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Utilization of strontium added NiAl$_2$O$_4$ composites for the detection of methanol vapors

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Abstract

Strontium added NiAl$_2$O$_4$ composites prepared by sol–gel technique was utilized for the detection of methanol vapors. X-ray diffraction, scanning electron microscopy (SEM), FT-IR spectroscopy and nitrogen adsorption/desorption isotherm at 77 K was employed respectively to identify the structural phases, surface morphology, vibrational stretching frequencies and BET surface area of the composites. The composites were prepared with the molar ratios of Ni:Sr as (1.0:0.0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, 0.0:1.0) keeping the aluminum molar ratio as constant for all the compositions and were labeled as NiSA1, NiSA2, NiSA3, NiSA4, NiSA5 and NiSA6, respectively. The samples sintered at 900 °C for 5 h were subjected to dc resistance measurements in the temperature range of 30–250 °C to study the methanol vapor detection characteristics. The results revealed that the sensitivity in detecting methanol vapor increased with increase in temperature up to 175 °C for the composites NiSA1 and NiSA6 while for the other composites up to 150 °C and thereafter decreased. The sensitivity increased with increase in methanol concentration from 100 to 5000 ppm at 150 °C. Among the different composites NiSA5 showed the best sensitivity to methanol detection at an operating temperature of 150 °C.
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1. Introduction

There is growing public concern over industrial impact on the environment due to the manufacture of various end products and monitoring environmental quality, therefore becomes mandatory. Global monitoring is generally related to the detection of trace chemicals such as green house gases, whereas local and indoor/outdoor monitoring includes determination of toxic and explosive gases as well as malodors, most of which are often volatile organic compounds (VOCs). There are various sources commonly responsible for the emission of these gases: the energy industry, production industry, transport, industrial processes, solvents, agriculture and landfill [1]. Thus the increased concern about environmental protection has led to continuous expansion in searching for new VOC sensor material

development. Different criteria are used for measuring sensitivity to gases like changes in mechanical, optical and electrical properties [2,3]. Electrical detection is most commonly used and is based on the change in resistance or capacitance of the sensor material on exposure to gases. Semiconducting oxides like zinc oxide, aluminum oxide, titanium oxide, etc. have been studied extensively and have emerged as economical sensors for monitoring toxic gases and vapors than the other available organic and polymeric material comparatively [4,5]. The sensitivity of these sensors to gases depends on the microstructure, which can be achieved by adopting special techniques of preparation or by doping impurities [6,7]. The oxide matrices, particularly alumina have gained importance due to their desirable characteristics such as chemical inertness, physical and thermal stability, low cost, long life, etc. and they have been investigated at both ambient and elevated temperatures [8,9]. The sol–gel technique is considered as the most promising technique for the preparation of metal oxides [9,10] as it allows for high purity ceramics with homogeneous distribution of components on the atomic scale, lower crystallization temperature and economy. Alcohols

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Table 1
Sample code, molar ratios and activation energy of Ni:Sr:Al for Sr added NiAl$_2$O$_4$ composites

S. no.	Sample code	Molar ratios of Ni:Sr:Al	E_a (eV)
1	NiSA1	1.0:0.0:2.0	0.338
2	NiSA2	0.8:0.2:2.0	0.312
3	NiSA3	0.6:0.4:2.0	0.296
4	NiSA4	0.4:0.6:2.0	0.272
5	NiSA5	0.2:0.8:2.0	0.234
6	NiSA6	0.0:1.0:2.0	0.292

broadly fall under the category of volatile organic compounds, which usually have very low boiling point, and highly reactive. Hence the development of an alcohol sensor having higher sensitivity along with optimization of selectivity, which can be operated at lower operating temperature, is the issue inviting much attention for research. Methyl alcohol (methanol) is a very useful organic solvent with widespread applications in automotive fuel and manufacturing of paints, colors, dyes, drugs, perfumes, etc. However it is highly toxic and often fatal to human beings as its metabolites formaldehyde and formic acid cause blindness and death. The wide range of applications, toxicity and clinical implications of methanol make imperative the need of development of a reliable and selective methanol sensor. It has been shown that the gas sensitivity is greatly improved as the grain size decreases by doping of metal oxides. Both single and mixed ceramic metal oxides have been used for the purpose of sensing alcohol vapors. The sensing behavior of methanol by metal oxides like TiO$_2$ [11], indium tin oxide [12], α-Fe$_2$O$_3$ [13] and CeO$_2$–Fe$_2$O$_3$ [14] focused our interest to utilize mixed metal composites containing metal aluminates for the above purpose. Though metal aluminate spinels were used as humidity sensors [15–17] there were no literatures found regarding metal aluminates for the purpose of sensing alcohols. Hence we focused our study to prepare nickel aluminate and Sr(II)-added nickel aluminate and utilize them for the detection of methanol vapor.

The main objective of the present work is to study the effect of addition of strontium on nickel aluminates rather than the isomorphic substitution. In the present paper the newly developed strontium added nickel aluminate composites by sol–gel technique were characterized by X-ray diffraction, scanning electron microscopy (SEM), FT-IR spectroscopy and nitrogen adsorption/desorption isotherm at 77 K. The dependence of electrical response of these composites to the methanol vapor was investigated.

2. Experimental

Strontium added NiAl$_2$O$_4$ composites with the molar ratios of Ni:Sr (1.0:0.0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, 0.0:1.0) keeping the aluminum molar ratio constant for all compositions as shown in Table 1 were prepared by the sol–gel route using nitrates of nickel, strontium and aluminum. Calculated amounts of these metal nitrates of analytical grade were dissolved in 100 ml of water and 1 M citric acid was added as the gelling agent. The resulting solution was stirred at room temperature until a clear

transparent solution was obtained. This clear solution was kept for gelation at 65 °C for 12 h and the gel was then dried at 110 °C, followed by calcination at 600 °C for 5 h. The calcined powders were subjected to dry milling and made in the form of cylindrical pellets of dimension 13 mm diameter and 3–4 mm thickness using a hydraulic press at a pressure of 400 MPa using 2% polyvinyl alcohol as the binder. The pellets were then sintered at 900 °C for 5 h in ambient air atmosphere. The samples were cooled down to room temperature at the natural cooling rate of the furnace. The sample code with their corresponding molar ratio is shown in Table 1.

The structural studies were carried out using a Philips X'pert diffractometer for 2θ values ranging from 10° to 80° using Cu Kα radiation at λ = 0.154 nm. A Perkin-Elmer Infrared spectrometer was used to identify the functional groups of the composites. The samples were scanned in the spectral range 4000–400 cm^{-1}. The surface morphology of the sintered porous compacts was determined by a Leo-JEOL scanning electron microscope at the desired magnification. The surface area and pore size distribution were derived from the nitrogen adsorption–desorption isotherms using liquid nitrogen at 77 K. The nitrogen adsorption–desorption isotherms of the composites were measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). The composites were degassed at 150 °C for overnight. The surface area of the composites was calculated using BET equation, which is the most widely used model for determining the specific surface area (m^2/g). The pore size distribution was determined using the BJH method. In addition, the t-plot method [18] was applied to calculate the micropore volume and external surface area. The total pore volume was estimated as liquid volume of adsorbate adsorbed at a relative pressure of 0.99. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be 0.162 nm^2.

Electrical conductance measurements of the samples were determined by two-probe method using conducting silver paste to ensure the ohmic contact of the electrodes. The samples were electrically connected to a dc power supply and a Keithley 485 picoammeter in series. Given the high resistivity of the materials under investigation, the potential inaccuracy due to contact resistance is assumed negligible. The temperature dependent resistance experiments were carried out to determine the activation energies of the samples using the linearised form of the expression, $I = I_o \exp^{-E_a/kT}$, where I was the current, E_a the activation energy, k the Boltzmann constant and T the temperature. For this purpose the samples were kept inside a cylindrical furnace, which was connected to a microprocessor, controlled temperature programmer. The activation energy of the composites was determined from the temperature dependence conductance experiments in the temperature range 120–300 °C under ambient conditions.

The sensitivity tests were carried out in a testing chamber that measures the surface resistance of the samples. Methanol was injected by a micro syringe into the test chamber and the sensing characteristics of the sensor were observed by measuring the electrical resistance change of the sensor when the latter
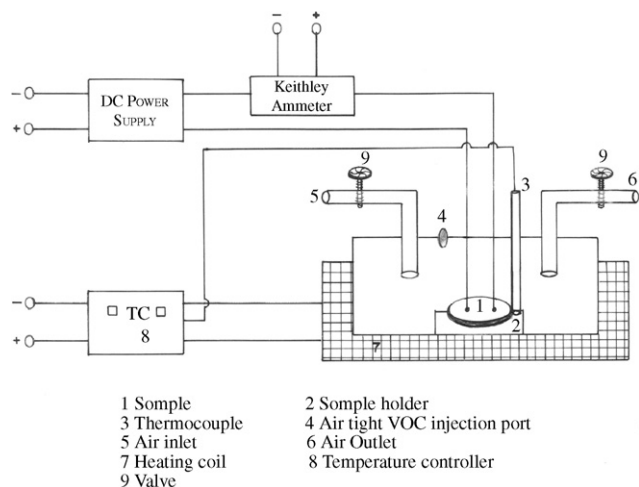
Fig. 1. Schematic diagram of the experimental set-up used to measure the methanol vapor responses.

was exposed to methanol. The volume of the test chamber was 0.003 m³. As 1 ml of liquid in 1 m³ volume corresponds to a concentration of 1 ppm, a typical injection of 0.3 ml of methanol in 0.003 m³ corresponds to the gas concentration of 100 ppm [19]. Under the exposure of reducing gas such as alcohol, its resistance decreases. Its sensitivity S_f is defined as,

$$S_f = \frac{R_{air} - R_{gas}}{R_{gas}}$$

where R_{gas} is the resistance of the sensor under gas exposure and R_{air} is the resistance of the sensor in air. The resistances of the samples were measured at different temperatures in the range of 30–200 °C and different concentration levels (100–5000 ppm) of methanol. The schematic representation of the experimental set-up is shown in Fig. 1.

3. Results and discussion

3.1. N₂ adsorption/desorption isotherms

Fig. 2 represents the nitrogen adsorption/desorption isotherms at 77 K of the nickel aluminate (NiSA1), strontium aluminate (NiSA6) and the mixed metal composite that
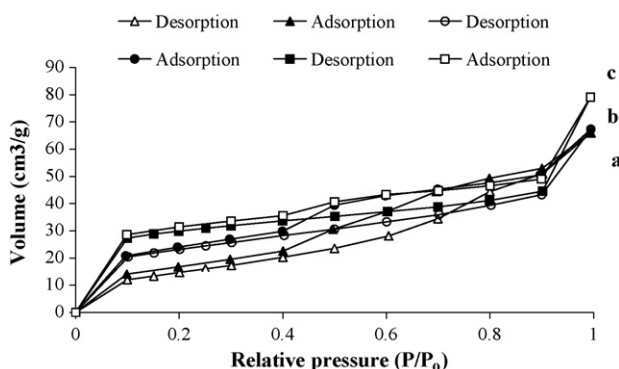

Fig. 2. Nitrogen adsorption/desorption isotherms of (a) NiSA1 (b) NiSA6 (c) NiSA5 at 77 K.

possessed maximum sensitivity (NiSA5) respectively. The isotherms of NiSA1 and NiSA5 and NiSA6 showed a hysterisis effect with the slope of the plateau increasing with a significant increase in the nitrogen uptake through the entire pressure range. The large increase in the nitrogen adsorption for NiSA1 at the higher relative pressures indicate that the NiSA1 composite have only a mesoporous character with a relatively larger pore size in the mesopore range of 2–50 nm. While the nitrogen adsorption for the composites NiSA6 and NiSA5 considerably increased at a low relative pressure indicating the formation of micropores in addition to the presence of mesopores. This increase in uptake of nitrogen in the samples is a result of the major increase in porosity created within the strontium aluminate and strontium added nickel aluminate components. The composite material NiSA5 exhibited the most prominent hysterisis effect, which can be characterized by the formation of intergranular pores as a result of strontium addition. The amount of nitrogen adsorbed increased to 79.10 cm³/g for NiSA5 and that for pure nickel aluminate (NiSA1) and strontium aluminate (NiSA6) composites were only 65.98 and 63.28 cm³/g, respectively.

3.2. Surface area and pore volume

The specific surface area was calculated using the BET model and the mesopore surface area was calculated by the *t*-plot method. The composite NiSA1 possessed a very low surface area of 55.02 m²/g while NiSA6 possessed 77.86 m²/g. But the mixed metal composite NiSA5 possessed an increase in BET surface of 94.56 m²/g. This increase in surface area for NiSA5 can be attributed to the decrease in particle size due to the addition of strontium in the nickel aluminate composites as a result of non-isomorphic substitution. The pores could be generated within the three components of oxides of nickel, strontium and aluminum matrices. Consequently pores of different dimensions are produced. The composite NiSA1 possessed only mesopores surface area while the composite NiSA6 and NiSA5 possessed both micro and mesopore surface area. The micropore surface area was obtained by subtracting mesopore surface area from the corresponding BET surface area. It was observed that there was a considerable increase in micropore surface area of 53.51 m²/g for NiSA5 while NiSA6 had 33.96 m²/g with NiSA1possessing no micropore surface area. These results suggest that strontium addition in the composites could lead to the modification of the intergranular pores controlling the range of surface area.

The mixed metal composite NiSA5 has a pronounced effect on the pore volume profile. The total pore volumes were estimated from nitrogen adsorption and micropore volumes were obtained by the *t*-plot method. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The incremental increase in total pore volume for the mixed metal composite NiSA5 was significantly observed than the other two NiSA1 and NiSA6 systems. NiSA1 possessed no micropore volume but only with mesopore volume while NiSA1 and NiSA6 possessed both micro and mesopore volumes. The increase in micropore and mesopore volume can be attributed to the decrease in particle size with more addition of strontium. The values from Table 2 indicate that the introduction of micro-

Table 2
Surface area parameters of NiSA1, NiSA5 and NiSA6 composites

S. no.	Parameters	NiSA1	NiSA6	NiSA5
1	S_{BET} (m^2/g)	55.02	77.86	94.56
2	S_{mic} (m^2/g)	0.00	33.96	53.51
3	S_{meso} (m^2/g)	55.02	43.9	41.05
4	Total pore volume (cm^3/g)	0.102	0.104	0.122
5	Micropore volume (cm^3/g)	0.000	0.020	0.028
6	Mesopore volume (cm^3/g)	0.102	0.084	0.094
7	Average pore diameter (nm)	7.42	5.34	5.01

S_{BET}: BET surface area, S_{mic}: micropore surface area, S_{meso}: mesopore surface area.

Fig. 3. Pore size distribution of NiSA1, NiSA5 and NiSA6 composites.

pores by the strontium addition in the NiSA5 matrices along with mesopores would lead to enhanced methanol adsorption with higher sensitivity than the pure nickel aluminate NiSA1 and strontium aluminate NiSA6 composites. The surface area parameters of NiSA1, NiSA5 and NiSA6 composites are shown in Table 2.

The mesoporosity values (percentage of mesopore compared to total pore volume, V_{meso}/V_{total}) of the composites were 100, 80.69 and 77.04% for NiSA1, NiSA6 and NiSA5, respectively. The microporosity values (percentage of micropore compared to total pore volume, V_{micro}/V_{total}) of the composites NiSA1, NiSA6 and NiSA5 were 0, 19.31, 22.96, respectively. The data suggested that the NiSA1 sample inherited intragranular pores only in the mesopore range while pure strontium aluminate NiSA6 possessed both micro and mesoporic ranges and thus the addition of strontium in the nickel aluminate species introduced intragranular micropores in addition to the mesopores in NiSA5 composite. In addition it was observed that NiSA5 possessed the highest micropore volume compared to the pure strontium and nickel aluminate composites. This suggests that the combination of mixed metals can introduce sufficient micropores in addition to the available mesopores which in turn indicate that the combination of mixed metals such as strontium, nickel and aluminum oxide can be considered as a suitable matrix for the production of microporous and mesoporous materials.

3.3. Pore size and pore distribution

Fig. 3 shows the pore size distribution of NiSA1, NiSA5 and NiSA6 composites. The average pore size distribution dependent mainly on one or more combination of metal oxides in the composites. The average pore diameters of NiSA1, NiSA6 and NiSA5 composites were 7.42, 5.34 and 5.17 nm, respectively. The average pore diameters obtained from the composites is due to the formation of intergranular pores within the combination of metal oxides. It is observed that the average pore diameter of pure strontium aluminate decrease by one order compared to that of the pure nickel aluminate species. This drop in pore diameter could be due to the reduction in the particle size of strontium aluminates. And still the pore diameter is reduced in the case of mixed metal composite (NiSA5) to 5.17 nm. This reduction in the average pore diameter is attributed to the addition of more strontium along with nickel aluminate composition as a result of
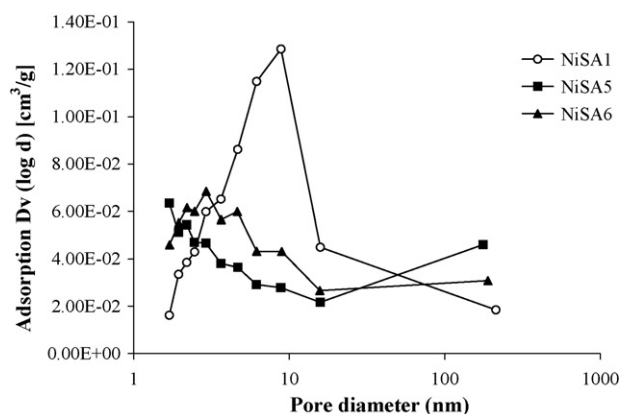
non-isomorphic substitution. The presence of strontium retards the growth of bulk nickel aluminate phase leading to an increase in porosity by introducing micropores.

3.4. X-ray diffraction studies

The XRD measurements were carried out to characterize the different phases of the composites. The X-ray diffraction patterns of nickel aluminate and strontium added nickel aluminate samples are shown in Fig. 4a–f. The XRD spectra of Fig. 4a showed peaks corresponding to nickel–aluminate spinel like phase (JCPDS: 20-0777). As the concentration of the strontium was increased, the evolution of SrAl$_2$O$_4$ peaks in addition to SrO phase (JCPDS: 01-0886) was observed. Single-phase ceramics of strontium aluminates were not obtained for the higher strontium added composites. The patterns were rather complicated which implied that the material was composed of mixture of phases. After a careful comparison between the standard JCPDS profiles and the experimental results it was found that the phases such as 5SrO·4Al$_2$O$_3$ (JCPDS: 09-38) and SrO·2Al$_2$O$_3$ (JCPDS: 25-1208) were recognized. The addition of more strontium retards the growth of bulk nickel aluminate phase on the surface and forms new phases 5SrO·4Al$_2$O$_3$ and SrO·2Al$_2$O$_3$. The presence of different phases in NiSA5 as shown in XRD was taken as the criteria for good methanol sensing.

3.5. FT-IR spectroscopy

The FT-IR spectra (Fig. 5) of the composites exhibit a broad band near 3400 cm^{-1} due to the γ(O−H) of free and hydrogen-bonded hydroxyl groups arising from the adsorbed water in the samples and a second typical absorption region at 1630 cm^{-1} is assigned to the deformative vibration of water molecules which is most probably due to water absorption during the compaction of the dry powder specimens with KBr [20,21]. The metal–oxygen stretching frequencies in the range 400–1000 cm^{-1}, are associated with the vibrations of Ni−O, Al−O, Sr−O and Sr−O−Al bonds [22]. The strontium added samples show the peak at 857 cm^{-1}, which is assigned to the formation of SrAl$_2$O$_4$ [23]. The two sharp bands at 560 and
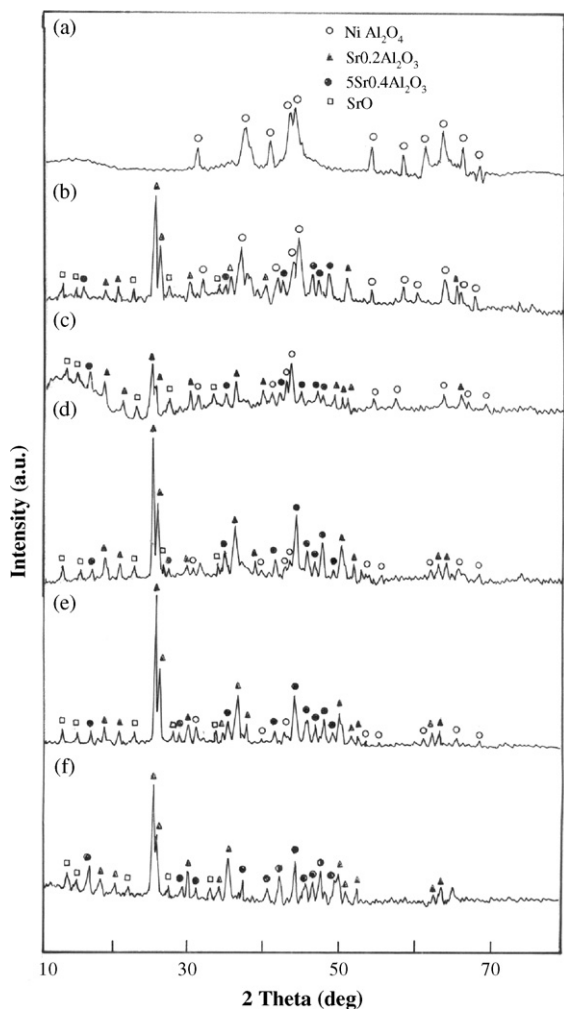
Fig. 4. X-ray diffraction spectra of (a) NiSA1, (b) NiSA2, (c) NiSA3, (d) NiSA4, (e) NiSA5, and (f) NiSA6.

Fig. 5. FT-IR spectra of (a) NiSA1, (b) NiSA2, (c) NiSA3, (d) NiSA4, (e) NiSA5, and (f) NiSA6.

$678\,cm^{-1}$ are due to the nickel aluminate spinels. These bands correspond to the AlO_6 group, which shows formation of the $NiAl_2O_4$ spinel [24].

3.6. Surface morphology (SEM)

Fig. 6a–c shows the surface morphology of the composites NiSA1, NiSA5 and NiSA6 and it depicts the intergranular porous structure of the composite materials qualitatively. The particle size of NiSA5 was found to be much smaller than NiSA6 sample also. The highly porous structure of NiSA5 compared to NiSA1 and NiSA6 suggest that the addition of more strontium in the nickel aluminate can reduce the particle size with the intergranular pores leading to microporosity in addition to the presence of mesopores.

3.7. Electrical conductance studies

The room temperature electrical conductance measurements of the composites prior to methanol-sensing measurements signified that the current increased linearly with the applied voltage, indicating the ohmic cont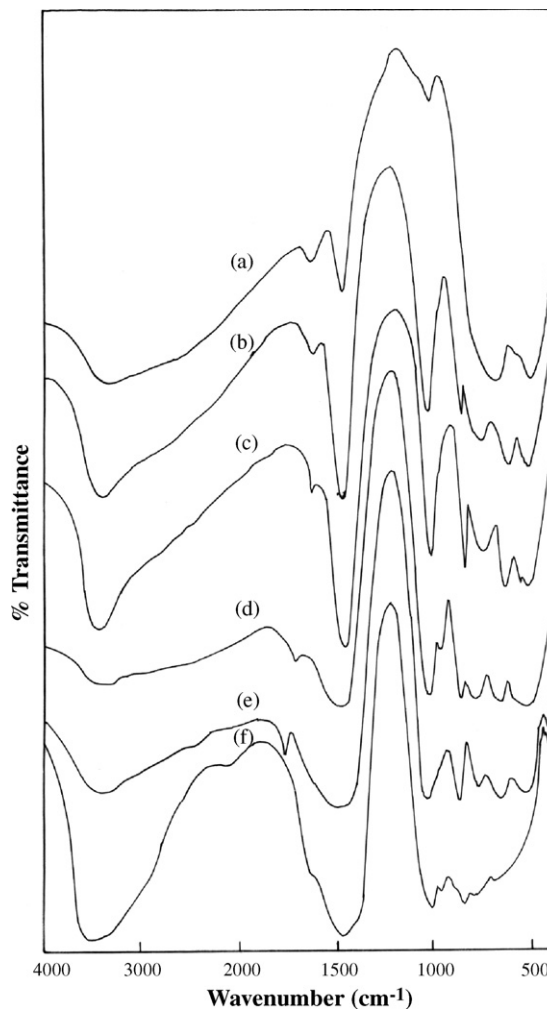act of the electrodes. The temperature dependence of electrical conductance carried out in the temperature range 120–300 °C suggested that the current (I) increased with an increase in temperature (T). The activation energies calculated from the temperature dependence conductance data are shown in Table 1. The activation energy for electrical conduction in polycrystalline materials generally involves the combination of the energy required to raise the carriers from the dominant levels to their corresponding transport bands and the energy required to create the carriers in the dominant levels. The lower activation energy predicts that the small polaron conduction dominates in the studied temperature range.

3.8. Methanol-sensing measurements

The sensitivity of strontium added $NiAl_2O_4$ composites to methanol at different concentrations (100–5000 ppm) and at different temperatures (30–250 °C) was studied through electrical conductance measurements. Fig. 7 shows the sensitivity of the composites at 1000 ppm of methanol concentration in the temperature range of 30–250 °C. The sensitivity increases with increase in temperature and the maximum sensitivity was obtained at an optimum temperature. The sensitivity thereafter
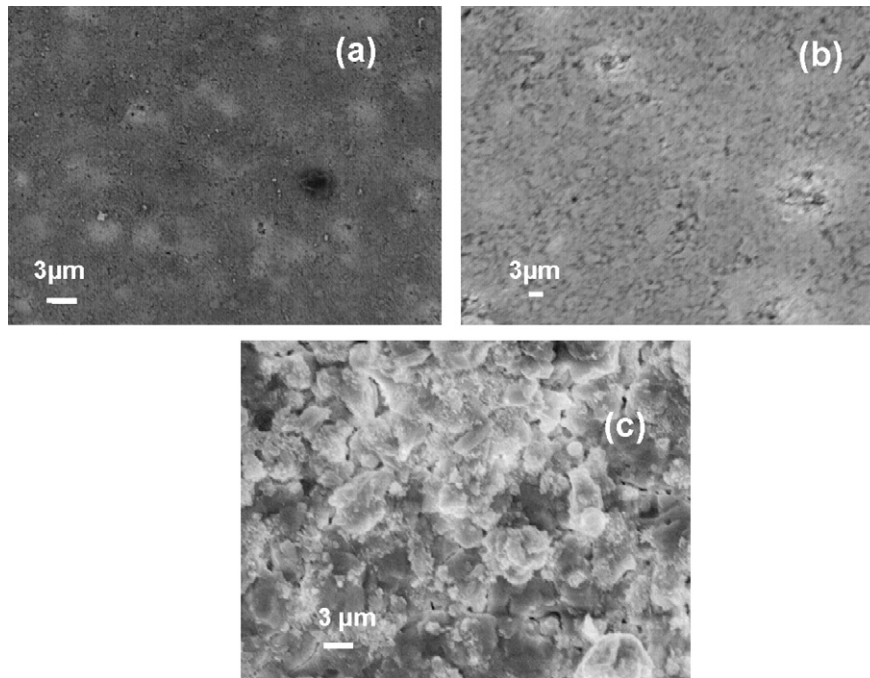
Fig. 6. SEM image of (a) NiSA1 (b) NiSA5 and (c) NiSA6 composites.

decreases for all the composites. It was observed that the sensitivity to methanol vapors of the pure $NiAl_2O_4$ was lesser than the strontium added composites. The optimum temperature for NiSA1 and NiSA6 was 175 °C and for all the Sr(II)-added nickel aluminates (NiSA2, NiSA3, NiSA4 and NiSA5) it was 150 °C. It shows that at an optimum temperature most of the adsorbed oxygen species would have reacted with the OH group of methanol vapor. This adsorbed oxygen creates a space charge region near the surface of the composite by extracting electrons from the material. Methanol, being reducing in nature, removes adsorbed oxygen species from the surface and re-injects the electrons back to the material, thereby decreasing the resistance. The maximum sensitivity at the respective operating temperature indicates that the equilibrium density of chemisorbed oxygen ions is maximum at this temperature. It is evident from Fig. 8 that varying in the concentration of methanol from 100 to 5000 ppm at 150 °C the sensitivity increases up to 1000 ppm with a higher rate of increase in sen-

sitivity and thereafter slows down reaching near equilibrium. The sensitivity at low concentration has a linear relationship with concentration, as there may be sufficient number of pores for methanol vapor adsorption. At higher concentration the rate of adsorption decreases due to less assess of methanol vapors into the filled pores leading to less increase in sensitivity values. The increase in porosity with increase in strontium content as evidenced from SEM image and BET studies confirmed the presence of more sites for methanol adsorption, which produces more charge carriers for electrical conduction. In addition the SEM photographs also reveal that increase in the strontium addition produces fine particles with smaller dimensions compared with the other indicative that smaller the particle size higher will be the surface energy and the adsorption capacity. Thus the composite NiSA5 possessed comparatively a higher sensitivity factor of 140 while that of the pure nickel aluminate NiSA1 and pure strontium aluminate NiSA6 had only 91 and 111, respectively, at their respective optimum temperature for 1000 ppm of methanol.
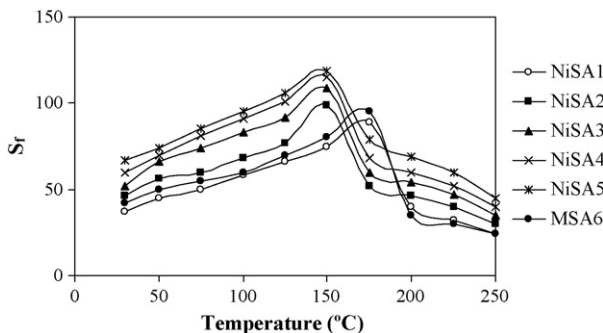

Fig. 7. Sensitivity of composites to 1000 ppm of methanol at different temperatures.
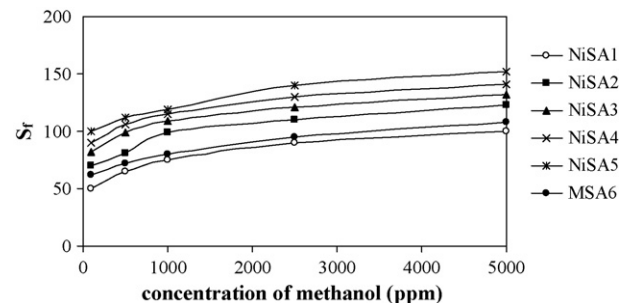

Fig. 8. Sensitivity of composites to methanol at different concentrations and at 150 °C.

3.9. Principle of methanol detection

The mechanism of the methanol detection by the composites can be described as follows.

The surface conductivity depends on the density of donors (oxygen vacancies) and acceptors (chemisorbed oxygen). In case of semiconductors like metal oxides, at first atmospheric oxygen is chemisorbed on the surface of the composite and forms ionic species such as O^{2-}, O_2^- and O^- and its conductivity increases when the incoming gas is reducing type and the proposed reaction pathway is,

$$O_{2(gas)} \Leftrightarrow O_{2(ads)} \tag{1}$$

$$O_{2(ads)} + e^- \Leftrightarrow O_{2(ads)}^- \tag{2}$$

$$O_{2(ads)}^- + e^- \Leftrightarrow 2O_{(ads)}^- \tag{3}$$

$$2O_{(ads)}^- + e^- \Leftrightarrow O_{2(ads)}^- \tag{4}$$

The reaction between methanol (reducing type) and ionic oxygen species yields formaldehyde and water in one case and formic acid and water in the other case. Two possibilities of reactions are:

$$CH_3OH_{(gas)} + O_{(ads)}^- \Leftrightarrow HCHO + H_2O + e^- \tag{5}$$

$$CH_3OH_{(gas)} + O_2^- \Leftrightarrow HCOOH + H_2O + e^- \tag{6}$$

Methanol is easily oxidized to formaldehyde and subsequently formic acid. When the methanol vapor comes in contact with the surface oxygen ions of the oxide surface, it reacts with either O^- or O_2^- ions and gets oxidized to formaldehyde or formic acid and water and liberates on electron which actually causes the conductivity to increase.

3.10. Influence of the combination of micro and mesopores

The results from our studies infer that the composite that possessed a mixture of micro and mesopores showed the higher sensitivity towards methanol. In this case, the adsorption process would have proceeded through a sequence of diffusion steps from the bulk phase into the mesopores ($2 < d < 50$ nm) and then to the micropores ($2 < d < 5$ nm). As the molecule size of methanol is about 0.35 nm [25], micropores would be a suitable site for the adsorption of methanol where it could be easily oxidized to aldehyde/acid and was favorable in the sample NiSA5 that possessed micropore surface area of 53.51 m^2/g and mesopore surface area of 41.05 m^2/g with an average pore diameter of 5.01 nm. The NiSA1 composite having comparatively low sensitivity with a reduced adsorption of methanol could be due to the less micropore surface area (33.96 m^2/g) and quite high mesopore surface area (43.90 m^2/g) comparatively to NiSA5 with an average pore diameter of 7.42 nm where desorption would also have been facilitated. Thus the addition of strontium into nickel aluminate matrix introduces micropore that leads to an enhanced adsorption followed by oxidation. If micropores have not been introduced in NiSA5 in addition to mesopores, then the average pore diameter might have been greater than 5.01 nm, which will lead to desorption. For the NiSA5 composite used in the present work, the presence of mesopores behaves as an entrance for the movement of methanol molecules from the bulk phase to the inner pores without any hindrance. Thus during the diffusion process the presence of mesopore is of great advantage enabling easy assess for the methanol molecule into the micropores not only for accelerating the diffusion into pores but also increasing the equilibrium coverage of such pore surface. If the composite would have possessed microporosity alone with no mesopore the average pore diameter would have been reduced to less than 2 nm but then the pore blockage might have occurred due to aggregation of adsorbate molecules or due to the smaller cross sectional area of the micropores at the pore entrances. Therefore a pure microporous or mesoporous material would not have favored higher sensitivity towards methanol. Thus the high sensitivity of NiSA5 can be explained by the fact that the composite containing considerable mesopore and micropore would result in favorable methanol adsorption to get easy assess to the composite interior.

3.11. Response and recovery characteristics

It is well known that the sensing mechanism of semiconductor gas sensor materials is a surface controlled process. The adsorption of test gases, which depends on the type of gas and the sensor material, might affect both response and recovery characteristics. Better response would be expected for larger concentration of the test gas adsorbed, because the reaction between the adsorbed reducing gas and oxygen species becomes more favorable. The response and recovery times are the important parameters of gas sensors and were studied for NiSA1 (pure nickel aluminate) and NiSA5 (the composite with higher sensitivity) and NiSA6 (pure strontium aluminate) composites at their corresponding operating temperatures for three cycles to ensure repeatability. The response and recovery time of NiSA1 was 270 and 230 s and for NiSA6 was 280 and 250 s, respectively. But for the composite NiSA5 the response and recovery time was only 240 and 210 s, respectively. This can be explained due to the presence of higher Sr(II) content on metal aluminate matrix and the high sensitivity of the composites. Thus by the addition of Sr(II) to pure metal aluminates, the speed or response and recovery time for sensing of methanol is alcohols is improved. The response and recovery plot of the maximum sensitivity composite NiSA5 is shown in Fig. 9.
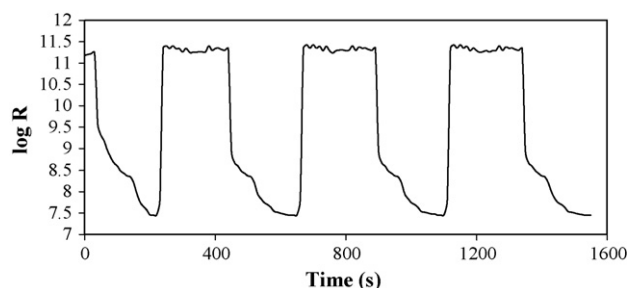

Fig. 9. Response and recovery plot of NiSA5 composite.

4. Conclusions

A study on the methanol detection characteristics of strontium added NiAl$_2$O$_4$ composites prepared by sol–gel technique have been carried out. The results suggest that increase in the concentration of strontium can increase the porosity resulting in higher sensitivity values. The XRD patterns suggested the formation of single phase for nickel aluminate composite while multiphasing was observed in the strontium added nickel aluminate composites. The vibrational stretching frequencies corresponding to the composites were confirmed by FT-IR spectroscopy. It was observed that the sensitivity of the composites to methanol was higher at 150 °C, which may be the saturation point of the redox reaction between the methanol vapor and the adsorbed oxygen species. The sensing properties of the composites were studied for different concentrations at 150 °C and found to be increasing with increase in methanol concentration. The increase in surface area and porosity as shown by nitrogen adsorption–desorption isotherms and pore size distribution, with the introduction of micropores makes the composite NiSA5 to be a better candidate for methanol detecting applications as evidenced by the comparatively higher sensitivity value. The results obtained are promising for the preparation of sensitive and low cost methanol sensor and harvesting of its properties may lead to dependable commercial products.

Acknowledgement

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