

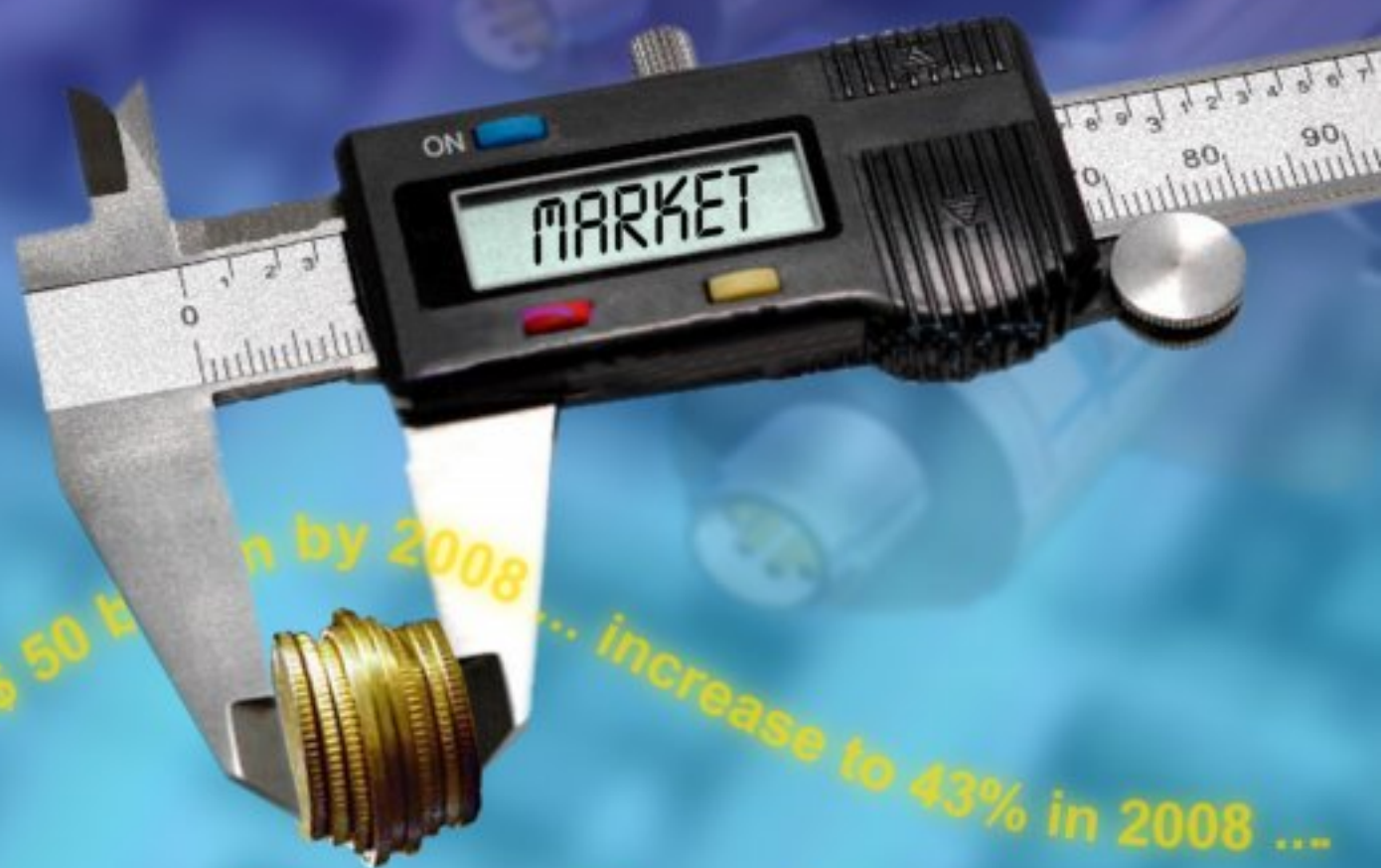
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## Sensor Market Trends

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## Methanol Sensing Behavior of Strontium(II) Added $MgAl_2O_4$ Composites Through Solid-State Electrical Conductivity Measurements

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**Abstract:** Strontium(II) added  $MgAl_2O_4$  composites prepared by sol – gel technique was utilized for the detection of methanol vapors. XRD, SEM and BET surface area measurements were employed to identify the structural phases and surface morphology. The composites were prepared with the molar 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 molar 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 methanol vapor detection characteristics. The results revealed that the sensitivity in detecting methanol vapor increased with increase in temperature up to 150 °C and thereafter decreased. The sensitivity increased with methanol concentration from 100-5000 ppm at 150°C. Among the different compositions of the composites MgSA5 showed the best sensitivity to methanol detection at an operating temperature of 150°C.

**Keywords:** Metal oxide composites; Ceramics; Sol – gel preparation; Methanol vapor; Electrical conductivity.

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## 1. Introduction

Methanol is a 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 [1]. The wide range of applications, toxicity and clinical implications of methanol make imperative the need of development of a reliable and selective methanol sensor. Semiconducting oxides have emerged as economical sensors for monitoring methanol 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] as it allows for high purity ceramics with homogeneous distribution of components on the atomic scale. The main objective of the present work is to study the effect of addition of Sr(II) on magnesium aluminates rather than the isomorphous 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 methanol vapor was investigated.

## 2. Experimental

Sr(II) added  $\text{MgAl}_2\text{O}_4$  composites with the molar 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 molar ratio constant for all compositions as shown in table 1, were prepared by the sol-gel route using nitrates of magnesium, strontium and aluminum.

**Table 1.** Sample code, molar ratios and activation energy of Mg: Sr: Al for Sr added  $\text{MgAl}_2\text{O}_4$  composites.

S.No.	Sample code	Molar 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

Calculated amounts of these metal nitrates of analytical grade were dissolved in water and citric acid was added as the gelling agent. 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 structural studies were carried out using a Philips X'pert diffractometer at  $\lambda = 0.154$  nm. The surface morphology of the sintered porous compacts was determined by a Leo-Jeol scanning electron microscope. The nitrogen adsorption-desorption isotherms of the composites were measured using an automatic adsorption instrument (Quantachrome Corp. Nova-1000 gas sorption analyzer). The surface area ( $\text{m}^2/\text{g}$ ) of the composites was calculated using BET equation and the pore size distribution was determined using the BJH method. In addition, the t-plot method [7] was applied to calculate the micropore volume and external surface area. 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. The temperature dependent conductance experiments were carried out to determine the activation energies of the samples using the linearised form of the expression,  $I = I_0 \exp^{-E_a/kT}$ , 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 sensitivity tests were carried out in a testing chamber designed for this study (Fig.1) 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 was exposed to methanol. A typical injection of 0.3ml of methanol corresponds to a gas concentration of about 100 ppm [8, 9]. 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 methanol.

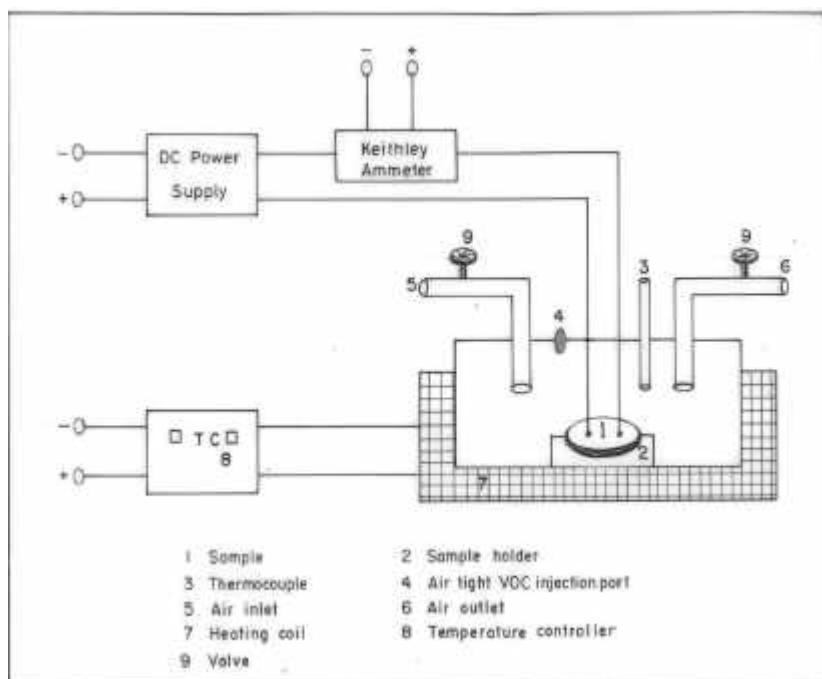


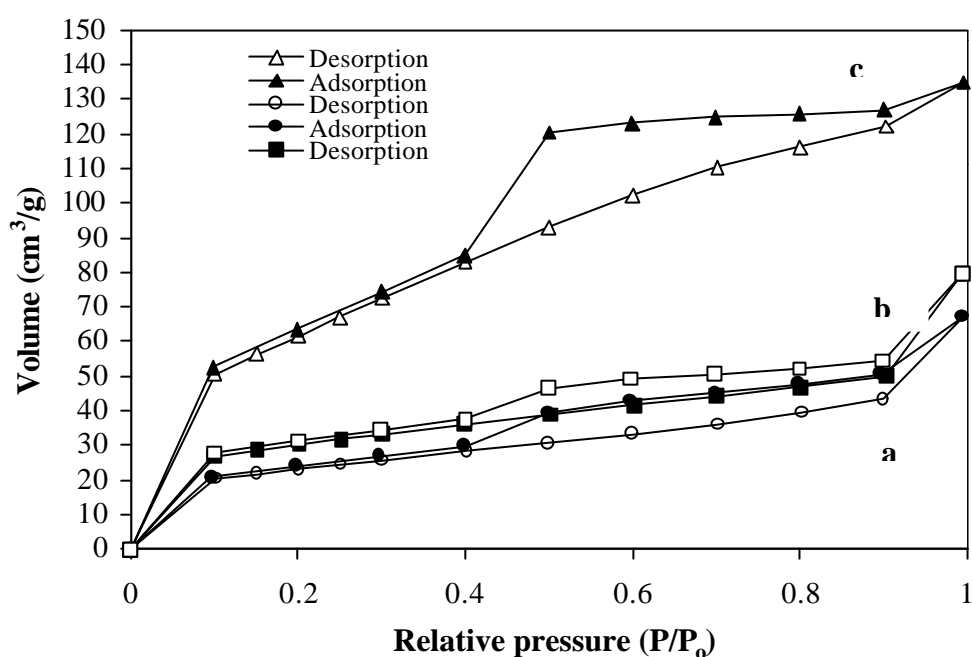
Fig. 1. Schematic diagram of the experimental set-up used to measure the methanol vapor responses.

### 3. Results and Discussion

#### 3.1 N<sub>2</sub> adsorption/desorption isotherms

Fig. 2 represents the nitrogen adsorption/desorption isotherms at 77K of the magnesium aluminate (MgSA1), strontium aluminate (MgSA6) and Sr(II) added magnesium aluminate composite that possessed maximum sensitivity (MgSA5) respectively. The amount of nitrogen adsorbed increased to 134.75 cm<sup>3</sup>/g for MgSA5 and that for pure magnesium aluminate (MgSA1) and strontium aluminate

(MgSA6) composites were only 79.52 and 67.28 cm<sup>3</sup>/g respectively. The composite MgSA1 possessed a low surface area of 100.50 m<sup>2</sup>/g while MgSA6 possessed 77.86 m<sup>2</sup>/g. But MgSA5 possessed an increase in BET surface of 230.10 m<sup>2</sup>/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 MgAl<sub>2</sub>O<sub>4</sub> composites as a result of non-isomorphic substitution. It was observed that there was a considerable increase in micropore surface area of 90.00 m<sup>2</sup>/g for MgSA5 while MgSA6 and MgSA1 had 33.96 m<sup>2</sup>/g 55.28 m<sup>2</sup>/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 increase in total pore volume for MgSA5 was significantly observed than the other two MgSA1 and MgSA6 composites. The increase in micropore and mesopore volume can be attributed to the decrease in particle size with more addition of Sr(II). The values from Table 2 indicate that the addition of more Sr(II) in magnesium aluminate matrix (MgSA5) would lead to enhanced methanol adsorption with higher sensitivity than the MgSA1 and MgSA6 composites. In addition it was observed that MgSA5 possessed the highest micropore volume compared to the MgSA1 and MgSA6 composites.



**Fig.2.** Nitrogen adsorption/desorption isotherms of a) MgSA6 b) MgSA1 c) MgSA5 at 77K.

**Table 2.** Surface area parameters of MgSA1, MgSA2 and MgSA6 composites.

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

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

Fig.3 shows the pore size distribution of MgSA1, MgSA5 and MgSA6 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 reduction in the average pore diameter in MgSA5 is attributed to the addition of more Sr(II) along with magnesium aluminate composition as a result of non-isomorphic 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.

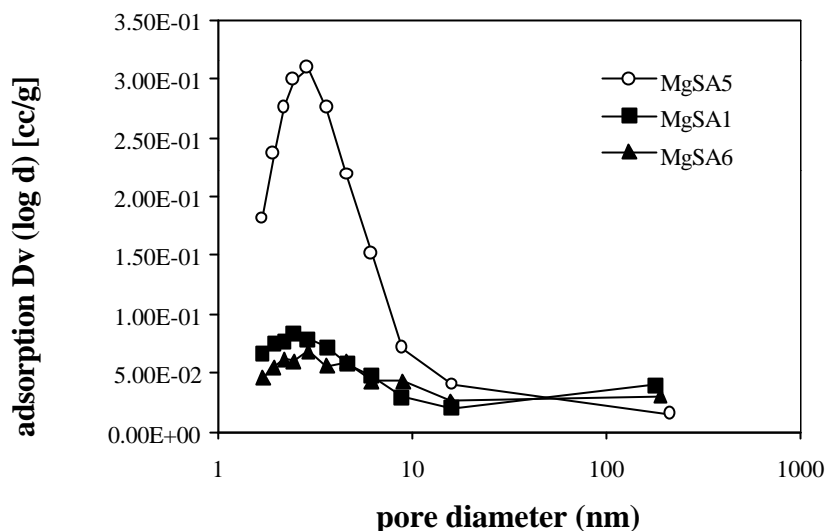
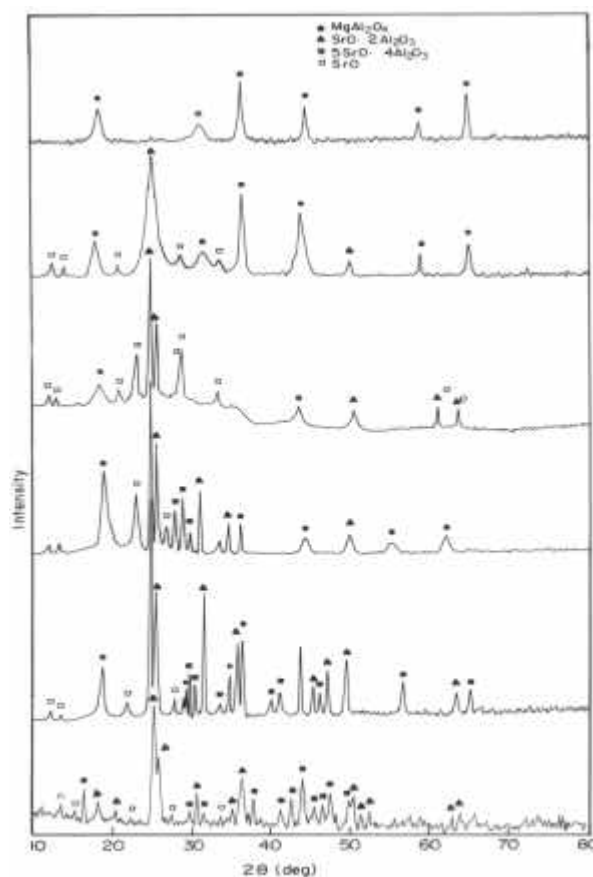


Fig. 3. Pore size distribution of MgSA1, MgSA5 and MgSA6 composites.

### 3.2 X-Ray diffraction studies

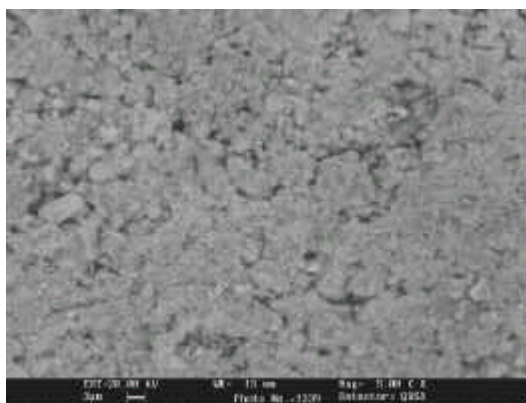
The XRD patterns of magnesium aluminate and Sr(II) added magnesium aluminate samples are shown in the Figs. 4a-f. The XRD spectra of Fig. 4a showed peaks corresponding to magnesium-aluminate spinel phase (JCPDS: 03-0901). As the concentration of the strontium was increased, the evolution of  $\text{SrAl}_2\text{O}_4$  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  $5\text{SrO}\cdot 4\text{Al}_2\text{O}_3$  (JCPDS: 09-38) and  $\text{SrO}\cdot 2\text{Al}_2\text{O}_3$  (JCPDS: 25-1208) were recognized for the higher Sr(II) added composites. The addition of more Sr(II) retards the growth of bulk magnesium aluminate phase on the surface and forms new phases  $5\text{SrO}\cdot 4\text{Al}_2\text{O}_3$  and  $\text{SrO}\cdot 2\text{Al}_2\text{O}_3$ . The presence of different phases in MgSA5 as shown in XRD was taken as the criteria for good methanol sensing [10].



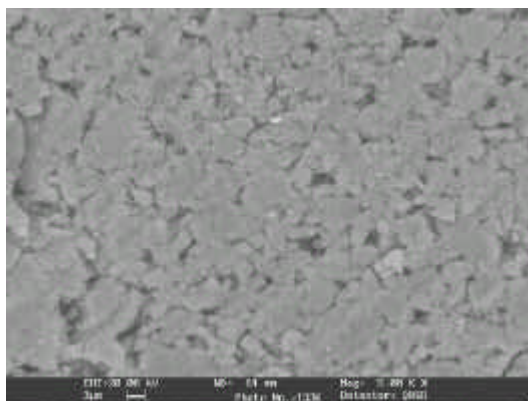
**Fig. 4.** X-Ray diffraction spectra of a) MgSA1, b) MgSA2, c) MgSA3, d) MgSA4, e) MgSA5, and f) MgSA6.

### 3.3 Surface morphology (SEM)

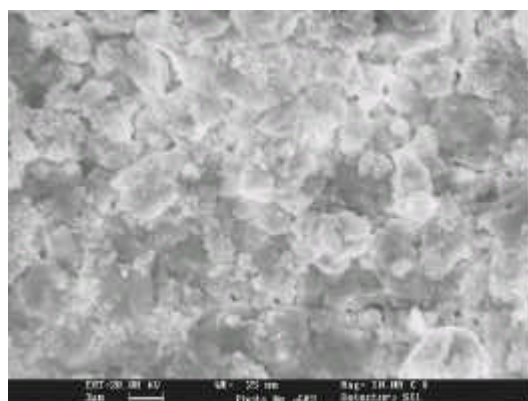
Figs. 5a-c shows the surface morphology of the composites MgSA1, MgSA5 and MgSA6 and it depicts the intergranular porous structure of the composite materials qualitatively. The highly porous structure of MgSA5 compared to MgSA1 and MgSA6 suggest that the addition of more Sr(II) in the magnesium aluminate can reduce the particle size with the intergranular pores leading to microporosity in addition to the presence of mesopores.



**Fig. 5a.** SEM image of MgSA1 composite.



**Fig. 5b.** SEM image of MgSA5 composite.



**Fig. 5c.** SEM image of MgSA6 composite.

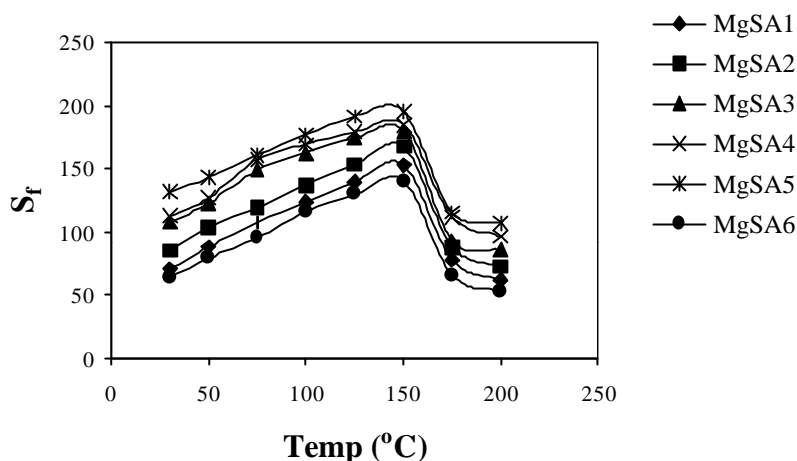
### 3.4 Electrical conductance studies

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 contact of the electrodes. 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 [11].

### 3.5 Methanol-sensing measurements

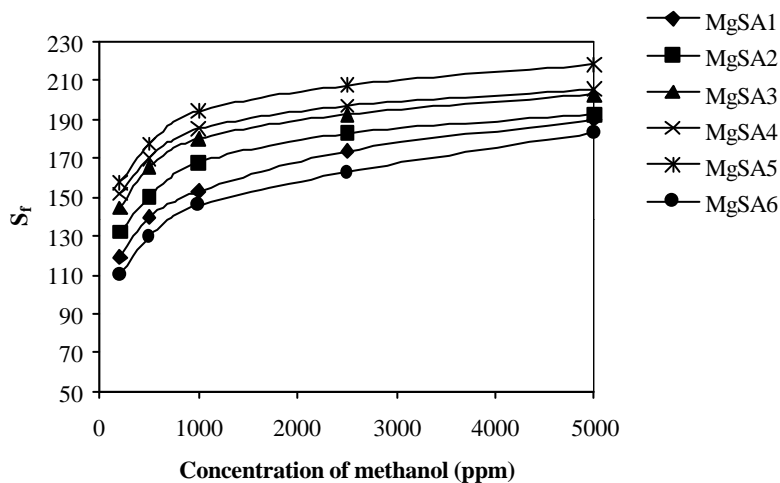
The sensitivity of Sr(II) added  $MgAl_2O_4$  composites to methanol at different concentrations (100-5000ppm) and at different temperatures (30-200°C) was studied through electrical conductance measurements. Fig.6 shows the sensitivity of the composites at 1000 ppm of methanol concentration in the temperature 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 methanol vapors of MgSA1 and MgSA5 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 methanol vapor was fixed as 150°C. It shows that at 150°C 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 150°C indicates that the equilibrium density of chemisorbed oxygen ions is maximum at this temperature.



**Fig. 6.** Sensitivity of composites to methanol (1000ppm) at different temperatures.

It is evident from Fig.7 that varying in the concentration of methanol 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 methanol vapor adsorption. At higher concentration the rate of adsorption decreases due to less access of methanol 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 methanol adsorption, which produces more charge carriers for electrical conduction. In addition the SEM photographs also reveal that increase in the Sr(II) addition produces fine particles with smaller dimensions compared with the other indicating that smaller the particle size higher will be the surface energy and the adsorption capacity. Thus the composite MgSA5 possessed comparatively a higher sensitivity factor of while that of the pure magnesium aluminate MgSA1 and pure strontium aluminate MgSA6 had only and 111 respectively at an optimum temperature of 150°C at 1000 ppm.



**Fig.7.** Sensitivity of composites to methanol at different concentrations and at 150°C.

### 3.6 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



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:



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 an electron which actually causes the conductivity to increase.

### 3.7 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 in to the mesopores ( $5 < d < 50$  nm) and then to the micropores ( $d < 2$  nm). As the molecular size of methanol is about 0.35 nm [12], 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 MgSA5 that possessed more micropores than the pure MgSA1 and MgSA6 composite. Thus the addition of Sr(II) into magnesium aluminate matrix introduces more micropores that leads to an enhanced methanol adsorption followed by oxidation. For the composite MgSA5 used in the present work, the presence of considerable range of mesopore volume 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 access for the methanol molecule into the narrow mesopores 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 then the pore blockage might have occurred due to aggregation of adsorbate molecules or due to the smaller cross sectional area of the micropores. Therefore a pure microporous or mesoporous material would not have favored higher sensitivity towards methanol. Thus the high sensitivity of MgSA5 can be

explained by the fact that the composite containing considerable mesopore and micropore would result in favorable methanol adsorption to get easy access to the composite interior.

## 4. Conclusions

A study on the methanol 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. It was observed that the sensitivity of the composites to methanol was higher at  $150^\circ C$ , 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  $150^\circ C$  and found to be increasing with methanol concentration. The increase in surface area and porosity with the introduction of micropores makes the composite MgSA5 to be a better candidate for methanol detecting applications as evidenced by the comparatively higher sensitivity value.

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## References

- [1]. T. Godish, Indoor Air pollution control, Lewis Publishers, MI, USA, (1991) pp. 310-320.
- [2]. C. Cantalini, M. Pelino, Microstructure and humidity sensitive characteristics of  $Fe_2O_3$  ceramic sensor, *J. Am. Ceram. Soc.*, 75 (1992) 546-551.
- [3]. H. Yagi, M. Nakata, Humidity sensor using  $Al_2O_3$ ,  $TiO_2$  and  $SnO_2$  prepared by sol-gel method, *J. Ceram. Soc. Jpn.*, 100 (1992) 152-156.
- [4]. F.J. He, T. Yao, B.D. Qu, J.S. han, A.B. Yu, Gas sensitivity of Zn doped  $\alpha-Fe_2O_3$  ( $SO_4$ -, Sn, Zn) to carbon monoxide, *Sens. Actuators B* 40 (1997) 183-186.
- [5]. E. Traversa, G. Gnappi, A.M. Gusmano, Ceramic thin films by sol-gel processing as novel materials for integrated humidity sensors, *Sens. Actuators B* 31 (1996) 59-70.
- [6]. C.O. Arian, M.P. Mentrui, E.E. Platero, F.X.L. Xamena, J.B. Parra, Sol-gel method for preparing high surface area  $CoAl_2O_4$  and  $Al_2O_3-CoAl_2O_4$  spinels, *Mater. Lett.*, 39 (1999) 22-27.
- [7]. S.J. Gregg, K.S.W. Sing, Adsorption, surface area and porosity, Academic Press, London, (1982) pp.100-125.
- [8]. M. Sunita, C. Ghanshyam, N. Ram, S. Singh, R.P. Bajpai, R.K. Bedi, Bull., Alcohol sensing of tin oxide thin film prepared by sol-gel process, *Mater. Sci.*, 25 (2002) 231-234.
- [9]. S. Pokhrel, L. Huo, H. Zhao, S. Gao, Sol-gel derived polycrystalline  $Cr_{10}Ti_{0.2}O_3$  thick films for alcohol sensing application, *Sens. Actuators B* (2006) (article in press).
- [10]. J. Judith Vijaya, L.J. Kennedy, G. Sekaran, B. Jeyaraj, K.S. Nagaraja, Effect of Sr addition on the humidity sensing properties of  $CoAl_2O_4$  composites, *Sens. Actuators B* (2006) (article in press).
- [11]. R. Sundaram, E. S. Raj, K.S. Nagaraja, Solid state electrical conductivity studies and humidity sensing studies on metal molybdate-molybdenum trioxide composites, *Sens. Actuators B* 101 (2004) 353-360.
- [12]. R. Tahery, J. Satherly, H. Modarress, Scaled particle theory: Relationships between compressibility, surface tension and molecular diameter, *Cell. Mol. Biol. Lett.* 9 (2004) 129-132.

