

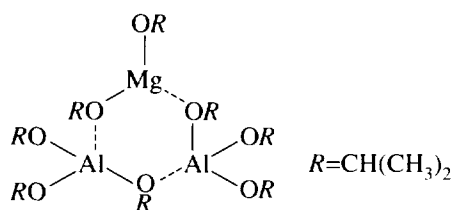
NOTE

Preparation and Characterization of High Surface Area $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ Solid Solutions

Mixed metal oxides with spinel-type structure are often used as model systems for catalytic studies, and some of them find current industrial usage. Magnesium aluminate, MgAl_2O_4 , acts as an efficient transfer catalyst for reducing sulfur dioxide emissions (1-3), and it can also be used as a convenient support for metal carbonyls (4, 5) and other catalyst precursor materials. For these applications, high surface area and accessible porosity are desirable properties.

The classical method to prepare MgAl_2O_4 involves high-temperature solid state reaction between MgO and Al_2O_3 , but severe sintering leads to very low surface areas. Suitable precursors have been sought to obtain a high surface area spinel. They include coprecipitated hydroxides or oxalates (2, 6) and γ -alumina impregnated with a magnesium nitrate solution (6). Reported surface areas of MgAl_2O_4 samples obtained from these precursors, after mild calcination at about 800 K, are in the 50-120 $\text{m}^2 \text{g}^{-1}$ range. We describe here the preparation and characterization of MgAl_2O_4 , and also $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ solid solutions, with surface areas of 250-300 $\text{m}^2 \text{g}^{-1}$. Interest in the solid solutions stems from the fact that gradual changes of chemical composition provide a means to modulate surface acidity.

Heterometallic magnesium-aluminium alkoxides were used as precursors of the metal oxides. Mg-Al isopropoxide, which was formulated (7) as



was prepared by reflux boiling a large excess of isopropanol (Fluka 99%) with stoichiometric amounts of Al and Mg; a trace of HgCl_2 was added to facilitate dissolution of the metals. Once total dissolution was accomplished, the excess of alcohol was distilled off. The metal alkoxide was thus obtained as a viscous liquid which retains the

last traces of isopropanol. A tiny drop of metallic mercury (formed from reduction of HgCl_2 during dissolution of Al and Mg) can easily be removed at this stage. The heterometallic alkoxide was then hydrolysed (at 303 K) with a large excess of an aqueous buffer (pH = 7.2) consisting of a 50% mixture of 50 mM tris-(hydroxymethyl)-methylamine and 50 mM nitric acid. Control of pH at this stage is important, since aluminium hydroxide can be quantitatively precipitated only within a narrow pH range. The gel thus obtained was thoroughly washed, air-dried in a desiccator, and calcined at 870 K for 4 h to yield the oxide product MgAl_2O_4 . Similarly, $\gamma\text{-Al}_2\text{O}_3$ and several mixed oxides with different Mg:Al ratio were obtained starting from aluminium isopropoxide or the corresponding alkoxides prepared from appropriate mixtures of the metals. The oxide products were analysed chemically, by complexometric titration, to determine the actual Mg:Al ratio. This was found to be slightly higher than the nominal value in the starting heterometallic alkoxide, except for the sample with Mg:Al = 1:16 where the low magnesium content did not allow enough precision in the chemical analysis. The results are shown in Table 1, which also summarizes the results of crystallographic and textural (surface area and porosity) characterization of the samples.

Powder X-ray diffractometry of all synthesized oxides revealed only a spinel-type phase. This cubic phase corresponds to MgAl_2O_4 for the sample with Mg:Al = 1:2, and to $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ solid solutions for samples with smaller Mg:Al ratio. The oxide product obtained from pure aluminium isopropoxide was termed $\gamma\text{-Al}_2\text{O}_3$ (Table 1) mainly on account (8, 9) of the very broad (111) diffraction line observed, but discrimination from $\eta\text{-Al}_2\text{O}_3$ (the other cubic form of active alumina) is not unambiguous. The cubic lattice parameter, a_0 , was found to vary approximately linearly with composition, as shown in Table 1. The same trend was reported by Navrotsky *et al.* (10) for highly crystalline $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ solid solutions, obtained by high temperature calcination (up to 1943 K) of reagent-grade mixtures of MgO and Al_2O_3 . The values reported by these authors for the solid solution end mem-

TABLE 1
Lattice Parameter and Textural Data for MgAl_2O_4 , $\gamma\text{-Al}_2\text{O}_3$, and $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ Solid Solutions (Samples Calcined at 870 K)

Sample	Mg: Al ratio		a_0 (nm)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	R_p (nm)	V_p ($\text{cm}^3 \text{g}^{-1}$)
	Nominal ^a	Found ^b				
MgAl_2O_4	1:2	0.52	0.809	250	3.5	0.45
Solid solution	1:4	0.30	0.803	250	4.0	0.51
Solid solution	1:8	0.13	0.797	260	4.0	0.54
Solid solution	1:16	0.06	0.794	290	3.5	0.53
$\gamma\text{Al}_2\text{O}_3$	—	—	0.790	260	3.5	0.47

^a Mg: Al ratio taken for the preparation of the parent alkoxide.

^b Ratio found in the complexometric chemical analysis of oxide product.

bers are $a_0(\text{MgAl}_2\text{O}_4) = 0.8084 \text{ nm}$ and $a_0(\gamma\text{-Al}_2\text{O}_3) = 0.7905 \text{ nm}$; our results (Table 1) are in agreement with theirs. Our oxide products, obtained at 870 K, gave broad diffraction lines as shown in Fig. 1 for MgAl_2O_4 . This precluded accurate determination of lattice parameters, although values reported in Table 1 were obtained using a silicon internal standard to correct for systematic errors. From several independent measurements on the same sample, the standard deviation on a_0 was estimated to be $\pm 0.002 \text{ nm}$. The observed continuous variation of a_0 with Mg: Al ratio of the different samples, together with the fact that no diffraction lines other than those corresponding to a spinel-type phase were observed in the diffractograms, provide strong evidence for solid solution formation at 870 K.

Gels obtained by hydrolysis of the parent metal alkoxides were found to be amorphous. The first signs of incipient crystallinity appear after calcination at 770 K, and the

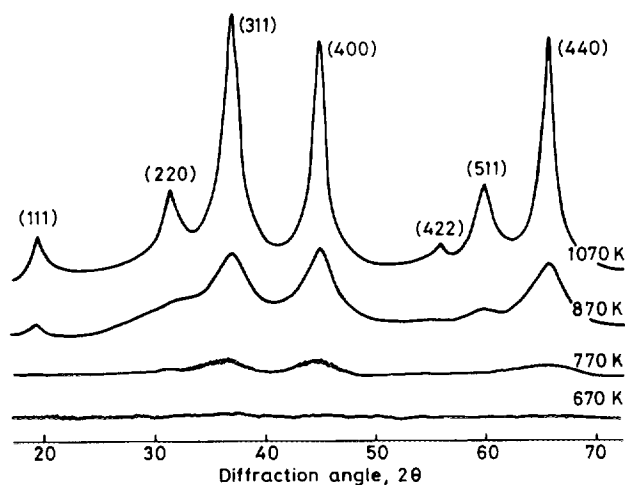


FIG. 1. X-ray diffractograms ($\text{CuK}\alpha$ radiation) showing development of crystallinity in a gel with Mg: Al = 1:2 calcined for 4 h at increasing temperature. Indexing corresponds to a spinel phase.

spinel-type structure is clearly discernible from 870 K upward, as shown in Fig. 1 for MgAl_2O_4 . As expected, higher calcination temperatures increase crystallinity, but surface area decreases. Data reported in Table 1 were obtained for samples fired at 870 K, in all cases.

Nitrogen adsorption at 77 K was used to determine specific surface area and porosity. The corresponding adsorption-desorption isotherms were obtained after outgassing the oxide samples at 473 K in a dynamic vacuum of 10^{-2} Pa . All of them were found to be very similar, and akin to type IV of the BDDT classification (11) as shown in Fig. 2 for two of the samples. The shape of the isotherms, and the presence of a hysteresis loop at high

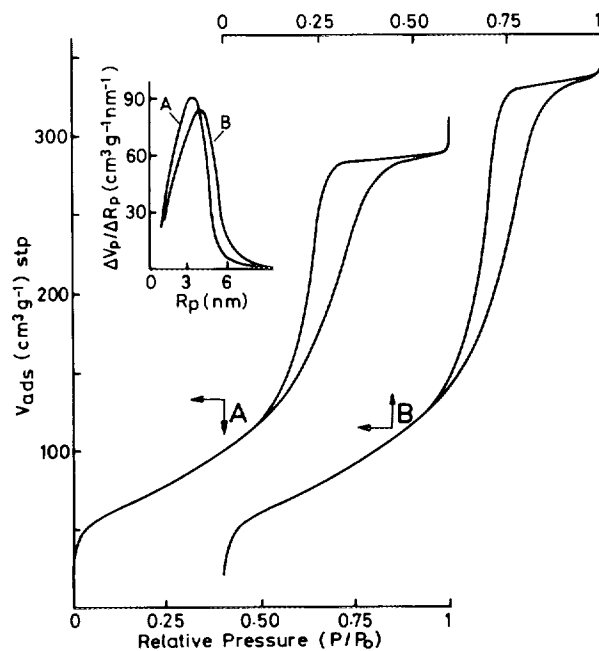


FIG. 2. Nitrogen adsorption-desorption isotherms at 77 K for (A) MgAl_2O_4 , and (B) the $\text{Al}_2\text{O}_3\text{-MgAl}_2\text{O}_4$ solid solution with Mg: Al = 1:8. Inset shows the corresponding pore-radii distribution curves of differential pore volume as a function of pore size.

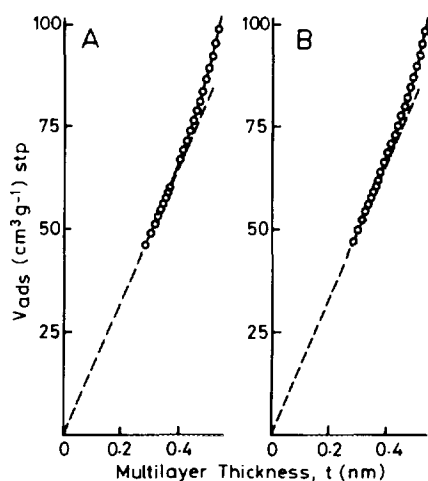


FIG. 3. V_a - t plots obtained from the isotherms shown in Fig. 2.

relative pressure, suggest that the oxides under study are mesoporous solids. Absence of significant microporosity was confirmed by using the V_a - t method (12, 13). Plots of multilayer thickness (t) versus the volume of adsorbed nitrogen (V_a) could be extrapolated through the origin, as shown in Fig. 3. This clearly indicates that microporosity does not contribute significantly to surface area. Porous texture was analysed following the BJH method (14) which was applied to the adsorption branch of each isotherm; this is preferred to the desorption branch for type IV isotherms (15, 16). The pore size distribution curve was found to be unimodal in all cases, and showed a rather narrow spectrum of pore radii as can be seen in Fig. 2.

Values of BET surface area, pore radius (R_p) and pore volume (V_p) for all of the oxides studied are summarized in Table 1. Preliminary results for an $MgAl_2O_4$ sample were published elsewhere (17). It is apparent that surface area and porosity are very similar for all samples, regardless of variations in chemical composition. The only possible exception is the rather higher surface area found for the oxide solid solution with $Mg:Al = 1:16$, but we do not consider the difference to be significant.

In summary it was shown that mesoporous magnesium aluminate and Al_2O_3 - $MgAl_2O_4$ solid solutions can be prepared in a high surface area form starting from metal alkoxide precursors. The method described here could have general validity for the preparation of other spinel-type metal oxides in a highly dispersed state, since many metals are known to form alkoxides. The main advantages of using alkoxide precursors for preparing multicomponent oxides are high purity and good chemical homogeneity, which allows one to obtain the oxide products at low calcination temperature. The present method also facilitates pH control during gelification. This is not al-

ways the case when ammonia or ammonium carbonate are used as precipitating agents with, for example, metal nitrate solutions. Since metal hydroxide (or hydroxycarbonate) formation is pH dependent, the classical coprecipitation route can lead to less homogeneous gels.

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