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Sol–gel derived $(Sr,Ni)Al_2O_4$ composites for benzene and toluene sensors

J. Judith Vijaya [a,*], L. John Kennedy [b], G. Sekaran [b], K.S. Nagaraja [a]

[a] Department of Chemistry, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai — 600 034, India
[b] Department of Environmental Technology, Central Leather Research Institute (CLRI), Chennai — 600 020, India

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Abstract

Strontium(II) added $NiAl_2O_4$ composites prepared by sol–gel technique was utilized for the detection of benzene and toluene vapors. XRD, SEM and BET measurements were employed to identify the structural phases, surface morphology and surface area. The $(Sr,Ni)Al_2O_4$ composites sintered at 900 °C were subjected to dc resistance measurements in the temperature range of 30–200 °C to study the benzene and toluene vapor detection characteristics. The maximum sensitivity of the composites was obtained at 150 °C. An increase in the sensitivity was observed with increase in benzene and toluene concentration from 100 to 5000 ppm at 150 °C. Among the different compositions, the $(Sr,Ni)Al_2O_4$ composites with higher strontium content (NiSA5) showed the best sensitivity towards benzene and toluene vapor detection.

Keywords: Ceramics; Composite materials; Electrical properties; Sensors; Sol–gel preparation; VOC vapor

1. Introduction

The increased concern about environmental protection has led to continuous expansion in searching for new volatile organic compounds (VOC) sensor materials [1]. Semiconducting oxides have emerged as economical sensors for monitoring toxic vapors than the other available organic and polymeric material comparatively [2,3]. 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 [4]. The sol–gel technique is considered as the most promising technique for the preparation of metal oxides [5,6] and among the VOCs, benzene and its derivatives were confirmed to cause diversiform cancers [7]. The sensing behavior of benzene and toluene by metal oxides like SnO_2 [8], TiO_2 [9], doped ZnO [10] and WO_3 [11] focused our interest to utilize mixed metal composites containing metal aluminates for the above purpose. Though magnesium aluminate spinels were used as humidity sensors [12,13] there are no literatures found regarding nickel aluminate and Sr(II) added nickel aluminates for the purpose of sensing VOCs. In the present paper the newly developed Sr(II) added nickel aluminate composites by sol–gel technique were investigated for their sensing behavior towards benzene and toluene vapor.

2. Experimental

Sr(II) added $NiAl_2O_4$ 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 aluminium molar ratio as a constant were labeled as NiSA1, NiSA2, NiSA3, NiSA4, NiSA5 and NiSA6 respectively. The composites in the form of pellets were sintered at 900 °C for 5 h. The structural studies were carried out using a Philips X'pert diffractometer and the surface morphology was determined by a Leo-Jeol scanning electron microscope. The nitrogen adsorption–desorption isotherms were measured using Quantachrome Corp. Nova-1000 gas sorption analyzer. Electrical conductance measurements were determined by two-probe method and the samples were electrically connected to a dc power supply and a Keithley 485 picoammeter in series. The temperature dependent conductance experiments were carried out to determine the activation energies of the samples. The sensitivity tests were carried out in a testing chamber and VOCs were injected by a microsyringe into

* Corresponding author. Tel.: +91 44 28178200; fax: +91 44 28175566.
E-mail addresses: jjvijayaloyola@yahoo.co.in (J.J. Vijaya), ksnagi@vsnl.net (K.S. Nagaraja).

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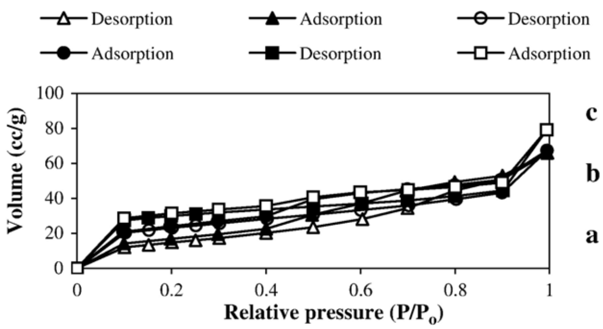

Fig. 1. Nitrogen adsorption/desorption isotherms of a) NiSA1, b) NiSA6, and c) NiSA5 at 77 K.

the test chamber. The sensing characteristics of the sensor were observed by measuring the electrical resistance change of the sensor when the latter was exposed to VOCs. A typical injection of 0.3 ml of VOCs corresponds to a gas concentration of about 100 ppm [14]. The sensitivity factor is defined as, $S_\mathrm{f} = \frac{R_\mathrm{air} - R_\mathrm{gas}}{R_\mathrm{gas}}$ where R_gas is the resistance of the sensor under gas exposure and R_air is the resistance of the sensor in air.

3. Results and discussion

3.1. N_2 adsorption/desorption isotherms

The nitrogen adsorption/desorption isotherms of NiSA1, NiSA6 and NiSA5 (mixed metal composite with maximum sensitivity) were carried out. The large increase in the nitrogen adsorption for NiSA1 at the higher relative pressures (Fig. 1) indicates that it contains only a mesoporous character. While the nitrogen adsorption for NiSA5 and NiSA6 considerably increased at a low relative pressure indicating the formation of micropores in addition to the presence of mesopores. The composite NiSA1 possessed a very low surface area of 55.02 m^2/g while NiSA6 and NiSA5 possessed 77.86 and 94.56 m^2/g respectively. This increase in surface area for NiSA5 can be attributed to the decrease in particle size due to the addition of Sr(II) in the nickel aluminate as a result of non-isomorphic substitution. The composite NiSA1 possessed only mesopore surface area while NiSA5 and NiSA6 had both micro and mesopore surface area. It was observed that there was a considerable increase in micropore surface area of 53.51 m^2/g for NiSA5 while NiSA6 had 33.96 m^2/g and NiSA1 had no micropore surface area. The introduction of micropores by the addition of Sr(II) in NiSA5 along with mesopores would lead to enhanced adsorption than NiSA1 and NiSA6 composites. This suggested that the NiSA1 sample inherited intragranular pores only in the mesopore range while NiSA6 possessed both micro and mesoporic ranges and thus the addition of Sr(II) in the nickel aluminate introduced intragranular micropores in addition to the mesopores in NiSA5 composite. It is observed that the average pore diameter of NiSA6 decreased by one order compared to that of NiSA1,

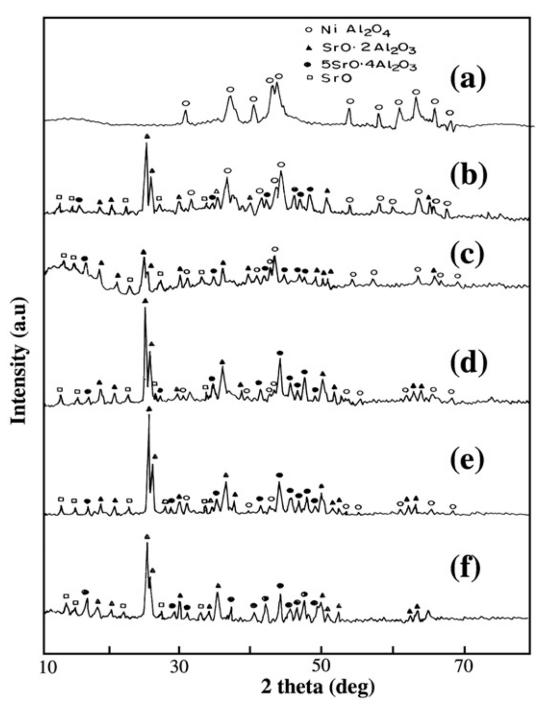

Fig. 2. X-ray diffraction spectra of a) NiSA1, b) NiSA2, c) NiSA3, d) NiSA4, e) NiSA5, and f) NiSA6.

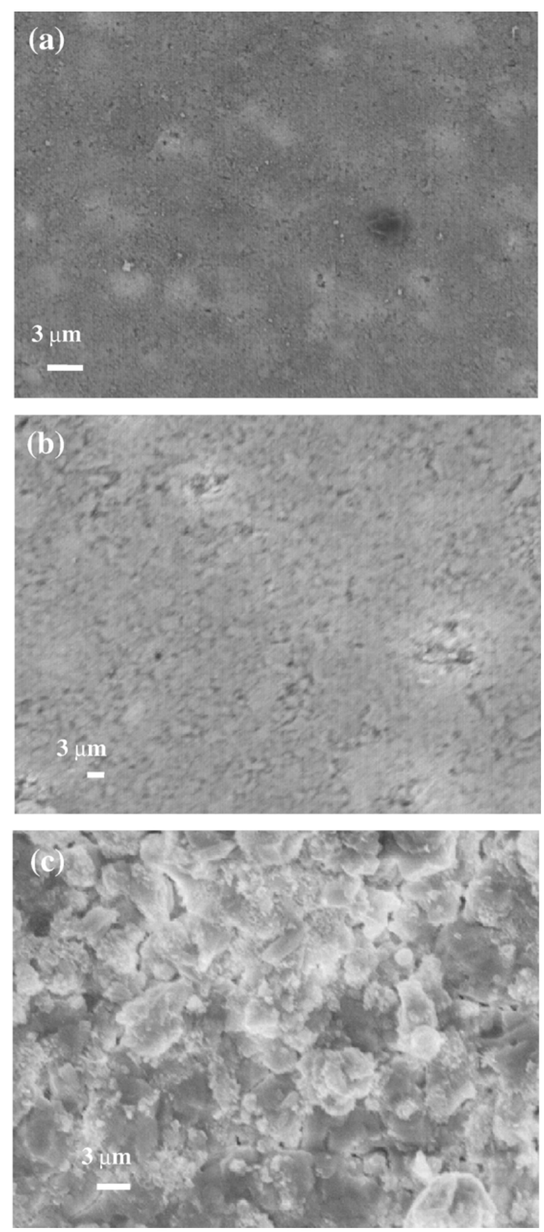

Fig. 3. SEM image of a) NiSA1, b) NiSA5 and c) NiSA6 composite.