Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 153 (2008) 767–774
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Utilization of strontium added $NiAl_2O_4$ composites for the detection of methanol vapors

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

[a] *Department of Chemistry, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai 600034, India*
[b] *Department of Environmental Technology, Central Leather Research Institute (CLRI), Chennai 600020, India*

Received 27 August 2006; received in revised form 9 April 2007; accepted 6 September 2007
Available online 8 September 2007

Abstract

Strontium added $NiAl_2O_4$ 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.

Keywords: Metal oxide composites; Ceramics; Sol–gel; Methanol vapor; Alcohol sensor

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

* 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).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.09.022

Table 1
Sample code, molar ratios and activation energy of Ni:Sr:Al for Sr added $NiAl_2O_4$ 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_2O_3 [13] and CeO_2–Fe_2O_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 $NiAl_2O_4$ 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 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 $\lambda = 0.154$ 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