December 2006 Volume 2 Issue 6

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 2(6), 2006 [215-222]

Strontium(II) Added $MgAl_2O_4$ Composites For Ammonia Detection

Corresponding Author

K.S.Nagaraja, J.Judith Vijaya
Department of Chemistry, Loyola Institute of Frontier Energy (LIFE), Loyola College, Chennai- 600 034, (INDIA).
Tel: +91-44-28178200, Fax: +91-44-28175566
E-mail: ksnagi@vsnl.net
jjvijayaloyola@yahoo.co.in

Co-Authors

L.John Kennedy, G.Sekaran
Department of Environmental Technology, Central Leather Research Institute (CLRI), Chennai - 600 020, (INDIA).

Received: 16th November, 2006
Accepted: 29th November, 2006

Web Publication Date: 27th December, 2006

ABSTRACT

Strontium(II) added $MgAl_2O_4$ composites prepared by sol–gel technique was utilized for the detection of ammonia vapors. XRD, SEM and BET surface area measurements were employed to identify the structural phases and surface morphology. The composites were prepared with the mole ratios of Mg: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 aluminium mole ratio as constant for all the compositions and were labeled as MgSA1, MgSA2, MgSA3, MgSA4, MgSA5 and MgSA6 respectively. The samples sintered at 900°C for 5 h were subjected to dc resistance measurements in the temperature range of 30-200°C to study the ammonia vapor detection characteristics. The results revealed that the sensitivity in detecting ammonia vapor increased with increase in temperature up to 150°C and thereafter decreased. The sensitivity increased with increase in ammonia concentration from 100-5000 ppm at 150°C. Among the composites MgSA5 showed the best sensitivity to ammonia detection at an operating temperature of 150°C.

KEYWORDS

Metal oxides;
Composites;
Ceramics;
Sol-gel;
Ammonia vapor.

INTRODUCTION

Ammonia is a kind of gas with high toxicity. But the determination of ammonia is needed and important for environmental monitoring and chemical processes controlling in industrial, agricultural and medical fields[1]. Recently their application in selective catalytic reduction (SCR) systems has gained importance[2]. SCR systems are employed in the exhaust system of commercial vehicles, combustion systems in power plants and in industrial boilers to monitor the emissions of NO_2 and NO. These gases are harmful by products of combustion processes. In an SCR converter ammonia serves as a reducing agent for nitrogen oxides converting them into environmentally safe nitrogen and water vapor. An ammonia sensor is required to calculate the amount of unreacted and excess ammonia, which is fed in to the inlet stream[3].

This necessitates the development of a selective ammonia sensor capable of detecting small quantities of ammonia. However the exposure to ammonia vapors irritates the skin and respiratory tract and causes potential lung damage[4]. The wide range of applications, toxicity and clinical implications of ammonia make imperative the need of development of a reliable and selective ammonia sensor. The main objective of the present work is to study the effect of addition of Sr(II) on magnesium aluminates rather than the isomorphic substitution. In the present paper the newly developed Sr(II) added magnesium aluminate composites by sol-gel technique were characterized by X-ray diffraction, scanning electron microscopy and nitrogen adsorption/desorption isotherm at 77K. The dependence of electrical response of these composites to the ammonia vapor was investigated.

EXPERIMENTAL

Sr(II) added $MgAl_2O_4$ composites with the mole ratios of Mg: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 mole ratio constant for all compositions as shown in TABLE 1, were prepared by the sol-gel route using nitrates of magnesium, strontium and aluminum. Calculated amounts of these metal nitrates of analytical grade were dissolved in water and 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 gellation 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 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 mole ratio is shown in TABLE 1.

TABLE 1: Sample code, mole ratios and activation energy of Mg:Sr:Al for Sr added $MgAl_2O_4$ composites

S.No.	Sample code	Mole ratios of Mg: Sr: Al	Ea (eV)
1	MgSA1	1.0:0.0:2.0	0.324
2	MgSA2	0.8:0.2:2.0	0.297
3	MgSA3	0.6:0.4:2.0	0.259
4	MgSA4	0.4:0.6:2.0	0.216
5	MgSA5	0.2:0.8:2.0	0.188
6	MgSA6	0.0:1.0:2.0	0.292

The structural studies were carried out using a Philips X'pert diffractometer for 2θ values ranging from 10 to 80° using CuKa radiation at λ=0.154 nm. The samples were scanned in the spectral range 4000-400cm^{-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 77K. 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 most widely used 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[5] was applied to calculate the micropore volume and external surface area. The total pore volume was estimated as liquid volume of adsor-

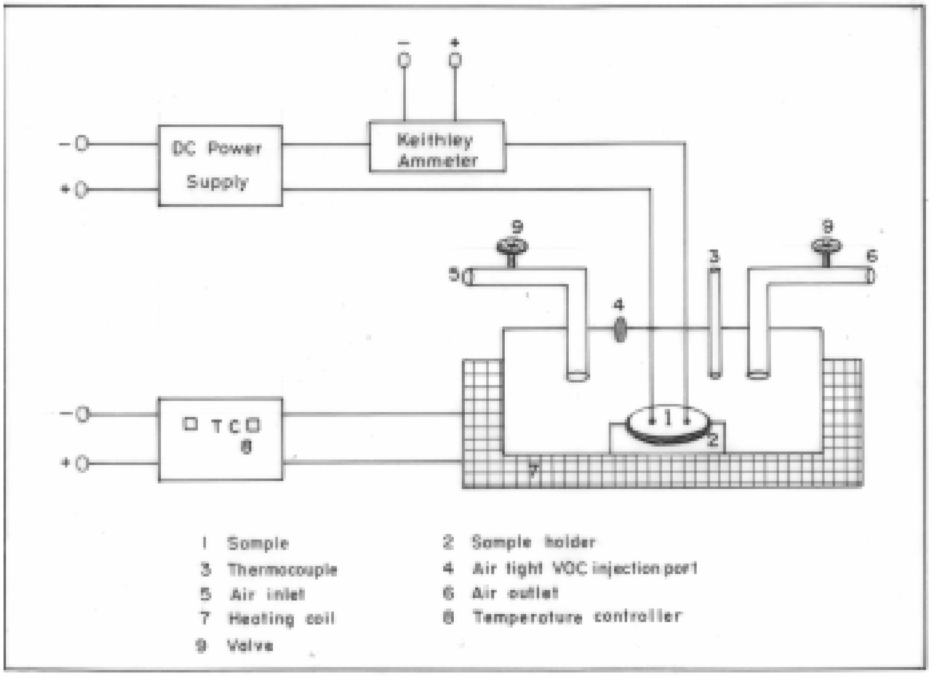

Figure 1: Schematic diagram of the experimental set-up used to measure the ammonia vapor responses

bate 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, $I = I_0 \exp^{-Ea/kT}$, 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 designed for the present study (Figure 1) that measures the surface resistance of the samples. Ammonia 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 was exposed to ammonia. A typical injection of 0.3ml of ammonia corresponds to a gas concentration of about 100 ppm[6]. Under the exposure of reducing gas such as alcohol, its resistance decreases. The sensitivity factor S_f is defined as,

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

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 to 5000 ppm) of ammonia.

RESULTS AND DISCUSSION

X-ray diffraction studies

The XRD measurements were carried out to characterize the different phases of the composites. The X-ray diffraction patterns of magnesium aluminate and strontium added magnesium aluminate samples are shown in the figures 2a-f. The XRD spectra of figure 2a showed peaks corresponding to magnesium-aluminate spinel like phase (JCPDS: 03-0901). As the concentration of the strontium was increased, the evolution of $SrAl_2O_4$ peaks in addition to SrO phase (JCPDS:01-0886) was observed. After a careful comparison between the standard JCPDS profiles and the experimental results it was found that the phases such as $5SrO{\cdot}4Al_2O_3$ (JCPDS: 09-38) and $SrO{\cdot}2Al_2O_3$ (JCPDS:25-1208) were recognized for the higher strontium added composites. The addition of more strontium retards the growth of bulk magnesium aluminate phase on the surface and forms new phases $5SrO{\cdot}4Al_2O_3$ and $SrO{\cdot}2Al_2O_3$. The presence of different phases in MgSA5 as shown in XRD

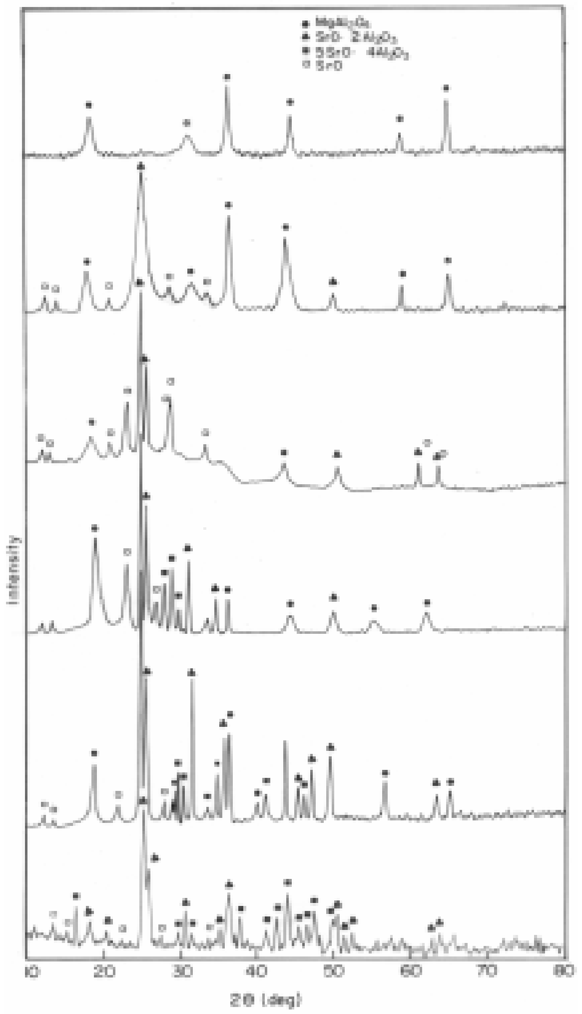

Figure 2: X-Ray diffraction spectra of (a) MgSA1, (b) MgSA2, (c) MgSA3, (d) MgSA4, (e) MgSA5, and (f) MgSA6

TABLE 2: Surface area parameters of MgSA1, MgSA2 and MgSA6 composites

S.No.	Parameters	MgSA1	MgSA6	MgSA5
1	S_{BET} (m^2/g)	100.50	77.86	230.10
2	S_{mic} (m^2/g)	55.28	33.96	140.00
3	S_{meso} (m^2/g)	45.22	43.9	90.00
4	Total pore volume (cm^3/g)	0.123	0.104	0.208
5	Micropore volume (cm^3/g)	0.030	0.020	0.076
6	Mesopore volume (cm^3/g)	0.093	0.084	0.132
7	Average pore diameter (nm)	4.89	5.34	3.624

S_{BET} BETsurface area, S_{mic} micropore surface area, S_{meso} mesopore surface area

was taken as the criteria for good ammonia sensing[7].

Surface morphology (SEM)

Figures 3a-c shows the surface morphology of the composites MgSA1, MgSA5 and MgSA6 and it depicts the intergranular porous structure of the composite materials qualitatively. The highly porous structure of MgSA5 compared to MgSA1 and MgSA6 suggest that the addition of more strontium in the magnesium aluminate can reduce the particle size with the intergranular pores leading to microporosity in addition to the presence of mesopores.

N_2 adsorption/desorption isotherms

Figure 4 represents the nitrogen adsorption/desorption isotherms at 77K of the magnesium aluminate (MgSA1), strontium aluminate (MgSA6) and the mixed metal composite that possessed maximum sensitivity (MgSA5) respectively. The isotherms of

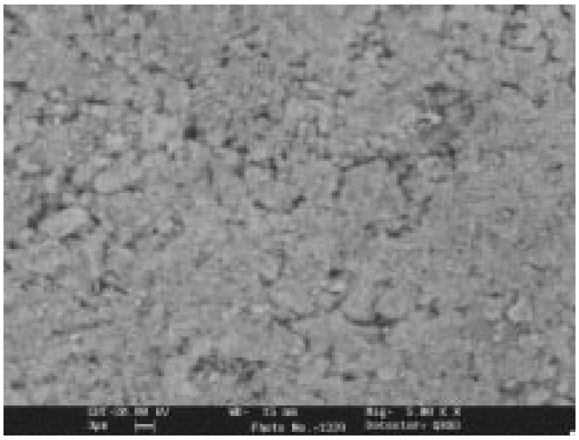

Figure 3a: SEM image of MgSA1 composite

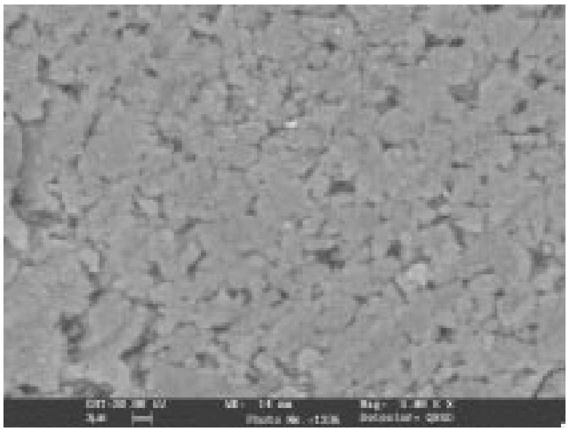

Figure 3b: SEM image of MgSA5 composite

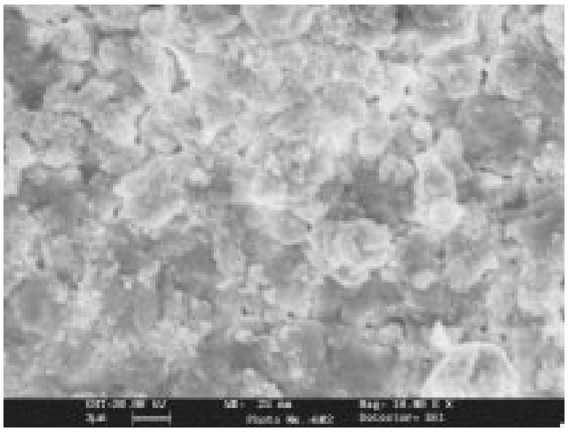

Figure 3c: SEM image of MgSA6 composite

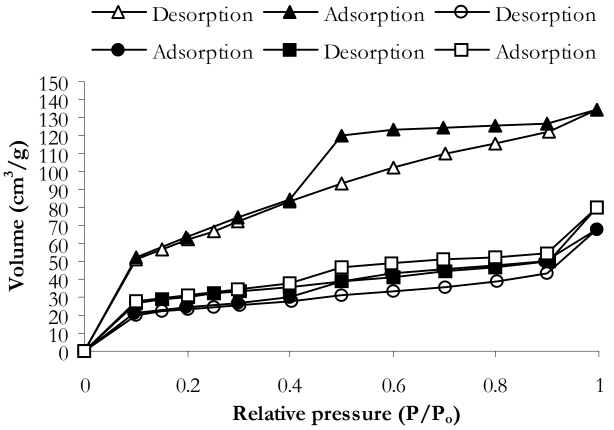

Figure 4: Nitrogen adsorption/desorption isotherms of a) MgSA6 b) MgSA1 c) MgSA5 at 77K

MgSA1 and MgSA5 and MgSA6 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 increase in uptake of nitrogen in the samples is a result of the major increase in porosity created within the magnesium aluminate, strontium aluminate and strontium added magnesium aluminate components. The composite material MgSA5 exhibited the most prominent hysterisis effect, which can be characterized by the formation of intergranular pores as a result of Sr(II) addition. The amount of nitrogen adsorbed increased to 134.75 cm^3/g for MgSA5 and that for pure magnesium aluminate (MgSA1) and strontium aluminate (MgSA6) composites were only 79.52 and 67.28 cm^3/g respectively.

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 MgSA1 possessed a low surface area of 100.50 m^2/g while MgSA6 possessed 77.86 m^2/g. But the mixed metal composite MgSA5 possessed an increase in BET surface of 230.10 m^2/g. This increase in surface area for MgSA5 can be attributed to the decrease in particle size due to the addition of Sr(II) in the magnesium aluminate composites as a result of non-isomorphic substitution. The pores could be generated within the three components of oxides of magnesium, strontium and aluminum matrices. Consequently pores of different dimensions are produced. 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 90.00 m^2/g for MgSA5 while MgSA6 and MgSA1 had 33.96 m^2/g 55.28 m^2/g respectively. These results suggest that Sr(II) addition in the composites could lead to the modification of the intergranular pores controlling the range of surface area.

The mixed metal composite MgSA5 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 MgSA5 was significantly observed than the other two MgSA1 and MgSA6 systems. 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 Sr(II) addition in the MgSA5 matrices along with the micropores and mesopores would lead to enhanced ammonia adsorption with higher sensitivity than the pure magnesium aluminate MgSA1 and strontium aluminate MgSA6 composites. The surface area parameters of MgSA1, MgSA5 and MgSA6 composites are shown in TABLE 2.

Thus the addition of strontium in the magnesium aluminate species introduced more intragranular micropores in addition to the mesopores in MgSA5 composite. In addition it was observed that MgSA5 possessed the highest micropore volume compared to the pure strontium and magnesium aluminate composites. This suggests that the combination of mixed metals can introduce more micropores in addition to the available mesopores which in turn indicate that the combination of mixed metal oxides such as strontium, magnesium and aluminium oxide can be considered as a suitable matrix for the production of microporous and mesoporous materials.

Pore size and pore distribution

Figure 5 shows the pore size distribution of MgSA1, MgSA5 and MgSA6 composites. The average pore size distribution dependent mainly on one or more combination of metal oxides in the composites. The average pore diameters of MgSA1, MgSA6 and MgSA5 composites were 4.89, 5.34 and 3.62 nm respectively. The average pore diameters obtained from the composites is due to the formation of intragranular pores within the combination of metal oxides. The pore diameter is reduced in the case of mixed metal composite (MgSA5) to 3.62 nm. This reduction in the average pore diameter is attributed to the addition of more Sr(II) along with magnesium aluminate composition as a result of nonisomorphic substitution. The presence of Sr(II) retards the growth of bulk magnesium aluminate phase leading to an increase in porosity by introducing more micropores along with mesopores.

Electrical conductance studies

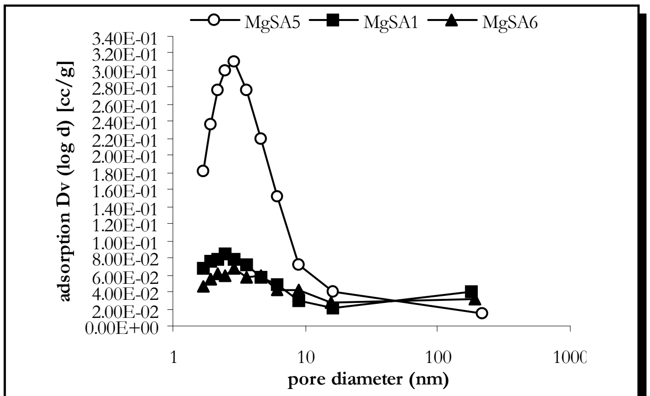

Figure 5: Pore size distribution of MgSA1, MgSA5 and MgSA6 composites

The room temperature electrical conductance measurements of the composites prior to ammonia sensing measurements signified that the current increased linearly with the applied voltage, indicating the ohmic contact 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.

Ammonia-sensing measurements

The sensitivity of Sr(II) added $MgAl_2O_4$ composites to ammonia at different concentrations (100-5000ppm) and at different temperatures (30-200°C) was studied through electrical conductance measurements. Figure 6 shows the sensitivity of the composites at 1000 ppm of ammonia concentration in the temperature range of 30-200°C. The sensitivity increases with increase in temperature from 30-150°C and thereafter decreases for all the composites. It was observed that the sensitivity to ammonia vapors of the pure $MgAl_2O_4$ was lesser than the Sr(II) added composites. The maximum sensitivity for all the composites was obtained at 150°C compared to the other studied temperatures. Hence the operating temperature for detecting ammonia vapor was fixed

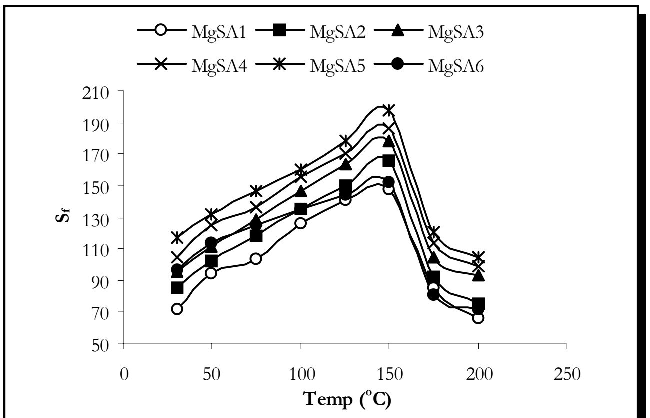

Figure 6: Sensitivity of composites to ammonia (1000ppm) at different temperatures

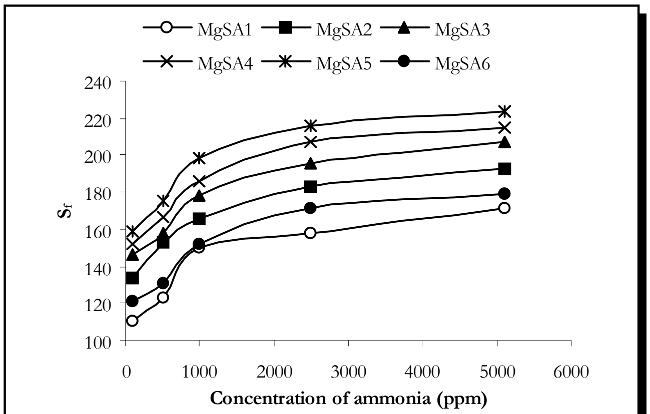

Figure 7: Sensitivity of composites to ammonia at different concentrations and at 150°C

as 150°C. It shows that at 150°C most of the adsorbed oxygen species would have reacted with the OH group of ammonia vapor. This adsorbed oxygen creates a space charge region near the surface of the composite by extracting electrons from the material. Ammonia, 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 150°C indicates that the equilibrium density of chemisorbed oxygen ions is maximum at this temperature.

It is evident from figure 7 that varying in the concentration of ammonia from 100-5000 ppm at 150°C the sensitivity increases up to 1000 ppm with a higher rate of increase in sensitivity 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 ammonia vapor adsorption. At higher concentration the rate of adsorption decreases due to less assess of ammonia vapors into the filled pores leading to less increase in sensitivity values. The increase in porosity with increase in Sr(II) content as evidenced from SEM image and BET studies confirmed the presence of more sites for ammonia adsorption, which produces more charge carriers for electrical conduction.

Principle of ammonia detection

The mechanism of the ammonia detection by the composites can be described as follows:

Semiconducting metal oxide gas sensors are based on the conductivity changes of he semiconductor materials upon interaction with target gas molecules. When gas molecules are adsorbed on the surface of a semiconductor, electron transfer occurs between the semiconductors and the adsorbates. The chemical reactions involved during the gas sensing can be summarized as follows:

The first step is the adsorption of oxygen molecules in air on the sensor surface. The electrons are obtained by the oxygen molecules adsorbed from the sensor. In the second step, ammonia is reacted with the adsorbed oxygen and the electrons are returned to the sensor. As the result, the sensor conductivity increases. Hence the adsorbed oxygen for sensor at first step is very important. If the electron density is high at the sensor surface, the concentration of adsorbed oxygen ($O^{-}_{(ads)}$) becomes high.

$$o_{2(ads)} + e^{-} \Leftrightarrow O_2{}^{-}{}_{(ads)} \quad (1)$$

$$o_{2(ads)} + e^{-} \Leftrightarrow 2O_2{}^{-}{}_{(ads)} \quad (2)$$

$$2NH_{3(ads)} + 5O^{-}{}_{(ads)} + O_2 \Leftrightarrow 2NO_2 + 3H_2O + 5e^{-} \quad (3)$$

CONCLUSIONS

A study on the ammonia detection characteristics of Sr(II) added $MgAl_2O_4$ composites prepared by sol-gel technique have been carried out. The results suggest that increase in the concentration of Sr(II) can increase the porosity resulting in higher sensitivity values. The XRD patterns suggested the formation of single phase for magnesium aluminate composite while multiphasing was observed in the

Sr(II) added magnesium aluminate composites. It was observed that the sensitivity of the composites to ammonia was higher at 150°C, which may be the saturation point of the redox reaction between the ammonia vapor and the adsorbed oxygen species. The sensing properties of the composites were studied for different concentrations at 150°C and found to be increase with ammonia concentration. The increase in surface area and porosity as shown by nitrogen adsorption-desorption isotherms and pore size distribution, with the introduction of more micropores makes the composite MgSA5 to be a better composite for ammonia detecting applications as evidenced by the comparatively higher sensitivity value.

ACKNOWLEDGEMENTS

We thank the Loyola college management for extending constant support throughout the study.

REFERENCES

[1] S.G.Wang, Q.hang, D.J.yang, P.J.Sellin, G.F.Zhong; Diamond Related Mater., **13**, 1327 **(2004)**.

[2] R.Moos, R.Muller, C.Plog, Evic, H.Leye, E.Irion, T.Bruan, K.Marquardt, K.Binder; Sens.Actuators B, **83**, 181 **(2002)**.

[3] A.K.Prasad, D.J. Kubinski, P.I. Gouma; Sens.Actuators B, **93**, 25 **(2003)**.

[4] B.Timmer, W.Olthuis, A.Berg; Sens.Actuators B, **107**, 666 **(2005)**.

[5] S.J.Gregg, K.S.W. Sing; 'Adsorption, Surface area and Porosity', 100-125, Academic Press, London, **(1982)**.

[6] M.Sunita, C.Ghanshyam, N.Ram, S.Singh, R.P.Bajpai, R.K.Bedi; Bull.Mater.Sci., **25**, 231 **(2002)**.

[7] J.Judith Vijaya, L.J.Kennedy, G.Sekaran, B.Jeyaraj, K.S.Nagaraja; Sens.Actuators B, (article in press), **(2006)**.