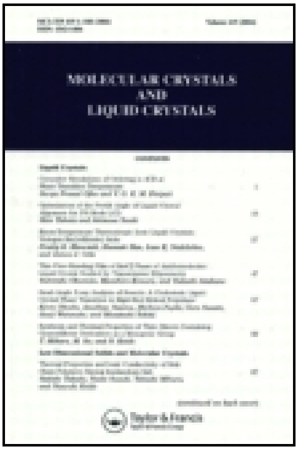

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EFFECT OF INTERMEDIATES ON THE NATURE OF POLYVANADATE-INTERCALATED LAYERED DOUBLE HYDROXIDES

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Abstract Layered double hydroxides with the hydrotalcite ($Mg_{(1-x)}Al_x(OH)_2(CO_3)_{x/2}.nH_2O$) structure intercalated with polyvanadate species have been prepared following different routes.X-ray diffraction, thermal analysis, transmission electron microscopy and infrared spectroscopy results indicate the layered structure of the material. A narrow mesopore size distribution was obtained when using terephtalate as swelling agent.

INTRODUCTION

Layered Double Hydroxides (LDHs) are of current interest for a variety of applications, ranging from anion scavengers and pharmaceuticals to adsorbents, heterogeneous catalysts and precursors of heterogeneous catalysts[1]. Recently a variety of procedures have been reported concerning the preparation of pillared LDH derivatives such that materials may be prepared with properties akin to those of the well-known pillared clays. In the present study, vanadium was chosen as the pillaring species of a Mg,Al LDH because such materials have been already reported[2-6] and mixtures of Mg and V oxides are effective catalysts for oxidative dehydrogenation[7]. Nevertheless, no full comparison of the properties of a V-pillared LDH has been made, especially when other factors (e.g., Mg/Al ratio) are fixed. The use of different pillaring/exchange procedures is expected to lead to useful variations in physical characteristics including ease of water loss and hydrophobicity. Furthermore, the intermediate swelling of the LDH by an organic guest has been claimed to favour exchange of carbonate by the much larger vanadate ($V_{10}O_{28}^{6-}$) species.

EXPERIMENTAL

Parent LDH (sample A) with a Mg/Al ratio close to 2 was prepared following conventional methods[8]; a calcined precursor oxide (B) was prepared by calcination[4] at 550°C for 18 h. Intercalates with terephtalate (TP) were prepared by direct synthesis (C), direct rehydration of B (D), and one-step rehydration in the presence of glycerol (E). Vanadate-exchanged materials (samples F, G and H) were obtained by anion exchange of C, D or E, respectively; also by rehydration of (B) in the absence (I) or presence (J) of glycerol, and anion exchange of A without (K) or with (L) glycerol. Details will be given elsewhere[9].

Chemical analyses for Mg, Al and V were performed in a Perkin Elmer Atomic Absorption Spectrometer 3100, and C was analyzed in a Perkin-Elmer 2400C analyzer. X-ray diffraction (XRD) profiles were recorded in a Philips APD 1700 instrument (Cu Kα radiation). Thermal Analyses (Thermogravimetric, TG, and Differential Thermal Analysis, DTA) were recorded in

TABLE I Properties of vanadate-pillared hydrotalcites

Sample	Mg/Al	V(%w/w)	c(Å)	S_{BET}(m^2g^{-1})
A	2.17	-	22.1	77
C	2.32	-	43.5	42
D	2.24	-	43.5	7
E	2.64	-	43.5	8
F	1.98	22.5	35.4	56
G	1.84	21.9	34.8	64
H	1.90	21.9	35.4	75
I	1.23	21.8	35.4	48
J	2.17	26.6	35.7	77
K	1.91	27.1	35.4	89
L	2.27	25.4	36.0	84

Perkin-Elmer apparatuses models TGS-2 and DTA 1700 coupled to a Data Station 3600. Specific surface area (S_{BET}) and mesopore distribution were monitored by N_2 adsorption at 77 K.

RESULTS

Main properties of the samples are summarized in Table I. XRD diagrams indicate the layered structure of all samples, except sample B, that is amorphous[10]. Chemical analyses for Mg, Al, V and C are consistent with the presence of terephtalate in samples C-E, and of $V_{10}O_{28}^{6-}$ species in samples F-H and J-L; the content of V in sample I was unexpectedly low. FT-IR spectra (Fig. 1) confirm the presence of the expected anion in each case. Bands are due to $\upsilon_3(CO_3^{=})$ (sample A, 1380 cm^{-1}), υ_{as} and υ_{sym} (COO-) terephtalate (sample C, 1570 and 1390 cm^{-1}) and decavanadate (sample F, 974 cm^{-1}). Representative XRD profiles are shown in Fig. 2. The basal spacings (c/3) have been cal-

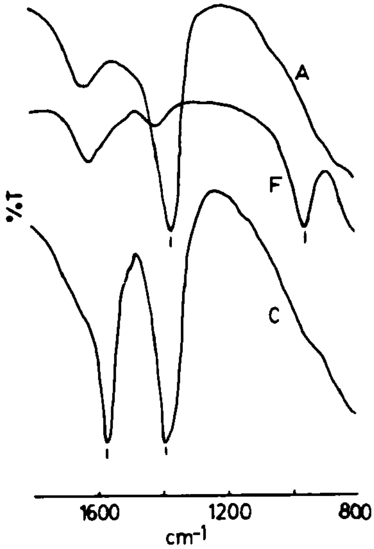

FIGURE 1 FT-IR spectra of representative samples studied.

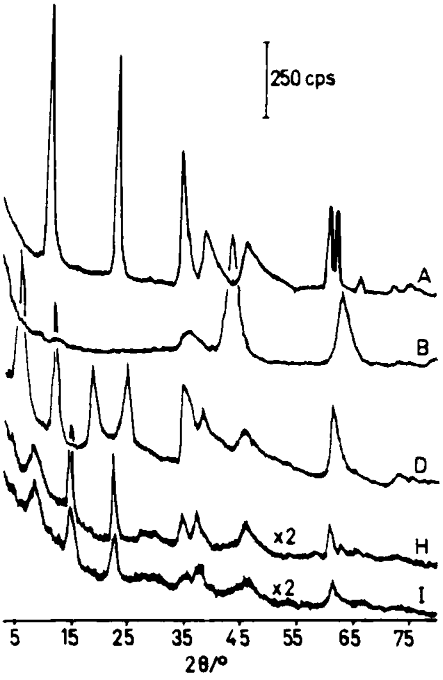

FIGURE 2 XRD profiles of vanadate-pillared hydrotalcite

culated averaging the positions for reflections (003), (006) and (009); for sample A coincides with that reported[11] for hydrotalcite, for samples C-E coincide with those reported previously[3] for similar compounds and those for samples F-L are very slightly low. TEM micrographs show hexagonal-shaped platelets in all cases, but for sample I two different types of particles seem to exist. The anomalous behaviour of this sample can be due to the way it had been obtained, by direct reconstruction of the hydrotalcite structure in vanadate solution at pH=4.5; in all other cases, vanadate was incorporated through anionic exchange (samples F-H, K and L) or reconstruction in the presence of glycerol (sample J).

TG and DTA curves were very similar for samples containing vanadium, and no difference was found between the weight losses recorded in air and in nitrogen; however, for those containing TP the weight loss was larger in air, due to combustion of the organic moiety. Decomposition takes place in all cases in two steps. For the TP-samples, the first one (up to ≈230°C) corresponds to removal of interlayer water molecules, and the second one is due to dehydroxylation and removal of the interlayer organic anion as CO_2 and H_2O when the analysis is carried out in air. Raman and XANES studies on a sample similar to F indicates[5] that the intercalate decavanadate ions partially depolymerise at 160-350°C, reaction to yield magnesium vanadates taking place only above 450°C, and this reaction has been recorded as exothermic DTA peaks in our case. So, calcination at 200-230°C will lead to dehydrated samples where the chemical nature of the interlayer decavanadate and the layers is maintained. It should be noticed that weight loss below ≈230°C was very similar in all cases (14-18% weight), indicating a fairly similar water content in the interlayers.

Nitrogen adsorption isotherms for samples outgassed at 200°C corresponded to type II in the IUPAC classification[12], but in almost all cases a type H2 hysteresis loop was recorded, indicating some degree of microporosity, specially for sam-

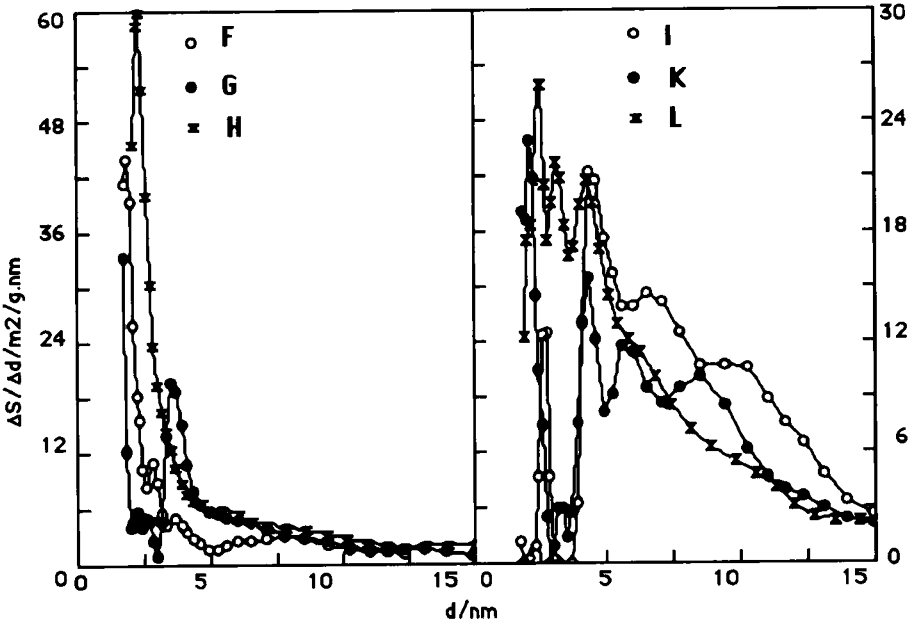

FIGURE 3 Pore-size distribution curves of vanadate-pillared hydrotalcite.

ples F and G. The values calculated for the specific surface areas (BET method) are included in Table I. The values were extremely low for samples D and E. It should be noted that for samples containing vanadium the values are similar for each couple of samples obtained from the same precursor (i.e., samples G and H, samples K and L), except for couple I and J, probably due to the heterogeneous nature of the former. Pore size distribution analysis, performed[13] following the method by Cranston and Inkley[14], leads to curves shown in Fig. 3. A very narrow pore size distribution is observed for samples F, G and H, with a maximum at ≈30 Å. On the contrary, a broad distribution of pore sizes is obtained for samples I, K and L. Similar microporosity has been reported by Wang et al.[6] for LDHs pillared with Keggin ions.

CONCLUSIONS

Synthesis of decavanadate-pillared LDHs can be attained by different methods; although most of them lead to compounds with similar structural properties, according to FT-IR and XRD data, porosity and pore size distribution appear to depend significantly on the method of preparation, intermediate swelling with terephtalate leading to a narrow pore size distribution.

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