

TABLE I
Characterization data for sulphoxides Ar-SO-CH₃

Ar	Yield, %	B.P./mm, (M.P.), °C		Reference	S=O (ν cm ⁻¹)*
		Found	Literature		
C ₆ H ₅	80	118-20/5	144/15	8	1030
<i>p</i> -CH ₃ C ₆ H ₄	86	138-40/12 (42)	113-4/2 (42-43)	8	1030
<i>o</i> -CH ₃ C ₆ H ₄	85	138-9/9.5	1032
<i>p</i> -ClC ₆ H ₄	86	135-6/5 (48)	135-6/5 (47-48)	8	1028
<i>p</i> -BrC ₆ H ₄	95	(87)	(86-87)	9	1033**
<i>p</i> -CH ₃ OC ₆ H ₄	75	152-3/5	153-4/5	8	1035
<i>o</i> -CH ₃ OC ₆ H ₄	77	148-50/5	1025

* IR spectra were recorded on Perkin-Elmer 257 (neat).

** IR spectra in KBr pellet.

TABLE II
Ar-SO₂-CH₃

Ar	Yield, %	M.P., °C		Reference
		Found	Literature	
C ₆ H ₅	60	88	88	1
<i>p</i> -CH ₃ C ₆ H ₄	65	88-89	89	11
<i>p</i> -ClC ₆ H ₄	62	96	96	12
<i>p</i> -BrC ₆ H ₄	70	99	99-100	9

solution of the aryl methyl sulphide (0.03 mole) in glacial acetic acid (25 ml), kept on a water-bath and allowed to stand for an hour. It was cooled, poured into crushed ice, stirred and the precipitated sulphone was collected on a filter and recrystallised from suitable solvents.

Kinetics of oxidation to sulphoxide are under investigation.

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CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL ON MgAl_{2-x}Fe_{2x}O₄

THE catalytic properties of transition metal ions (Ni, Cr) in the environment of a diamagnetic matrix (MgAl₂O₄) has attracted a lot of attention in recent years^{1,2}. Reports on the catalytic activity of the system MgAl_{2-x}Fe_{2x}O₄ are not available although this system shows interesting variation in the electrical and magnetic properties as x varies from 0 to 2^{3,4}. This system is also interesting structurally, as while MgAl₂O₄ is a normal spinel,

the end member MgFe_2O_4 with $x = 2$, is an inverse spinel. The present investigation is a part of our earlier studies on the catalytic activity of spinels⁵.

The catalysts have been prepared by the co-precipitation of hydroxides of Mg, Al and Fe at an optimum pH (9.5) from the respective nitrates. The completion of precipitation of each ion was checked independently. The precipitates were dried at 100° C and calcined at 950° C for 24 hours. The solid solutions formed were characterized by TGA, DTA and chemical analyses as well as by X-ray diffraction patterns. Isopropyl alcohol (BDH AnalaR) was distilled before use and its purity checked by using a chromatograph.

The decomposition of isopropyl alcohol was followed in a fixed bed flow type integral reactor and the liquid and gaseous products were analysed by chromatograph (Varian 1800), and gas analysis techniques respectively. The reaction was studied in the temperature range 300–370° C. From the plots of contact time *versus* concentration, the initial rates were computed and used for making the Arrhenius plots.

Analysis of the dehydration and dehydrogenation reaction products showed that when x has values of 0 or 0.02, the system exhibited only dehydration activity to the complete exclusion of dehydrogenation, although traces of the condensation product, namely, di-isopropyl-ether (< 0.5 mole %) was also noticed. All the other catalysts exhibited both dehydration and dehydrogenation activities, though with varying selectivities. Fig. 1 shows the varia-

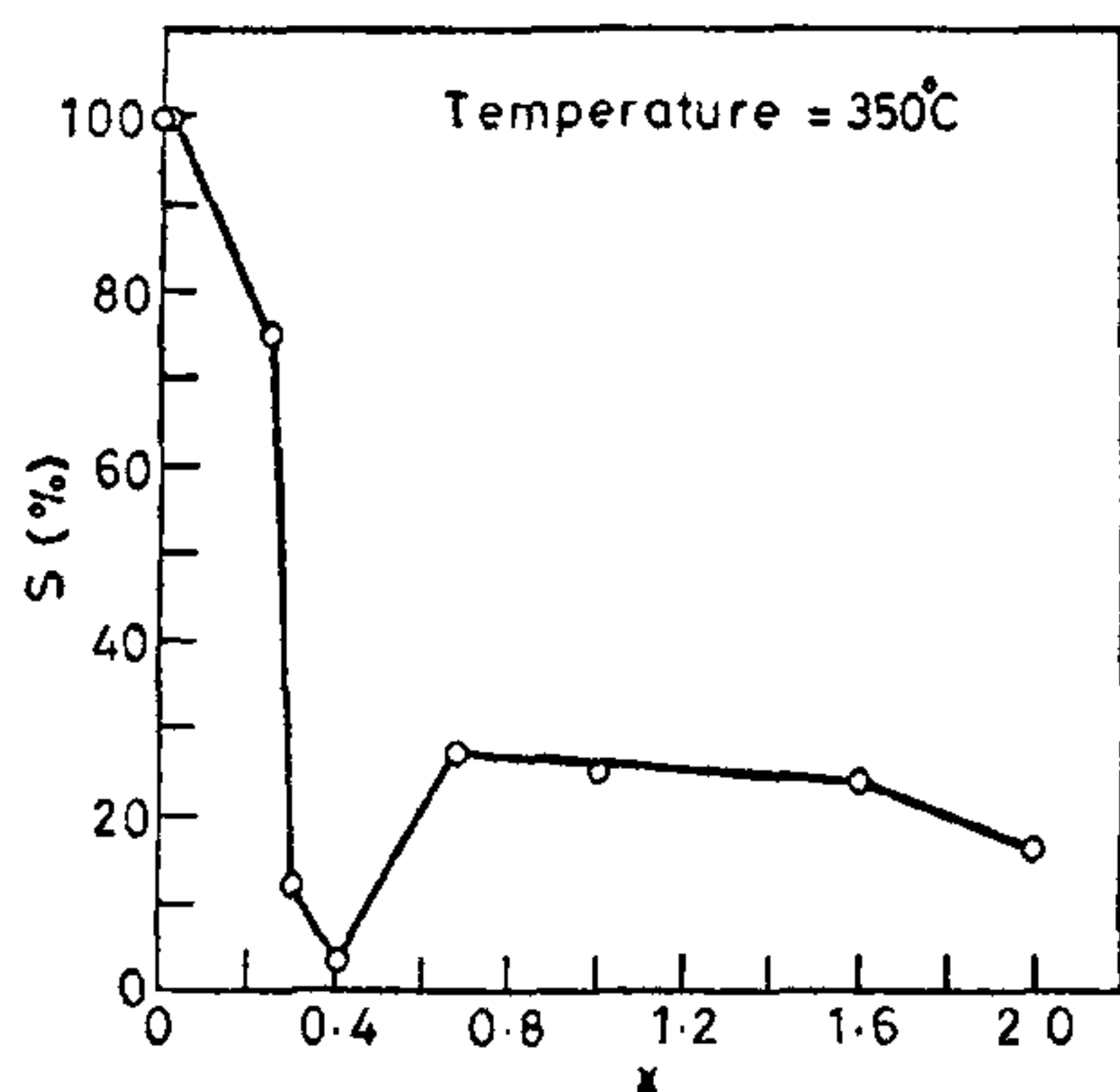


FIG. 1. Selectivity for Dehydration of Isopropyl Alcohol vs. x plot on $\text{MgAl}_{2-x}\text{Fe}_x\text{O}_4$ ($x = 0 \rightarrow 2$).
tion of selectivity for dehydration activity (s) at 350° C with change in titration metal ion (t.m.i) concentration. Selectivity was calculated as the ratio of the concentration of dehydration product

to total decomposition. The selectivity reaches a minimum at $x = 0.4$ and then picks up to a value of 25% at $x = 0.667$ and afterwards remains practically the same though it drops down a bit in the case of pure MgFe_2O_4 .

Arrhenius plots for the dehydration reaction for the various samples showed that for all catalysts with $x < 0.4$, the activation energy values lie in the range of 26–32 kcal/mole, while the corresponding activation energies for the catalysts with $x > 0.4$ are in the range of 8–15 kcal/mole. The activation energy for the catalyst with $x = 0.4$ could not be obtained as the dehydration product was negligible and hence rates could not be calculated with accuracy.

From the activation energy values mentioned above, it may be postulated that the active sites for dehydration could be different on either side of minimum (Fig. 1) changing presumably from a surface coordinatively unsaturated Al^{3+} ions as in Al_2O_3 ⁶ to Fe^{3+} ions as in Fe_2O_3 which are relatively weak Lewis acid sites. This postulate gains further strength from the fact that, whereas, water inhibits greatly the dehydration activity for catalysts with $x < 0.4$, it does not have measurable effect on dehydration activity for catalysts with $x > 0.4$. The change-over of selectivity towards predominant dehydrogenation in the case of the catalysts with high concentration of iron could be attributed to predominant n -type semiconductivity of these catalysts, as revealed by our conductivity studies.

Any further comparison of dehydrogenation activities of the catalysts should take into account factors like the magnetic behaviour and the distribution of t.m.i in the matrix MgAl_2O_4 and these studies are in progress.

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