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Development of room temperature ammonia sensor based on CNF/ Nano-ZSM-5 composites

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ABSTRACT

This study deals with ammonia sensing performance of nanocomposites. NanoZSM-5 zeolite is synthesized by microwave assisted hydrothermal process and is modified to have modified forms of ZSM-5 namely D-ZSM-5, H-ZSM-5, Fe-ZSM-5 and Cu-ZSM-5 via either dealumination or ion exchange process. The composites are developed by blending modified zeolites with cellulose nanofibers (CNF) as a dispersing medium. The composites are prepared with fixed proportions; 80 %CNF and 20% modified zeolites by wt%. Composite films, prepared by solution casting method, are used for ammonia detection. The films are characterised by XRD and FTIR to identify the phases and the presence of functional groups. The thermal behaviour of these composites are studied by TGA. Sensing parameters such as operating temperature, response and recovery time, gas concentration variation and gas uptake capacity are determined. The operating temperature for ZSM-5 is found to be 30°c with highest sensitivity. These sensors can be used as potential ammonia sensors.

1. Introduction

The scientific community in both, developed and developing countries, is increasingly concerned with the detection and monitoring of environmental hazards and chemical pollutants. Every year, numerous organic and inorganic chemical pollutants are released into the air, water and soil, causing various kinds of pollutions [1]. Specifically air pollution, one of the most important global problems, is nothing but the contamination of air due to presence of variety of pollutants like volatile organic compounds, carbon monoxide, nitrous oxide, sulfur oxide, formaldehyde, hydrogen sulphide, carbon dioxide, nitrogen dioxide and ammonia. Among these, ammonia is found to be the most dangerous gaseous pollutant. Ammonia gas is colourless irritant gas with a pungent odour which is readily soluble in water. The prominent ammonia use is in the agricultural sector which includes cold storage, food storage and food prevention. Ammonia is highly toxic in nature it causes serious nuisance like eye, throat, skin and respiratory track irritation, lung disease, rhinorrhea. Therefore, it is very necessary to detect the ammonia gas [2-6]. Zeolite is an inorganic crystalline material having three dimensional frame work structure. It is formed due to interconnected aluminosilicate building units resulting in large empty spaces like structure inherent channels & cages. The aluminosilicate structure is negatively charged and attracts large cations which can electrostatically bound to the framework for charge compensation moreover water molecules recide inside the pores and channels. The key properties of zeolites are ion exchange ability, high adsorption capacity, high surface area and high porosity. It is due to these properties zeolite is widely used in commercial and domestic, applications namely agricultural environmental protection, petroleum industry, medical, specifically sensor field [5-8]. From the literature survey, it is observed that Y-zeolite, Fe-zeolite, Na-Y, Na-X, Ca-A, acidic ZSM-5, pure silica zeolite, clinoptilolite have been used to sense ammonia [9-16]. In addition zeolite composites namely Poly(p-phoneline)/(H-ZSM-5), LPFG/(H-ZSM-5), metal oxide/(ZSM-5) have also been employed to detect ammonia with improved sensing parameters. Therefore, the preference is given to ZSM-5 based

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composites [17-19]. Cellulose is a natural biopolymer that is abundantly available in plant cell walls and is secreted in its pure form by many bacteria. Due to their unique features, cellulose materials are considered as an efficient replacement for conventional polymers. Cellulose nanofibers (CNF) have attracted wide interest due to their nano size, ease of preparation, low-cost, tuneable surface properties and enhanced mechanical properties. CNF is biodegradable, biocompatible with high surface area. From the literature survey, it is observed that CNF/PVA/PANI, CNF/HAP composites have been used for the ammonia sensing applications [20–23]. It is a suitable candidate in sensor and composites fields by acting as a filler material. Hence, in this study CNF is blended with ZSM-5 matrix to have ecologically friendly novel zeolite composites to meet the requirements of desired features like high sensitivity and low working temperature.

2. Experimental

The NanoZSM-5 zeolite is synthesized via microwave assisted templet free hydro thermal method as reported earlier [16]. Cellulose is purchased from the Sigma Aldrich. These ingredients are used without further purification [24].

2.1. Modification of ZSM-5

ZSM-5 is modified to have delaminated and ion exchange forms. Dealumination is known post-synthesis method of removing aluminum from zeolites structure with the use of chemical agents or by hydrothermal treatment. The synthesized nanozeolite is treated with hydrochloric acid (1 M) by allowing ZSM-5 to be in contact with acid for 5 hr. to extract aluminium ion from zeolite framework. This is followed by washing by distilled water and drying at 100 °c to have delaminated (D-ZSM-5). The modification in ZSM-5 zeolite is also carried out through aqueous ion exchange process. Synthesized of ZSM-5 (5 g) is stirred with NH_4OH, $FeCl_3$ and $Cu(NO_3)_2{\cdot}H_2O$ solutions (0.1 M) with vigorous shaking for 24 hr at room temperature for incorporation of various cations in ZSM-5 structure. After ion exchanged process, zeolites are recovered by filtration and washed with double distilled water for removal of non-exchanged ions. The obtained filtrate is dried at 100 °c with the aid of hot air oven to have H-ZSM-5, Fe-ZSM-5 and Cu-ZSM-5[24].

2.2. Film preparation

The composite films are prepared using modified zeolites and CNF with a fixed ratio of 20:80 by wt%. Initially homogeneous CNF suspension is obtained using water as a solvent with constant stirring. Modified zeolites are added and again stirring process is carried out for proper blending. Composites films namely CNF/D-ZSM-5, CNF/H-ZSM-5, CNF/Fe-ZSM-5 and CNF/Cu-ZSM-5 are prepared by solution casting method. These films are further used as sensors to detect ammonia.

2.3. Characterization

Using Rigaku-make X-ray diffractometer with Cu-Kα radiation, the crystallinity of the sintered ZSM-5, CNF, and modified zeolite composites are confirmed. The X-ray diffraction peaks are obtained in the range of 5 to 60^0. Using a Shimadzu-make FTIR spectrophotometer, the FTIR spectra of ZSM-5, CNF, and modified zeolites samples are obtained by scanning the sample form 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. Sensing performance testing method

The ability of designed sensor to detect ammonia is evaluated using a homemade static gas unit. Sensor resistance in air is measured at an intervals of 5 °C temperature after the sensor is heated with the aid of a heater from room temperature to 70 °C. The measurement of resistance with respect to temperature change is then calculated (air + ammonia) environments. By measuring the variation in electrical resistance of the sensor film in air (R_a) and in an (ammonia + air) combination (Rg), the detecting characteristics of each sensor are identified. The following equation is used to determine the sensitivity (response) to ammonia.

$$\text{Sensitivity (\%)} = (R_g\text{-}R_a)\ /R_a \times 100$$

By plotting the change in film's sensitivity as a function of temperature, the operating temperature that corresponds to maximum sensitivity, is determined. By subjecting the film to varying ammonia concentrations (ppm) and measuring the change in resistance (sensitivity) with ammonia concentrations, the maximum ammonia adsorption capacity of the sensor film is ascertained. When each composite film is exposed to air and a fixed concentration of (ammonia -air) combination alternately, the sensor's response time and recovery time required to come-back to its initial state are also measured.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents the XRD profiles of ZSM-5, CNF and composite films wherein the XRD pattern of ZSM-5 is included for reference. The XRD profile of pure ZSM-5 zeolite shows the presence of characteristic peaks at 2θ values of 23 and 30^0. This is in good agreement with the literature data. In case of CNF, the two broad peak shows slightly amorphous nature. Peaks corresponding to ZSM-5 do not appear in all composite films whereas the major peak corresponding to CNF shows its existence in all composite films. It is due to higher CNF content (80%) in composites [24]. During ion exchange process, Na^+ cation is replaced by H^+, Fe^{3+}, and Cu^{2+}. Hence, the difference in ionic radii and proper blending of CNF with various zeolite structures may be responsible for shift in peaks (see Fig. 2).

3.2. FTIR Analysis:

The FTIR spectrum of ZSM-5 shows the presence of absorption peaks at 3700 cm^{-1} (Si-OH stretching) and 1642 cm^{-1} (OH bonding of absorb water molecules). The peaks at 1063 cm^{-1}, 1001 cm^{-1}, 792 $cm^{-1}$and 696 cm^{-1} are due to symmetric TO4 tetrahedron. Absorption band due to Si-O-Si stretching occurs at 470 cm^{-1}. The structure-sensitive band at around 1220 cm^{-1} for ZSM-5, is related to the stretching vibrations of T-O bond. The FTIR spectrum of CNF includes typical absorption peaks near 3400 cm^{-1}(OH stretching), 2903 cm^{-1} (C–H stretching), 1369 cm^{-1} (C–H bending), and 1030 cm^{-1} (C-OH stretching vibration).In CNF/H-ZSM-5 composite film the peaks occurring at 2903 cm^{-1} (C–H stretching), 1369 cm^{-1} (C–H bending), and 1030 cm $^{-1}$ (C-OH stretching vibration), which is clearly visualized, can be assigned to CNF. In CNF/D-ZSM-5 film only two absorption peaks are observed at 1369 cm^{-1} (C–H bending), and 1030 cm^{-1} (C-OH stretching vibration) and are attributed to CNF. In CNF/Cu-ZSM-5 composite film, peaks appearing at 3400 cm^{-1} (OH stretching), 2903 cm^{-1} (C–H stretching), 1369 cm^{-1} (C–H bending), and 1030 cm^{-1} (C-OH stretching vibration) show decrease in intensity. In case of CNF/Fe-ZSM-5, the sharp absorbance peaks observed at 2903 cm^{-1} and 1369 cm $^{-1}$

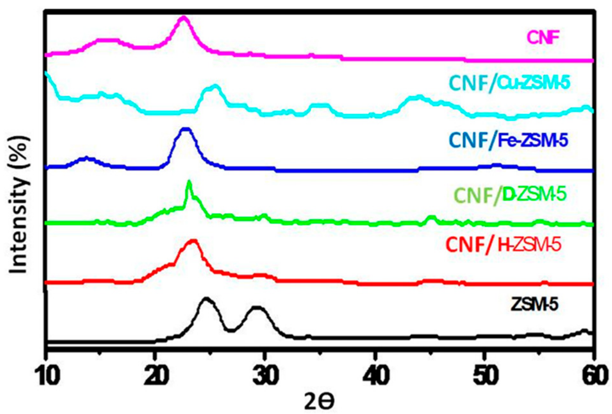

Fig. 1. XRD patterns for ZSM-5, CNF and composite films.

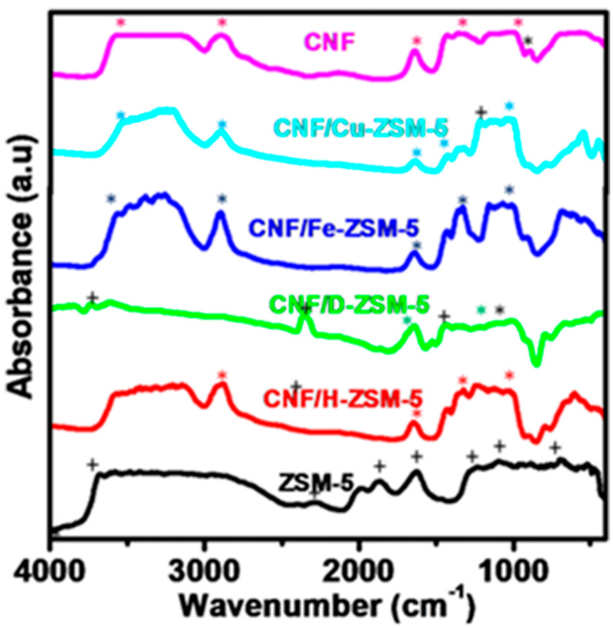

Fig. 2. FTIR spectra for ZSM-5, CNF and composite films.

confirm the presence of functional groups (C–H stretching & C–H bending) corresponding to CNF. The FTIR spectra for all composite films contain a peak at 550 cm^{-1} due to double five member of the ZSM-5 structure. The band at around 435 cm^{-1} can be attributed to the pore opening or motion of the tetrahedral ring in zeolites. Thus, it can be concluded that the FTIR spectra of composite films depict appearance of peaks both, due to ZSM-5 and CNF [24]. It indicates the amalgamation of CNF and modified ZSM-5.

3.3. TGA analysis

The TGA plots for composites are shown Fig. 3. The TGA study for ZSM-5 indicates its thermal stability upto 500 °c. It shows first mass losse above or near to 200°c indicating the elimination of water molecules. The loss due to the removal of internal water molecules in the zeolites can be attributed for the weight losse that occur at high temperature near about 450°c. CNF's thermal degradation results in the temperature range 250 to 325°c. All the composites show weight loss in the same temperature range due to thermal degradation process. It is quite obivious because of a significant percentage of CNF (80%) in a composite [25,26].

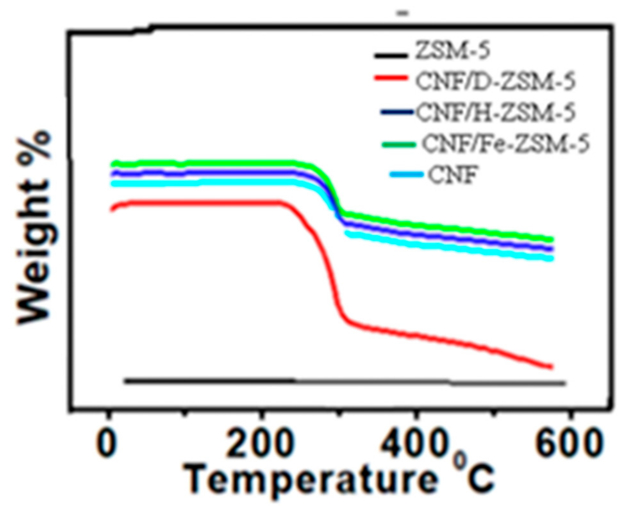

Fig. 3. Weight loss as function of temperature showing thermal behaviour of ZSM-5, CNF and composite films.

3.4. Gas sensing performance

3.4.1. Operating temperature

The typical variation of response for 10 ppm ammonia as function of temperature for ZSM-5, CNF and modified zeolite based composite film sensors is shown in Fig. 4. ZSM-5 film sensor gives high sensitivity at low operating temperature. Almost all composite materials exhibit the highest gas sensitivity at lower temperature of 33 ^{0}C. The sensitivity for each sensor decreases with increase in temperature. The sensitivities of ZSM-5, CNF, CNF / D-ZSM-5, CNF/H-ZSM-5, CNF/Fe-ZSM-5, CNF/Cu-ZSM-5 are found to be 2000, 112, 69, 81, 50, and 73 respectively. Higher sensitivity for ZSM-5 may be due to high porosity, large surface area and presence of more active sites on the surface leading to more interactions of surface atoms with ammonia molecules. It is observed that response to ammonia decreases due to the addition of CNF in ZSM-5. It indicates the availability of less no of surface active sites compare to ZSM-5.

3.4.2. Determination of response and recovery time

The change in ammonia gas response as a function of time for ZSM-5, CNF and their composite sensors is shown in Fig. 5. The response and recovery times for ZSM-5 and CNF sensor are found to be 10 /3 min and 7/3 min respectively. It is observed that all composite films give fast response to ammonia compared to that by ZSM-5 and CNF films. CNF/D-ZSM-5 gives quick response within 3 min compared to all other sensors for ammonia vapour and get back to its initial value within 1 min.

3.4.3. Transient response

Fig. 6 depicts the transient response for ZSM-5, CNF & composite sensors towards the ammonia vapours at their working temperature for variable concentration of ammonia gas. The three different concentrations used are 10, 50, 100 ppm. It can be concluded that the response goes on increasing with increase in ammonia vapour concentration for all sensor films.

3.4.4. Determination of gas uptake capacity

Gas uptake capacity of ZSM-5, CNF and composite film sensors as a function of ammonia concentration is presented in Fig. 7. The gas response increases with increase in gas concentration, later attains a constant value, described as saturation value or maximum gas uptake. The gas response for ZSM-5 and CNF is found

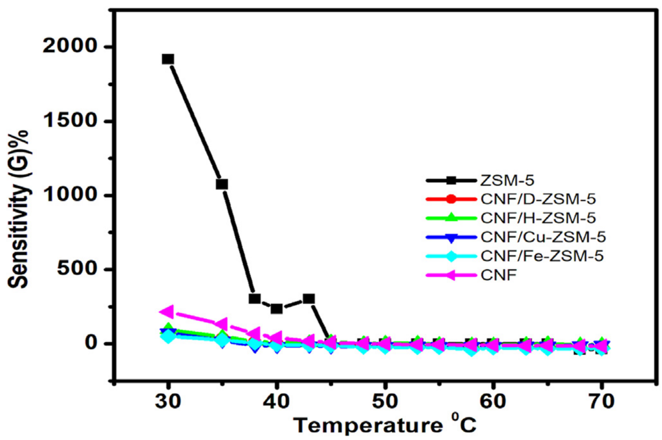

Fig. 4. Variation of gas response with temperature for fixed ammonia gas concentration (10 ppm).

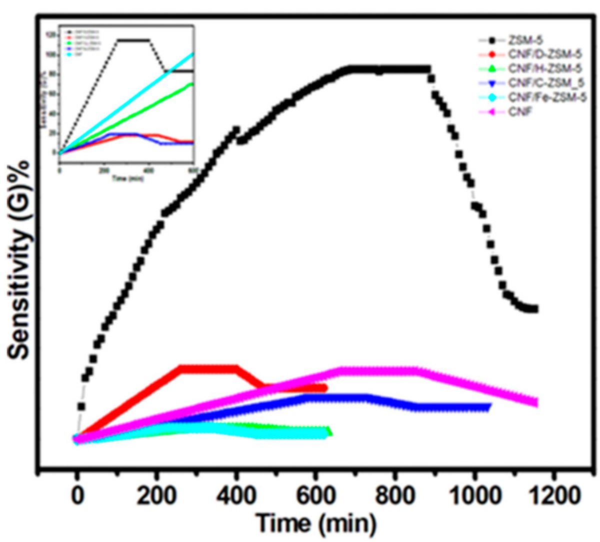

Fig. 5. Response and recovery behaviour of ZSM-5, CNF and composites towards 10 ppm ammonia.

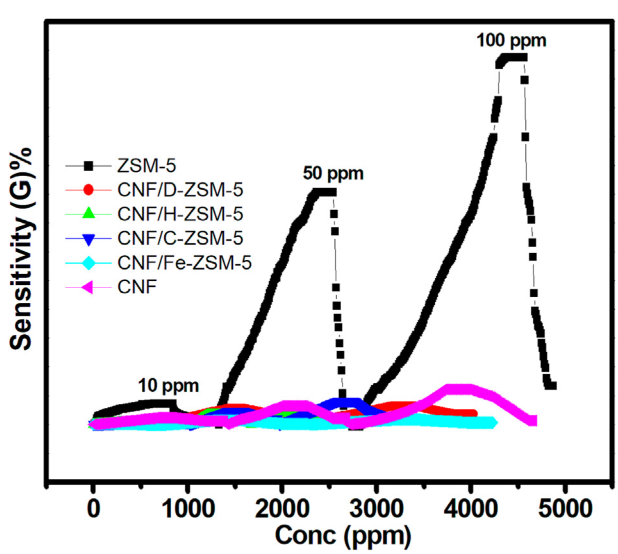

Fig. 6. Sensitivity of ZSM-5, CNF and composite sensors upon exposure to ammonia at their respective operating temperature.

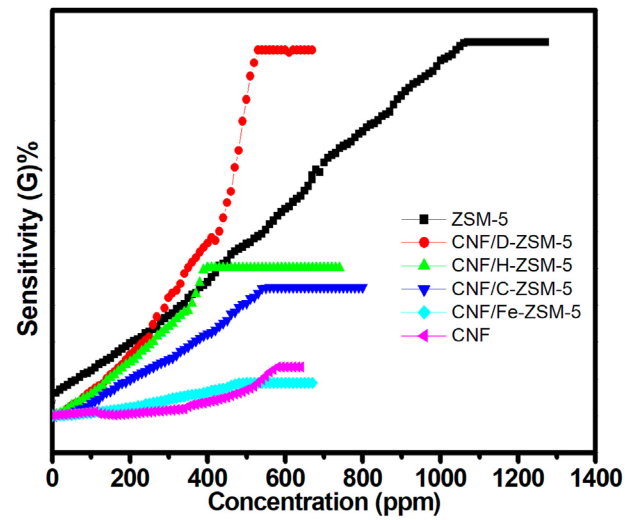

Fig. 7. Gas uptake capacity of ZSM-5, CNF and composite film sensors as a function of ammonia concentration.

to be 1075 ppm and 530 ppm respectively. In case of composites, the gas uptake is in the range of 520–545 ppm. However, ZSM-5 shows much higher uptake capacity. Moreover, all sensors are able to detect 1 ppm minimum ammonia concentration.

The sensor data is provided in Table 1.

4. Conclusion

Modified zeolite based novel CNF/ZSM-5 composites have been developed to detect ammonia gas. ZSM-5 film sensor reveals highest sensitivity at 30°c. Composite films, prepared using solution casting method, are found to be sensitive to ammonia with an operating temperature of 33°c. In comparison with ZSM-5, composite films show low response towards ammonia. ZSM-5 sensor is found to have a higher ammonia uptake capability (1075 ppm). Excluding ZSM-5, all other sensors possess low uptake capacities. Among various composites, CNF/H-ZSM-5 composite film exhibits highest response. All sensors are able to sense ammonia with the lowest concentration of (1 ppm). It can be concluded that CNF/modified ZSM-5 composite sensors, with a dynamic range of 1 ppm to 500–545 ppm and at low operating temperature can be used as the potential ammonia sensors**.**

CRediT authorship contribution statement

Kishori Naik: . **Vikas Kutte:** Data curation, Formal analysis. **Madhuri Lakhane:** Formal analysis, Software. **Malikarjun Wakade:** Data curation, Formal analysis. **Megha Mahabole:** .

Data availability

The data that has been used is confidential.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Table 1
The Ammonia sensing parameters of Pure ZSM-5, CNF and modified zeolite composite films sensors.

Materials	Operating Temperature	Sensitivity	Response Time	Recovery Time	Concentration Saturation
ZSM-5	30	2056	10 min	3 min	1075 ppm
CNF/D-ZSM-5	33	69.3	3 min	1 min	545 ppm
CNF/H-ZSM-5	33	81.68	9 min	2 min	500 ppm
CNF/Fe-ZSM-5	33	50.21	4 min	2 min	519 ppm
CNF/Cu-ZSM-5	33	73.20	5 min	2 min	526 ppm
CNF	33	112	7 min	3 min	530 ppm

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