadzu make FTIR spectroscopy in the frequency range 400-4000 cm^{-1}. Atomic force microscopy (AFM) is used to get information of nano scale topography of the sensor substrate.

C. Gas Sensitivity Measurements

A two probe (copper electrode) gas sensor system is used for the measurement of the gas sensitivity of the NaA zeolite thick films as described elsewhere. The thick film sensor is mounted on two probe sample holder placed on heater. The film area is kept constant for all the samples prepared for measurement of gas sensitivity. The temperature of the gas sensor system is held at the temperature of 200ºC for a brief time and the voltage across the known resistance, kept in series with sensor, is measured by reducing the temperature from 200ºC to 45ºC. Later on, the known amount of ethanol is injected into the system and the change in electrical resistance of film is measured. The resistance is measured using following the formula.

$$R\,sensor = (V\,input - V\,output / V\,output) \times R\,ref. \quad \ldots..(1)$$

Consequently the gas response S (%) is calculated by using following formula [20]-[22]

$$Gas\,response S(\%) = (Rg - Ra/Ra) \times 100 \ldots\ldots(2)$$

Where Ra is resistance in air and Rg is resistance in gas. The operating temperature is defined as the temperature at which the sensor film has maximum gas response S (%). The film is kept at the operating temperature and then ethanol (20ppm) is injected into the system and the change in electrical resistance of the films is measured. After getting constant value, glass dome is opened to recover the initial value of resistance in air. The response time of sensor upon ethanol gas is also determined which is defined as the time of the sensor need to get 90% sensitivity of the equilibrium value (saturated region). Similarly recovery time is the taken to get back 90% of the original conductance in air.

III. RESULTS AND DISCUSSION

A. X-ray Diffraction Studies

Fig. 1 shows the XRD pattern of NaA zeolite records in the 2θ range of 20° to 80°. The important peaks of zeolite are located at various 2θ values and their respective planes are identified and tabulated in table I. [23]-[24]. X-ray diffraction study confirms that NaA zeolite material with appropriate crystal structure. The average crystalline size of NaA zeolite is calculated by Debye Scheres's formula, which is found to be 66.24 nm.

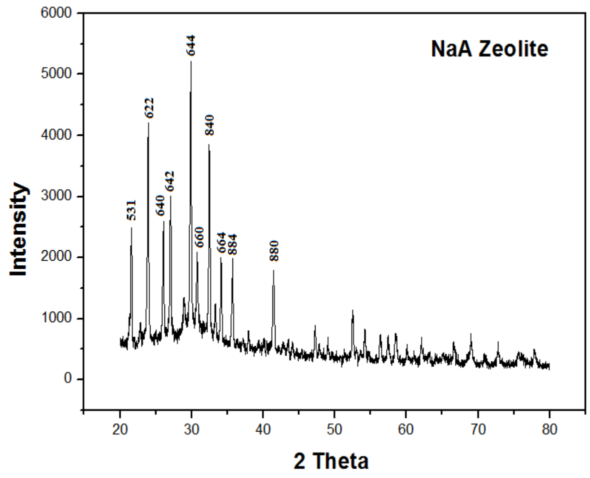

Fig 1. X-ray Diffraction pattern for sodium A zeolite powder, depicting major planes.

Sr. No.	2θ value	plane
1	21.3	531
2	24.0	622
3	26.1	640
4	27.1	642
5	29.9	644
6	30.8	660
7	32.5	840
8	34.1	664
9	35.7	884
10	41.5	880

Table I. shows the 2θ value and its planes are tabulated for NaA zeolite matrix.

B. TG-DTA Analysis

TG-DTA of sodium A-zeolite is displayed in fig.2 showing linear TG (curve A) and differential TG (curve B). With the application of heat, the desorption from the sample commenced at 50ºC upto 300ºC continuously (curve A) and remains almost constant afterwards at higher temperature.

The first endothermic peak at about 70°C (curve B) may be due to desorption of loosely held water molecules in the NaA zeolite. The appearance of second endothermic peak at 200°C is due to dehydration of the hydrated sodium ions located in the cages of the A-zeolite framework. The newly appeared exothermic peak near by 300°C is related to the changes in chemical composition in the NaA zeolite material.

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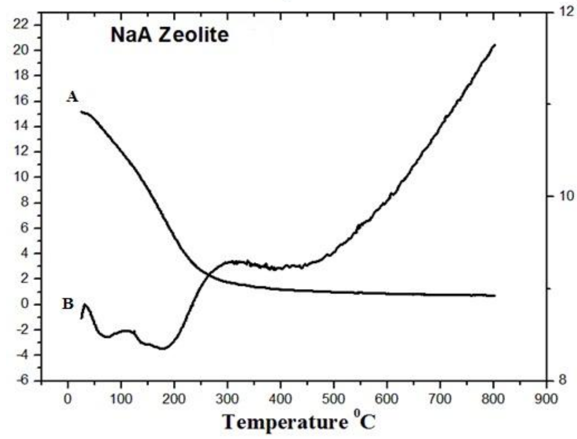

Fig 2. Thermogrvimetric profiles for sodium A zeolite powder displaying thernogravimetry curve (A) and differntial thermogravimetry curve (B)

C. *FT-IR Analysis*

Figure 3 represents the FT-IR spectra of the NaA zeolite. The FT-IR spectrum is recorded in the energy range from 400 to 4000 cm^{-1}. The characteristic band for zeolite framework at 664 cm^{-1} is due to the internal vibration of T (Si, Al) - O symmetric stretching. The next absorption frequency for the internal vibration of T-O bonding is appeared at the energy of 1005cm^{-1} [25]. The peaks at 1497 cm^{-1} and 1648cm^{-1} are assigned to internal tetrahedral symmetrical stretching and external linkage asymmetrical stretching respectively [26]. The peak at 2360cm^{-1} is assigned to the internal (TO_4) tetrahedral bending. The characteristics band of absorbed isolated mono coordinated OH group is at 3733cm^{-1}[26].

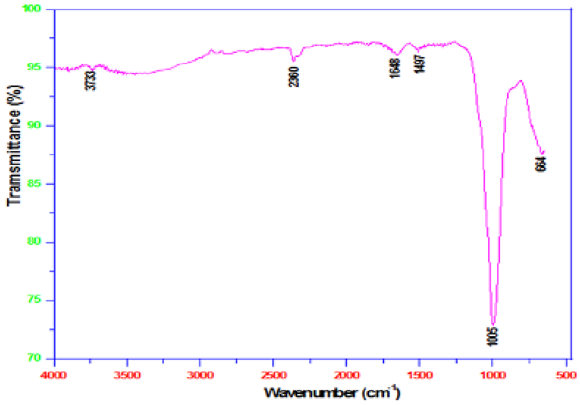

Fig 3. FT-IR spectra for sodium A zeolite powder showing related functional groups at various vibrational energies.

D. *AFM Topography*

Atomic force microscopy is performed in non-contact mode using silicon tips at room temperature of about 25°C. AFM image shows the nano-meter size events at porous surfaces. It is seen that pore size of more than 200nm exists between the clustered growths of zeolite grains. Such a large pore size certainly provides large adsorption sites for test gases and vapors.

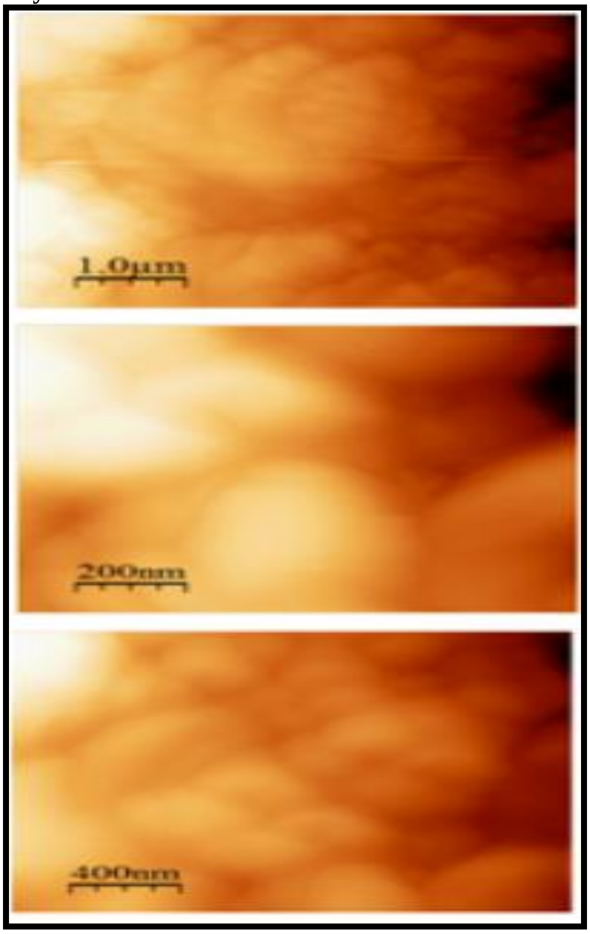

Fig 4. Atomic Force Microscopy of sodium A zeolite powder material at three different scales viz., 1.0 µm, 200 nm, 400 nm respectively.

E. *Sensing performance*

Figure5. shows that sensing performance of ethanol for NaA zeolite thick film. It is observed that NaA zeolite thick film has maximum sensitivity at 65°C for ethanol gas with other peaks at 95°C and 135°C which can be due to decomposition of ethanol species in to its related fragments.

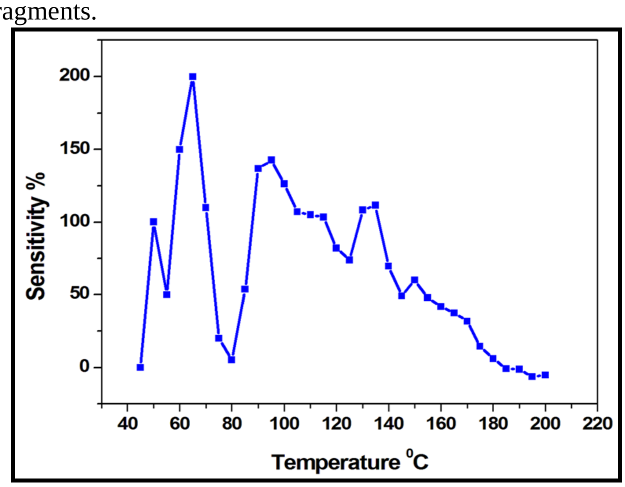

Fig 5. Ethanol gas response of sodium A zeolite thick film with temperature

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F. Response and Recovery time

The response and recovery behaviour of NaA zeolite thick film sensor are represented in figure 6. The response is quite rapid (70 seconds) and recovery is about 60 seconds for 20ppm of ethanol when the substrate is held at operating temperature of 65°C. The fast response may be due to faster oxidation of gas as well as plenty of available nano porous in the zeolite as seen in AFM. The response for such a negligible quantity of the ethanol vapours (20ppm) explains the suitability of NaA zeolite as an ideal sensor substrate

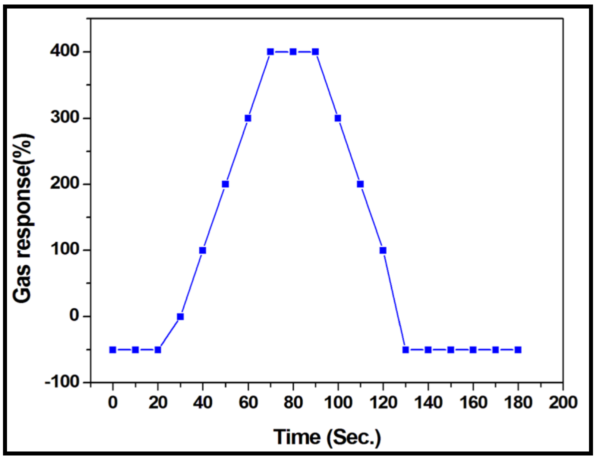

Fig 6. Ethanol response and recovery of sodium A-zeolite thick film with constant operating temperature 65°C.

G. Sensor Saturation Study

The change in sensitivity factor with ethanol gas concentration is presented in fig 7. The active region for sensing of ethanol concentration is in the range of 5ppm to 70ppm. The first region shows sharp initial rise up to 20ppm i.e. high sensitivity region. The second intermediate region from 20ppm to 70ppm shows nearly steady increment in gas uptake. Beyond 70ppm, there is negligible increase in sensitivity depicting less uptake of adsorbents (gas) leading to saturation of open sites. Thus the zeolite sensor is useful in sensing the low ppm of ethanol.

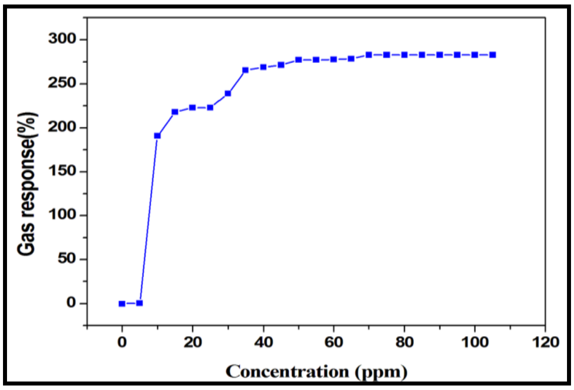

Fig 7. Ethanol gas saturation (uptake capacity) of sodium A zeolite thick film with constant operating temperature 65°C.

VI. CONCLUSION

The NaA zeolite has a functional operating temperature of 65ºC for ethanol sensing which is quite lower when compared to the existing ethanol sensors in the market. Secondly it is one of the unique devices for sensing low concentration of ethanol up to 70ppm. A high sensitivity for ethanol gas is attributed to large pore sizes up to 200nm available in the zeolite matrix depicting the NaA zeolite as an ideal nanomaterials for sensor device.

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