



XRD and ^1H MAS NMR spectroscopic study of mixed oxides obtained by calcination of layered-double hydroxides

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Abstract

Three Mg/Al, Mg/Ga and Mg/Al,Ga layered-double hydroxides were synthesized and characterized from their X-ray diffraction (XRD) patterns. Calcination of these solids at 773 K yielded a mixture of oxides ($\text{MgO}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Ga}_2\text{O}_3$ and $\text{MgO}/\text{Al}_2\text{O}_3/\text{Ga}_2\text{O}_3$) that was also characterized by the XRD technique. Surface proton sites in these mixed oxides were determined by ^1H MAS NMR spectroscopy. The results are compared with those for the pure oxides. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrotalcite, $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3) \cdot 4\text{H}_2\text{O}$, is a layered-double hydroxide (LDH) belonging to the anionic clay family [1] that is structurally analogous to brucite, $\text{Mg}(\text{OH})_2$; Mg^{2+} cations occupy the centres of octahedra, which are superimposed and joined by hydrogen bonds between hydroxyl groups at octahedron vertices. In hydrotalcite, some Mg^{2+} ions are replaced by Al^{3+} ; this produces a charge deficiency in the layers that is neutralized by anions in the interlayer region, which also contains crystallization water. Replacement of the magnesium or aluminium with another cation (Mg, Ni, Zn or Cu in the former case and Ga, Cr, Fe or Mn in the latter) yields the

so-called layered-double hydroxides, of general formula $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. These solids are being used in many catalysed processes including condensation [2,3], hydrogenation [4,5] and nitrogen oxide decomposition reactions [6,7], among others.

Characterizing surface active sites in catalysts is one of the primary goals in catalysis that has so far been pursued by using a wide variety of instrumental techniques such as IR, Raman, NMR, ESR, ESCA and X-ray diffraction (XRD) spectroscopies. Thus, ^1H MAS NMR spectroscopy was recently used by our group for the structural elucidation of catalytically active solids such as sepiolites [8], Pt/MgO systems [9], $\text{SiO}_2/\text{AlPO}_4$ systems [10] and Pd/ SiO_2 catalysts [11].

This paper reports on the synthesis and XRD spectroscopic characterization of Mg/Al, Mg/Ga

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and Mg/Al,Ga layered-double hydroxides, as well as on the identification of the surface proton sites in their calcination products at 773 K by ^1H MAS NMR spectroscopy. The spectra thus obtained are compared with those for pure magnesium, aluminium and gallium oxide.

2. Experimental

2.1. Preparation of LDHs

2.1.1. Mg / Al LDH

Two solutions containing 0.03 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.01 mol of $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively, in 25 ml of deionized water were mixed and the mixture was then slowly dropped over 75 ml of a Na_2CO_3 solution at pH 10 at 333 K, under vigorous stirring. The pH was kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was allowed to stand at 353 K for 24 h, after which it was filtered and the solid washed with 2 l of deionized water.

2.1.2. Mg / Ga LDH

The procedure used to prepare this solid was identical with the previous one except that the solutions used contained 0.03 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.01 mol of $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

2.1.3. Mg / Al,Ga LDH

This LDH was obtained by the same procedure as the previous two, using a solution containing 0.03 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on one hand and 0.005 mol each of $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ on the other.

Once synthesized, the three LDHs were exchanged with carbonate in order to remove nitrate ions from the interlayers. For this purpose, an amount of 2.5 g of each LDH was dispersed in 125 ml of distilled water. The dispersion was supplied with 250 mg of Na_2CO_3 and refluxed for 2 h, after which the solid was separated by centrifugation and the water discarded. This operation was repeated and the supernatant analysed for nitrate, which gave a negative test. The resulting solids, named HT-Mg/Al, HT-Mg/Ga and HT-Mg/Al,Ga, were dried at 373 K and calcined in a nitrogen atmosphere at 773 K for 8

h. This treatment provided the solids designated HT-Mg/Al-773, HT-Mg/Ga-773 and HT-Mg/Al,Ga-773, respectively.

The magnesium, aluminium and gallium oxides were obtained by calcination of the corresponding hydroxides in a nitrogen atmosphere at 773 K.

2.2. Elemental analysis

The elemental composition of the samples was determined on a Perkin-Elmer 1000 ICP spectrophotometer under standard conditions.

2.3. X-ray diffraction

XRD patterns were recorded on a Siemens D-500 diffractometer using CuK_α radiation. Scans were performed over the 2θ range from 2° to 80° .

2.4. ^1H MAS NMR spectroscopy

^1H MAS NMR spectra were recorded at 400.13 MHz on a Bruker ACP-400 (9.4 T) spectrometer using zirconia rotors. All measurements were made at room temperature. Spectra were obtained by using an excitation pulse of $\pi/2$ (5 ms) and a recycle time of 10 s. An overall 1000 free induction decays were accumulated. Chemical shifts were measured relative to a tetramethylsilane standard. Prior to measurement, samples were dehydrated by evacuation to a pressure below $3\text{ }\mu\text{m Hg}$ in a Micromeritics ASAP-2000 instrument at 373 K overnight. The samples were then transferred, in a nitrogen atmosphere, to a moisture-free nitrogen glove box and used to fill the zirconia rotors. The rotors were spun at 4 kHz during MAS NMR measurements. ^1H MAS NMR spectra were interpreted on the assumption that no atmospheric water would penetrate from the rotor into such highly hygroscopic samples. In order to confirm the accuracy of this assumption, ^1H MAS NMR spectra for an HT-Mg/Al-773 sample were recorded immediately upon synthesis and a few days after being transferred to the rotor. The two spectra were identical and rather different from those for samples exposed to moisture, so the risk of water penetrating into the sample was excluded. The ^1H background resonance from the probe itself, identified by recording the ^1H MAS NMR spectrum for an empty rotor,

consisted of a broad, very weak resonance — apparently a static resonance. All ^1H MAS NMR spectra were corrected for this background resonance by subtracting the empty rotor spectrum.

3. Results and discussion

3.1. Elemental analysis

Elemental analyses of the LDHs performed after ion exchange with carbonate and drying at 393 K provided the following element ratios: 3:1 Mg/Al in HT-Mg/Al, 3:0.84 Mg/Ga in HT-Mg/Ga and 3:0.5:0.4 Mg/Al/Ga in HT-Mg/Al,Ga. The resulting formulae for the LDHs were thus $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.125} \cdot m\text{H}_2\text{O}$, $[\text{Mg}_{0.78}\text{Ga}_{0.22}(\text{OH})_2](\text{CO}_3)_{0.110} \cdot m\text{H}_2\text{O}$ and $[\text{Mg}_{0.78}\text{Al}_{0.13}\text{Ga}_{0.10}(\text{OH})_2](\text{CO}_3)_{0.115} \cdot m\text{H}_2\text{O}$, respectively.

3.2. X-ray diffraction

The XRD patterns for the LDHs (Fig. 1) exhibit some common features of layered materials (e.g. narrow, symmetric, strong lines at low 2θ values and weaker, less symmetric lines at high 2θ values). The presence of the intense and sharp lines at low values of 2θ is due to the basal reflections. These basal reflections correspond to successive orders of the basal spacing c . The presence of both sharp and diffuse non-basal reflections was taken as indication of a partially disordered structure, above all in the stacking superposition of the regular unit layers. A comparison of the XRD patterns for the samples containing gallium with that for the aluminium sample reveals that the former possess the same layered structure as the Mg/Al hydrotalcite. From the position of the strongest lines, of crystallographic indices (003), the lattice distance, d_{003} , was calculated and used to determine the lattice parameter c . The lattice parameter a was determined from the (110) diffraction line. The values for these lattice parameters, given in Table 1, suggest that the insertion of a Ga^{3+} cation, a bulkier cation than Al^{3+} , in the LDH structure increases the spacing between layers. Also, the values for HT-Mg/Al,Ga are in between those for the pure Ga and Al LDHs.

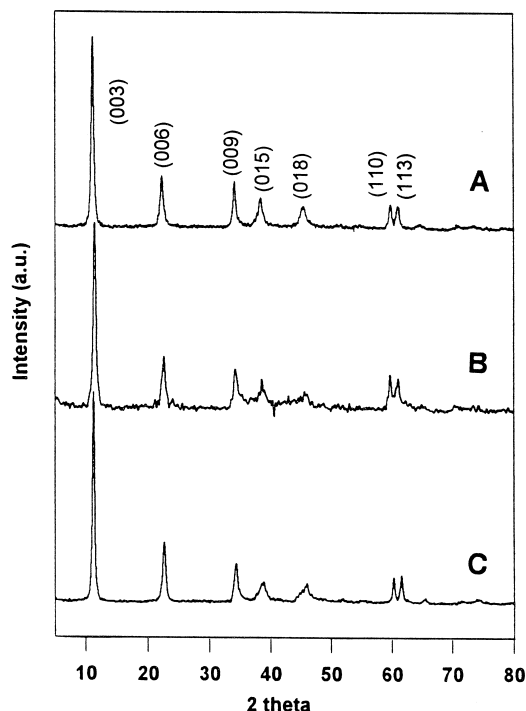


Fig. 1. XRD patterns for solids: (A) HT-Mg/Al, (B) HT-Mg/Ga and (C) HT-Mg/Al,Ga.

Calcination of these LDHs at 773 K destroyed the layered structure and led to solids consisting of periclase MgO and amorphous Al_2O_3 and/or Ga_2O_3 phases (Fig. 2). These results are consistent with reported values for other LDHs [12–14], calcination at 773 K of which yields periclase MgO as the sole crystalline phase.

3.3. ^1H MAS NMR spectroscopy

As noted in the previous section, calcination of the LDHs led to the formation of $\text{MgO}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Ga}_2\text{O}_3$ and $\text{MgO}/\text{Al}_2\text{O}_3/\text{Ga}_2\text{O}_3$ mixed oxides, where only MgO was crystalline. Consequently, the ^1H MAS NMR study of these mixed oxides was preceded by that of periclase MgO, Al_2O_3 and Ga_2O_3 obtained by calcination of the corresponding hydroxides [viz. $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{Ga}(\text{OH})_3$], in commercially available form.

Fig. 3 shows the ^1H MAS NMR spectra for the oxides. As can be seen, the spectrum for periclase MgO (Fig. 3A) exhibits two major signals at 4.6 and

Table 1
Lattice parameters for the synthesized LDHs

Sample	d_{003} (Å)	a (Å)	c (Å)
HT-Mg/Al	7.721	3.061	23.163
HT-Mg/Ga	7.797	3.077	23.391
HT-Mg/Al,Ga	7.759	3.069	23.277

0.2 ppm, the latter (and also the stronger) corresponding to OH groups, of a basic character judging by their upfield shift. The signal at 4.6 ppm suggests the presence of hydrogen bonds between surface OH groups, which exhibit a slightly acidic character. The signal at 0.2 ppm includes several shoulders at -1.0 , 0.6 , 1.1 and 1.5 ppm, which suggests a wide distribution of surface hydroxyl sites of variable basic strength. Fig. 3B shows the ^1H MAS NMR spectrum for alumina, which consists of two overlapped peaks with maxima at -0.9 and 2.6 ppm, respectively. The peak at -0.9 ppm was previously assigned by Mastikhin et al. [15] to OH groups bonded to an octahedrally coordinated aluminium atom. The upfield shift

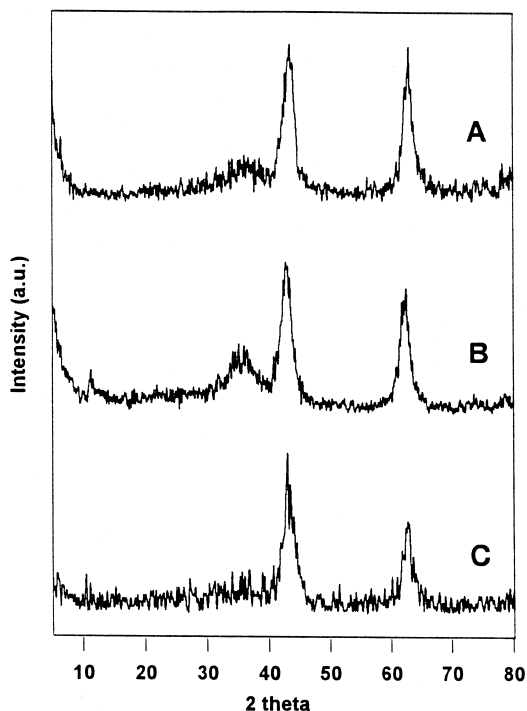


Fig. 2. XRD patterns for solids: (A) HT-Mg/Al-773, (B) HT-Mg/Ga-773 and (C) HT-Mg/Al,Ga-773.

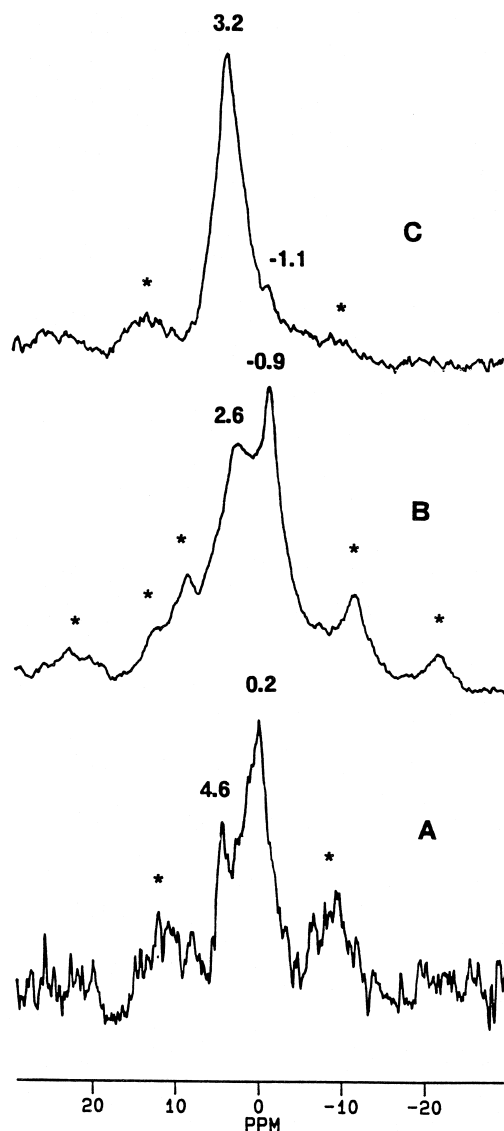


Fig. 3. ^1H MAS NMR spectra for solids: (A) MgO , (B) Al_2O_3 and (C) Ga_2O_3 . Asterisks denote spinning side bands.

of this signal at -0.9 ppm suggests that these OH groups are of a basic character. The peak at 2.6 ppm is highly asymmetric owing to the overlap of the lines corresponding to OH groups bonded to two or three octahedral aluminium atoms and an octahedral and a tetrahedral atom [15]. Finally, the ^1H MAS NMR spectrum for the gallium oxide (Fig. 3C) comprises a strong signal at 3.2 ppm and a weak one at -1.1 ppm. Based on previous assignments for

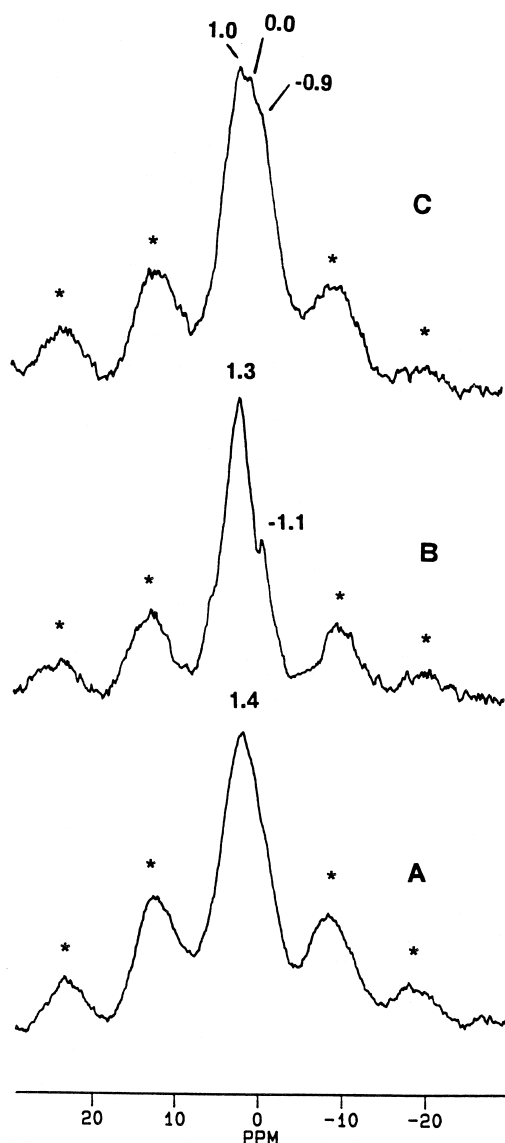


Fig. 4. ^1H MAS NMR spectra for solids: (A) HT-Mg/Al-773, (B) HT-Mg/Ga-773 and (C) HT-Mg/Al,Ga-773. Asterisks denote spinning side bands.

alumina [15–17], the signal at -1.1 ppm can be ascribed to basic OH groups bonded to an octahedrally coordinated gallium atom, whereas that at 3.2 ppm can be assigned to OH groups bonded to several octahedrally and tetrahedrally coordinated gallium atoms.

Fig. 4 shows the ^1H MAS NMR spectra for the LDH calcination products. All three spectra exhibit a

strong, broad band at 1.0 – 1.4 ppm. The width of this band suggests homogeneity in the distribution of surface OH groups in the different mixed oxides. It is therefore impossible to distinguish the signals for OH groups in periclase. Solid HT-Mg/Ga-773 exhibits a signal at -1.1 ppm, which, as noted earlier, was assigned to basic OH groups bonded to an octahedrally coordinated gallium atom. This band is also observed, as a shoulder, in the spectrum for HT-Mg/Al,Ga-773. On the other hand, no alumina signal can be clearly distinguished in the spectra for the two solids that contain this oxide. These results also seemingly suggest that the fraction of OH groups bonded to several octahedrally and tetrahedrally coordinated gallium atoms in the solids containing Ga_2O_3 is negligible since the strongest signal for the pure oxide (3.2 ppm, Fig. 3C) does not appear now (Fig. 4B and C).

From Fig. 3, it is apparent that the signal-to-noise ratio for MgO is much lower than those for the aluminium and gallium oxides; this suggests that the number of OH groups present in the latter oxides is much greater than that in the magnesium oxide. Consequently, the strong signal at 1.0 – 1.4 ppm in the spectrum for the mixed oxides can be assigned to OH groups in Al_2O_3 and Ga_2O_3 .

In conclusion, the calcination of Mg/Al and Mg/Ga LDHs yields mixtures of oxides of increased Brönsted basic character relative to the individual pure oxides.

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