

## 2-Propanol Decomposition on Substituted Copper Aluminate Catalysts

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Catalytic decomposition of propan-2-ol has been studied in the temperature range 473–673 K on  $\text{CuAl}_2\text{O}_4$ ,  $\text{Li}_2\text{O}$  impregnated  $\text{CuAl}_2\text{O}_4$  and lithium, nickel and magnesium substituted  $\text{CuAl}_2\text{O}_4$  catalysts. Selectivity of the catalyst towards dehydrogenation is increased by impregnation with Li due to an increase in the number of  $\text{Cu}^{2+}$  ions on the catalyst surface, which is the active site for dehydrogenation. The active sites for the dehydration process are the coordinatively unsaturated  $\text{Al}^{3+}$  ions of the catalyst.

Copper aluminate spinel, either alone or in the presence of other oxides has been widely used as a catalyst for the dehydrogenation of alcohols<sup>1,2</sup>. Alkali and alkaline earth metal-impregnated copper aluminate is a selective catalyst for the dehydrogenation of cyclohexanol<sup>1</sup>. However, no attempt has been made yet to determine whether the additives, act as promoters or simply maintain the stability of the catalyst. Thus, in order to study the effect of such additives, the present work on pure  $\text{Li}_2\text{O}$ -impregnated copper aluminate catalysts and some of its solid solutions with  $\text{MgAl}_2\text{O}_4$ ,  $\text{Li}_{0.5}\text{Al}_{2.5}\text{O}_4$  and  $\text{NiAl}_2\text{O}_4$  used as catalysts for the decomposition of propan-2-ol was taken up, involving the competing reactions of dehydration and dehydrogenation.

### Results and Discussion

X-Ray diffraction patterns of all the catalyst samples show that they are single phase solids. The results of the surface area measurements (Tables 1 and 2) show that as  $\text{Li}^+$  (CAL) or  $\text{Ni}^{2+}$  (CAN) is progressively substituted in  $\text{CuAl}_2\text{O}_4$ , the surface area does not show an increasing or decreasing trend. However, the values for the CAN samples are much smaller than those of the CAL samples. The results (Table 1) indicate that impregnation of  $\text{CuAl}_2\text{O}_4$  catalyst with  $\text{Li}_2\text{O}$  improves its catalytic activity towards dehydrogenation of isopropanol as was reported by Bel'skaya *et al.*<sup>1</sup> for cyclohexanol decomposition. These authors suggested that impregnation probably leads to decomposition of the  $\text{CuAl}_2\text{O}_4$  spinel phase which may be responsible for the improved activity. However, Ghose and Rao<sup>3</sup> showed that on impregnating  $\text{CuAl}_2\text{O}_4$  with  $\text{Li}_2\text{O}$ , compounds with spinel structures, having the composition  $\text{Cu}_{0.84}\text{Li}_{0.08}\text{Al}_{2.08}\text{O}_4$  (sintered at 673 K) and  $\text{Cu}_{0.47}\text{Li}_{0.265}\text{Al}_{2.265}\text{O}_4$  (sintered at 1173 K) are formed. This indicates that in  $\text{Li}_2\text{O}$ -impregnated  $\text{CuAl}_2\text{O}_4$  catalyst, the  $\text{Li}^+$  is incorporated in the spinel lattice and the catalytic activity is due to the presence of a copper-lithium-aluminate spinel phase in the catalyst and not due to either the destruction of the spinel phase or due to a separate  $\text{Li}_2\text{O}$  phase acting as a promoter to  $\text{CuAl}_2\text{O}_4$  catalyst.

On the oxide surfaces, usually dehydrogenation is found to occur on sites whose acidity or positive character

is small<sup>4</sup>. This may also be found in  $\text{CuAl}_2\text{O}_4$ , and its cations exposed at the surface may possess lower oxygen coordination and surplus positive charge. Dehydrogenation may then occur by a heterolytic dissociative mechanism, in which two metal ions and an oxide ion of the catalyst surface take part as has been proposed for dehydrogenation on basic oxide<sup>5</sup> and metal oxide<sup>6</sup> catalysts.

TABLE 1—COMPOSITION, SURFACE AREA AND SELECTIVITY TOWARDS DEHYDROGENATION OF Cu–LiAl SAMPLES

Composition	Code name CAL	Surface area $\text{m}^2\text{g}^{-1}$	Selectivity towards dehydrogenation %
$\text{CuAl}_2\text{O}_4$	CAL 100	18.2	92
$\text{Cu}_{0.9}\text{Li}_{0.05}\text{Al}_{2.05}\text{O}_4$	CAL 90	10.8	68
$\text{Cu}_{0.8}\text{Li}_{0.1}\text{Al}_{2.1}\text{O}_4$	CAL 80	7.6	63
$\text{Cu}_{0.6}\text{Li}_{0.2}\text{Al}_{2.2}\text{O}_4$	CAL 60	8.5	65
$\text{Cu}_{0.4}\text{Li}_{0.3}\text{Al}_{2.3}\text{O}_4$	CAL 40	13.1	–
$\text{Cu}_{0.2}\text{Li}_{0.4}\text{Al}_{2.4}\text{O}_4$	CAL 20	21.3	–
$\text{Li}_{0.5}\text{Al}_{2.5}\text{O}_4$	CAL 0	17.5	–
$\text{CuAl}_2\text{O}_4 + 1.5 \text{ wt}\% \text{Li}_2\text{O}$ (sintered at 673 K)	CuLi 673	12.5	98
$\text{CuAl}_2\text{O}_4 + 1.5 \text{ wt}\% \text{Li}_2\text{O}$ (sintered at 1173 K)	CuLi 1173	–	–

TABLE 2—COMPOSITION AND SURFACE AREA OF Cu–Ni–Al SAMPLES

X	Composition	Code name CAN	Surface area, $\text{m}^2\text{g}^{-1}$
0	$\text{CuAl}_2\text{O}_4$	CAL 100	18.2
0.9	$\text{Cu}_{0.9}\text{Ni}_{0.1}\text{Al}_2\text{O}_4$	CAN 90	1.0
0.8	$\text{Cu}_{0.8}\text{Ni}_{0.2}\text{Al}_2\text{O}_4$	CAN 80	1.0
0.6	$\text{Cu}_{0.6}\text{Ni}_{0.4}\text{Al}_2\text{O}_4$	CAN 60	1.0
0.4	$\text{Cu}_{0.4}\text{Ni}_{0.6}\text{Al}_2\text{O}_4$	CAN 40	1.0
0.2	$\text{Cu}_{0.2}\text{Ni}_{0.8}\text{Al}_2\text{O}_4$	CAN 20	3.9
0	$\text{NiAl}_2\text{O}_4$	CAN 10	1.4

The results in Fig. 1A show the effect of incorporation of  $\text{Li}^+$  in the  $\text{CuAl}_2\text{O}_4$  spinel lattice on the latter's catalytic activity towards dehydrogenation of propan-2-ol. The

results show that on incorporating  $\text{Li}^+$  into the  $\text{CuAl}_2\text{O}_4$  lattice, the dehydrogenation activity of the samples progressively decreases. This is expected as lithium has a tendency to combine strongly with alcohols<sup>7</sup>, giving rise to adsorbed alcoholate type of species which tend to inhibit dehydrogenation. However, the activity seems to be increasing between CAL 80 and CAL 60. This is rather unusual as the dehydrogenation activity is usually attributed to  $\text{Cu}^{2+}$  ions, and the  $\text{Cu}^{2+}$  content in CAL 60 is less than in CAL 80. These results suggest that the catalytic activity of these catalysts may not be dependent only on their  $\text{Cu}^{2+}$  content. The higher activity of CAL 60 cannot be justified even in terms of its surface area, which is small.

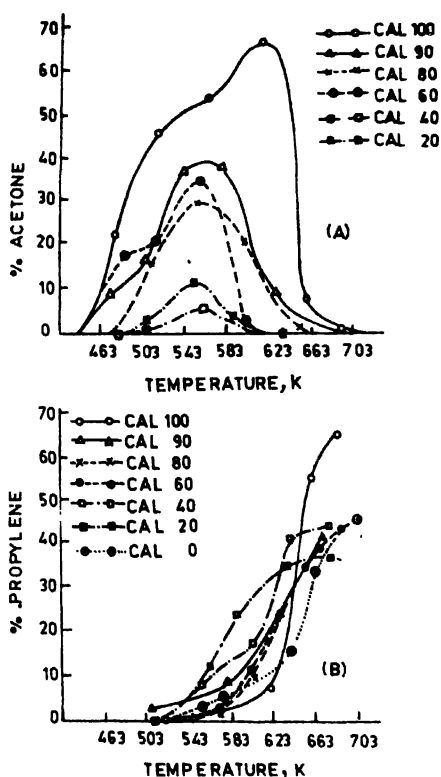


Fig. 1. Dehydrogenation (A) and dehydration (B) activities of CAL samples at different temperatures.

$\text{CuAl}_2\text{O}_4$  is a semiconductor and shows almost a linear decrease in resistivity when heated in air (Figs. 2A and B). On incorporation of  $\text{Li}^+$ , however, the aluminate becomes a mixed conductor, i.e. conduction is both ionic and electronic and that ionic conduction dominates from CAL 40 downwards. In CAL 60, therefore, the ionic and electronic conductivities may be comparable, which probably favours the dehydrogenation process. Thus CAL 60 shows better activity than CAL 80, although the copper content in the latter is higher. From these results it may be suggested that the improved activity of  $\text{Li}_2\text{O}$  impregnated  $\text{CuAl}_2\text{O}_4$  towards dehydrogenation could be due to induc-

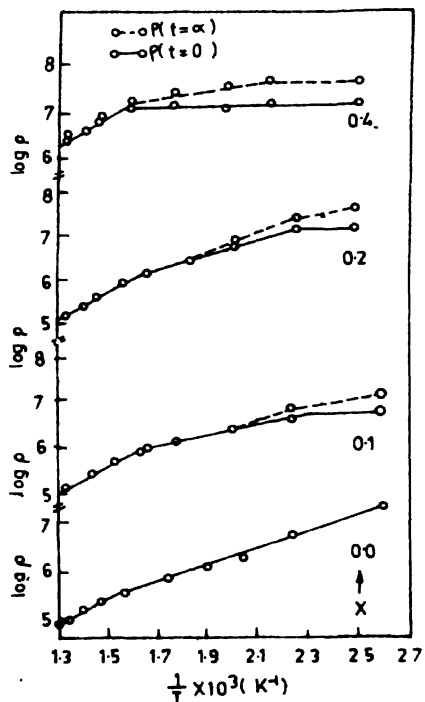


Fig. 2A.  $\log p$  vs  $1/T$  plots of  $\text{Cu}_1 - x\text{Li}_{x/2}\text{Al}_{2+x/2}\text{O}_4$ .

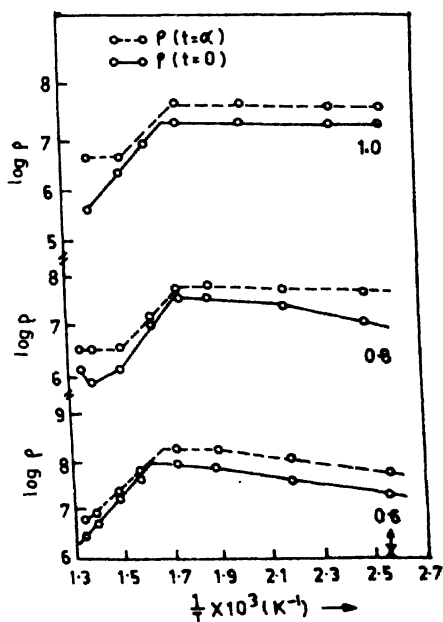


Fig. 2B.  $\log p$  vs  $1/T$  plots of  $\text{Cu}_1 - x\text{Li}_{x/2}\text{Al}_{2+x/2}\text{O}_4$ .

tion of ionic conductivity in the copper aluminate spinel catalyst. A considerable bulk ionic conductivity implies that lithium is mainly present in the bulk of the catalyst, al-

lowing more copper ions to be present at the catalyst surface. Thus, the activity of CAL 60 is not reduced due to the presence of  $\text{Li}^+$  ions.

To ascertain the effect of ionic conductivity on the catalytic activity of substituted copper aluminate catalysts, studies on nickel and magnesium substituted copper aluminate catalysts were taken up. With nickel substitution, there is no possibility of ionic conduction, but even then the results show a decrease in catalytic activity. This is expected, since sites like  $\text{Ni}^{2+}\text{-O-Al}^{3+}$  are not as active as  $\text{Cu}^{2+}\text{-O-Al}^{3+}$  because of the greater tendency of  $\text{Cu}^{2+}$  to acquire the  $d^{10}$ -configuration by adding an electron. The results in Fig. 3B however show that the activity does not decrease continuously with decreasing  $\text{Cu}^{2+}$  ion in the whole solid solution range. After an initial fall, the activity shows a slight increase from CAN 80 to CAN 40 and then rises rapidly. The initial decrease is definitely due to the decrease in copper ion concentration in the catalyst, but after that the tendency of nickel to transfer copper on to the tetrahedral sites which are more active, prevents further

decrease in activity. Furthermore,  $\text{Ni}^{2+}$  has a tendency to penetrate into the subsurface layers, leading to the  $\text{Cu}^{2+}$  surface enrichment as has been shown by XPS and magnetic measurements<sup>8</sup>.

Catalytic studies show that during decomposition of propan-2-ol on all the catalysts, both dehydrogenation and dehydration occur (Figs. 1A and B). Fig. 1B shows that below 523 K there is practically no dehydration activity and above 593 K the dehydration activity increases very rapidly. Fig. 1A shows that above 593 K dehydrogenation is very little except for the copper-rich samples and above 623 K even this is negligible. Thus  $\text{CuAl}_2\text{O}_4$  and all the lithium-containing catalysts show a selectivity towards dehydrogenation at lower temperatures and towards dehydration at higher temperatures.

The results in Figs. 3A and B clearly indicate that both in CAL and CAN systems, the catalysts show very little dehydration activity at temperatures where the dehydrogenation activity is very high. In the CAL system, there is little change in the activity with a change in the copper content. This probably implies that the dehydration activity is not dependent on the copper content but may be dependent on the aluminium content. In the CAN system there is no change in the aluminium content, yet Fig. 3B shows that the dehydration activity initially decreases and then increases as  $\text{Ni}^{2+}$  is progressively substituted for  $\text{Cu}^{2+}$ . The activity shown by nickel-rich samples is probably due to the presence of coordinatively unsaturated (CUS) $\text{Ni}^{2+}$ .

Crystal field considerations suggest that coordinatively unsaturated  $\text{Ni}^{2+}$  will have a stronger tendency to complete six-fold coordination by the adsorption of an alcohol molecule than (CUS) $\text{Al}^{3+}$  ions, and thus with the introduction of  $\text{Ni}^{2+}$  in  $\text{CuAl}_2\text{O}_4$  the activity will decrease although the total  $\text{Al}^{3+}$  does not decrease. However, with increasing  $\text{Ni}^{2+}$ , some  $\text{Al}^{3+}$  may be adjacent to  $\text{Ni}^{2+}$ , i.e.  $\text{Ni}^{2+}\text{-Al}^{3+}$  (CUS), and this acts as a stronger Lewis acid than  $\text{Al}^{3+}$  (CUS) as was found with  $\text{Cr}^{3+}$  ions having the same crystal field stabilisation energy as  $\text{Ni}^{2+}$ <sup>9</sup>. Thus, the nickel-rich crystals are found to exhibit high dehydration activity.

**Conclusion :** It may be suggested that in the  $\text{CuAl}_2\text{O}_4$  spinel oxide, the surface copper ions are the active species in the catalyst for the dehydrogenation of an alcohol. When substituted by other ions, i.e.  $\text{Li}^+$  or  $\text{Ni}^{2+}$ , which bring about an increase in the amount of surface  $\text{Cu}^{2+}$  ions, an improvement in the dehydrogenation activity is observed.

### Experimental

A 1.5 wt.%  $\text{Li}_2\text{O}$  impregnated  $\text{CuAl}_2\text{O}_4$  samples and  $\text{Cu}_{1-x}\text{Li}_{x/2}\text{Al}_{2+x/2}\text{O}_4$  solid solution samples were prepared<sup>3</sup>. Solid solution samples of  $\text{Cu}_{1-x}\text{Ni}_x\text{Al}_2\text{O}_4$  ( $x = 0.1, 0.2, 0.4, 0.6, 0.8$  and  $1.0$ ) were prepared by mixing the solutions of stoichiometric amounts of cupric nitrate, nickel nitrate and aluminium nitrate (all AnalaR). The mixture was dried, decomposed at about 743 K, powdered and pelleted. The pellets of  $\text{NiAl}_2\text{O}_4$  were calcined at 1473 K while all other solid solution samples were calcined at 1183 K for 24 h.

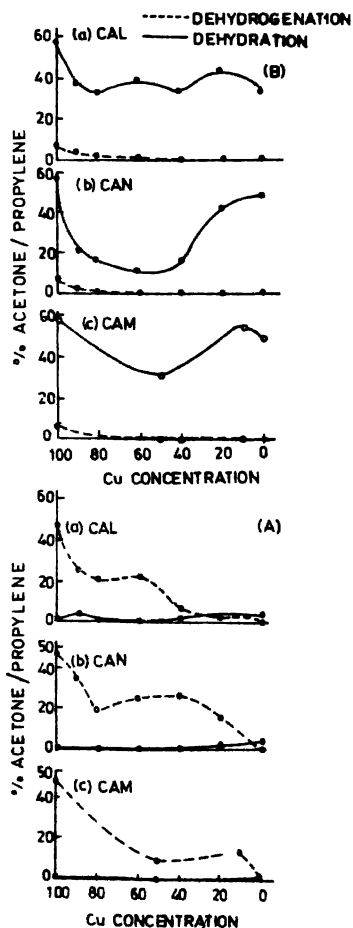


Fig 3 Dehydrogenation (A) and dehydration (B) activities of CAL, CAN and CAM samples at (A) 523 K and (B) 663 K.

Solid solution samples of  $\text{Cu}_{1-x}\text{Mg}_x\text{Al}_2\text{O}_4$  ( $x = 0.5, 0.9$  and  $1.0$ ) were also prepared by the same method. Code names of the samples are given in Table 1.

X-Ray diffraction study was done by the Debye-Scherrer powder technique using a Philips PW 1012/10 unit with Straumann mounting;  $\text{CuK}\alpha$  radiation with a nickel filter was used. Surface area was measured using the BET apparatus.

*Catalytic studies* : The catalytic vapour phase decomposition of propan-2-ol was studied in a flow type, fixed-bed, differential reactor using the catalyst (1 g) for each run. Chromatographically pure propan-2-ol was used. The liquid product acetone and unreacted propan-2-ol were analysed using a Pye-Unicam 104 gas chromatograph (pega 10% column and nitrogen as carrier gas). The liquid product was also tested for di-isopropyl ether. The gaseous product propylene was analysed by the Orsat apparatus using mercuric sulphate in concentrated sulphuric acid as absorbent. The presence of  $\text{CO}_2$  was tested by sending the gaseous product into baryta solution.

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