

# Comparison of the structural and acid–base properties of Ga- and Al-containing layered double hydroxides obtained by microwave irradiation and conventional ageing of synthesis gels

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Structural and acid–base properties of Mg/Al and Mg/Ga layered double hydroxides (LDH's) obtained by microwave irradiation of the co-precipitated gels have been investigated and compared to those of samples conventionally aged by prolonged hydrothermal treatment of the gels. Similar crystallinities and chemical compositions were obtained whatever the synthesis method used. Besides, all samples, and remarkably the Ga-containing LDH's with a molar ratio Mg : Ga = 4.5, exhibited pure lamellar phases. The acid–base properties of the mixed oxides obtained by calcination of the LDH's have been examined by microcalorimetric adsorption of CO<sub>2</sub> and by FTIR spectroscopy upon CH<sub>3</sub>CN interaction. These techniques gave evidence that the number and strength of acid and basic sites were influenced by the nature and amount of the trivalent cation, as well as by the preparation method.

## Introduction

Layered double hydroxides (LDH's) are laminar solids which have been claimed to be basic catalysts in reactions such as aldol, Knoevenagel and Claisen–Schmidt condensations,<sup>1–5</sup> Michael additions,<sup>6</sup> phenol alkylations,<sup>7</sup> epoxidation of olefins<sup>8</sup> or halide exchanges.<sup>9</sup>

The general formula of the LDH's is  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} [A_{x/m}]^{m-} \cdot mH_2O$ , with layers composed by the superposition of positively charged metallic hydroxide sheets, where M<sup>2+</sup> is a divalent cation such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, and M<sup>3+</sup> is a trivalent cation such as Al<sup>3+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup>, Ga<sup>3+</sup> with an appropriate M<sup>2+</sup> : M<sup>3+</sup> molar ratio ranging from 1.5 to 4.5. The positive charge is compensated by anions (CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, OH<sup>-</sup> etc.) located in the interlayer spaces.<sup>10</sup> The Mg/Al hydroxycarbonate LDH corresponds to the naturally occurring hydroxycarbonate mineral, which has been extensively characterised and easy to synthesise in the laboratory by a co-precipitation technique. By controlled thermal decomposition of LDH's, mixed oxides exhibiting homogeneous interdispersion of the elements and high specific surface areas can be obtained. Moreover, mixed oxides exhibit basic properties which can be tailored by changing the calcination temperature, the nature and amount of structural cations and compensating anions, as well as the method of synthesis of the LDH's.<sup>10–12</sup>

Concerning this latter point, in the case of the Mg/Al LDH's Fetter *et al.*<sup>13,14</sup> have found that microwave irradiation of the co-precipitated gel, instead of the hydrothermal treatment usually performed, allows well crystallised and pure hydroxycarbonate-like phases to be obtained, and for the ageing time

to be reduced from 18–24 h to 2–10 min. However the influence of microwave treatment in the synthesis of LDH's containing trivalent cations other than Al<sup>3+</sup> has not been investigated. In this respect Ga<sup>3+</sup> is particularly interesting. We have previously shown that in contrast to Al<sup>3+</sup>, Ga<sup>3+</sup> gives pure lamellar phases with a Mg : Ga ratio of 4.5,<sup>15</sup> these solids leading in turn to highly active catalysts.<sup>15,16</sup> This was an incitement to prepare Al- and Ga-containing LDH's with Mg : Al = 3 and Mg : Ga = 4.5, respectively, either by conventional hydrothermal treatment or by microwave irradiation of the co-precipitated gels and to compare their physico-chemical properties. We have particularly focused our attention on the acid–base properties of the mixed oxides obtained from these different LDH's. With this aim, adsorptions of CO<sub>2</sub> and CH<sub>3</sub>CN probes have been followed using microcalorimetry and FTIR spectroscopy, respectively.

## Experimental

### Preparation of materials

All the LDH samples were synthesised following the same procedure until the gel was obtained. They were prepared using a Mg : M(III) ratio of 3 and 4.5, when M(III) was Al<sup>3+</sup> or Ga<sup>3+</sup>, respectively. An aqueous solution of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.75 M) and of Al(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.25 M) or Ga(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.17 M) (Aldrich), and a 2 M NaOH aqueous solution were added dropwise to a polypropylene reactor at constant pH = 9.5 under vigorous stirring. In the case of the samples hereafter designated as conventionally prepared, and noted as

Mg/M(III)cv, the gel obtained after the complete addition of the nitrate solutions and NaOH was aged while magnetically stirring for 18 h at room temperature (RT). In the case of the samples hereafter designated as microwave irradiated, and noted Mg/M(III)mw, the gel was treated in a commercial microwave oven (MIC-I, SEV) operating at a power level of 168 W for 7 min. The solids obtained were washed several times with water, recovered by decanting, and dried in an open air oven at 340 K. Mixed Mg/Ga/Al samples with Mg : (Ga + Al) = 3.2 and Ga : (Ga + Al) = 0.18 were also prepared following the same procedures and designated as, e.g. Mg/Ga/Alcv.

### Characterisation techniques

Elemental analyses were performed at the Service Central d'Analyse du CNRS (Solaize, France). The powder X-ray diffraction (XRD) patterns were obtained with a CGR Theta 60 diffractometer using monochromatized Cu-K $\alpha$ 1 radiation ( $\lambda = 1.542 \text{ \AA}$ , 40 kV and 50 mA). Patterns were recorded over the  $2\theta$  range from 4 to 70°. BET specific surface areas were determined with a Micromeritics ASAP 2100 instrument by N<sub>2</sub> adsorption at 77 K on samples calcined in synthetic air at 723 K and outgassed at 523 K (10<sup>-4</sup> Pa). TG-DSC experiments were carried out in a Setaram TG-DSC-111 apparatus, with fully programmable heating and cooling sequences, sweep gas valves switchings, and data analysis. About 50 mg of an as-prepared sample were placed in a platinum crucible and dried at 393 K in a stream of He (flow: 20 cm<sup>3</sup> min<sup>-1</sup>). The sample was heated from 393 to 873 K (heating rate: 1 K min<sup>-1</sup>), in a stream of He (flow: 20 cm<sup>3</sup> min<sup>-1</sup>). The composition of gas outflowing the TG-DSC apparatus was monitored continuously on-line with a Leybold Transpector SQX quadrupole mass spectrometer (0–200 amu), monitoring the masses of 18 (H<sub>2</sub>O), 30 (NO) and 44 g (CO<sub>2</sub>).

The microcalorimetric measurements of adsorption and desorption (TPD) of CO<sub>2</sub> were performed using a Setaram TG-DSC-111 instrument. The samples were previously outgassed at 723 K, cooled to 373 K, and placed in contact with flowing CO<sub>2</sub>. Thermal events in the microcalorimeter cell were recorded. Weakly adsorbed CO<sub>2</sub> was removed in He flow at 373 K, and temperature programmed desorption (TPD) experiments were then performed following the weight loss in the He flow as the temperature was raised from 373 to 723 K (heating rate, 10 K min<sup>-1</sup>). Absorption/transmission IR spectroscopy experiments were performed on a Perkin-Elmer FT-IR 1760-X spectrophotometer equipped with a Hg–Cd–Te cryodetector (number of scans 60) upon adsorption of CH<sub>3</sub>CN (Carlo Erba, RPE) at RT. The powdered samples were prepared as pellets in self-supporting discs (10 mg cm<sup>-2</sup>), activated by heating under vacuum at 723 K, then heated in dry O<sub>2</sub> at 723 K and cooled down in oxygen. For the purpose of comparison, experiments were also performed on the following reference oxides: Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Rhône-Poulenc), Ga<sub>2</sub>O<sub>3</sub> and MgO (obtained by calcination of Ga(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> (Strem Chemicals), respectively, at 723 K).

## Results and discussion

### Investigation of the chemical and structural properties of LDH samples

The chemical compositions of the resulting LDH samples are given in Table 1. It is noteworthy that the use of microwave irradiation during the crystallisation step leads to LDH's with roughly the same compositions as those prepared by the conventional ageing by reflux. This shows that it is likely that the composition depends on the precipitation step, and particularly on parameters such as pH, concentration and rate of addition of solutions, rather than on the crystallisation step.

The Mg : M(III) ratios determined in the solids are very similar to those measured in solution. This is a common feature of Mg/Al LDH's. Conversely it should be noted that inconsistent results concerning this point are reported in the literature for Ga-containing LDH's. On the one hand, Mg : Ga molar ratios determined in solution and in solids are similar, ranging from 3 to 4.5, when precipitations are performed at pH = 11–12.<sup>17–19</sup> On the other hand, discrepancies are obtained in the case of syntheses performed at pH values above 10. In particular, incomplete incorporation of Mg<sup>2+</sup> is reported in some cases,<sup>19</sup> and attributed to the high solubility of Mg(OH)<sub>2</sub>. In contrast, incomplete incorporation of Ga<sup>3+</sup> is reported in other cases,<sup>16,20–22</sup> leading to solids with Mg : Ga ratios in the range 3.5–4.5 when starting from Mg : Ga ratios = 3 in solution. One can believe that this results from an underestimation of the degree of hydration of the precursor Ga nitrate salt.

All the LDH samples prepared showed XRD patterns typical of hydroxalcalite-like compounds (JCPDS card 22-0700) (Fig. 1). The reflections observed are indexed as hexagonal lattices with R3m rhombohedral symmetry as is usual for the LDH structure. It should be noted that the (003) and (006) lines are broader in Al- than in Ga-containing LDH's. Specifically, the mean particle sizes calculated from the (003) linewidth using the Scherrer equation increase from 4.4–4.8 to 24 nm on changing from Mg/Al to Mg/Ga samples. This is consistent with the differences already observed between XRD patterns of Ga- and Al-containing LDH's in their nitrate form.<sup>16</sup> This emphasizes the influence on the crystallinity of either the Mg : M(III) ratio or the nature of the trivalent cation. Very different crystallinities were found for Co/M(III)/CO<sub>3</sub> LDH's when M(III) = Al, Fe or Cr.<sup>23</sup> In contrast they do not vary significantly for Zn/Al<sup>24</sup> and Mg/Fe<sup>25</sup> LDH's with different M(II) : M(III) ratios in the 2–4 range. Therefore the nature of the trivalent cation appeared to be the influential parameter on which the crystallinity depends. It is noteworthy that the crystallinity of the conventionally prepared and microwave irradiated samples with similar chemical compositions is identical.

The (110) and (113) lines in the range  $2\theta = 60$ – $62^\circ$  were clearly distinct for Ga-containing samples only, revealing their higher intralayer ordering in comparison with the Al-containing ones. When going from the Mg/Al to the Mg/Ga samples, due to the increase in the Mg : M(III) molar ratio,

Table 1 Chemical compositions, structural and textural parameters of LDH samples

Samples	Chemical composition	Mg : (Al+Ga)					
		Solution	Solid	a/nm	c/nm	D(003)/nm	S <sub>BET</sub> <sup>a</sup> /m <sup>2</sup> g <sup>-1</sup>
Mg/Almw	Mg <sub>0.751</sub> Al <sub>0.249</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.015</sub> (NO <sub>3</sub> ) <sub>0.264</sub> ·0.57H <sub>2</sub> O	3	3	0.3145	2.46	4.4	160
Mg/Alcv	Mg <sub>0.748</sub> Al <sub>0.252</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.042</sub> (NO <sub>3</sub> ) <sub>0.213</sub> ·0.62H <sub>2</sub> O	3	2.97	0.3155	2.45	4.8	203
Mg/Ga/Almw	Mg <sub>0.762</sub> Al <sub>0.196</sub> Ga <sub>0.042</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.073</sub> (NO <sub>3</sub> ) <sub>0.235</sub> ·0.60H <sub>2</sub> O	3.2	3.20	0.3165	2.45	5.8	176
Mg/Ga/Alcv	Mg <sub>0.760</sub> Al <sub>0.197</sub> Ga <sub>0.043</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.014</sub> (NO <sub>3</sub> ) <sub>0.200</sub> ·0.63H <sub>2</sub> O	3.2	3.17	0.3185	2.42	4.8	200
Mg/Gamw	Mg <sub>0.822</sub> Ga <sub>0.178</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.015</sub> (NO <sub>3</sub> ) <sub>0.196</sub> ·mH <sub>2</sub> O	4.5	4.62	0.3200	2.38	24	120
Mg/Gacv	Mg <sub>0.821</sub> Ga <sub>0.178</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>0.015</sub> (NO <sub>3</sub> ) <sub>0.236</sub> ·mH <sub>2</sub> O	4.5	4.61	0.3215	2.38	24	90

<sup>a</sup>Determined on samples calcined at 723 K.

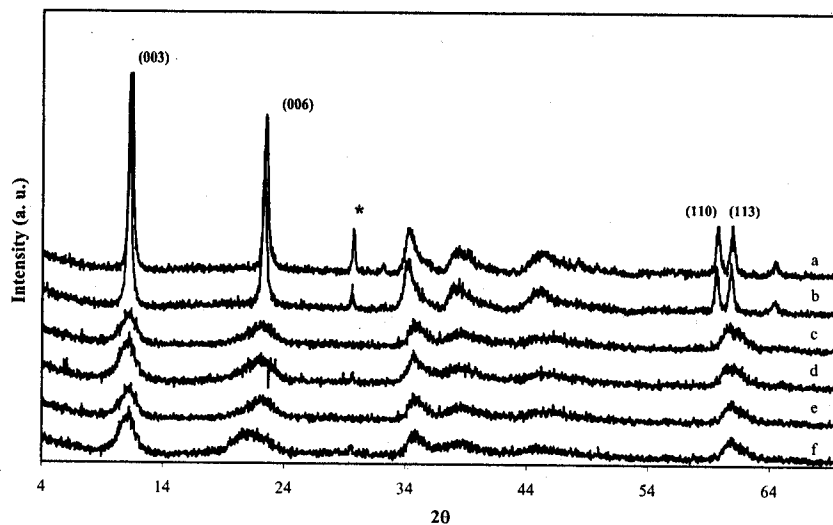


Fig. 1 XRD patterns of (a) Mg/Gacv; (b) Mg/Gamw; (c) Mg/Ga/Alcv; (d) Mg/Ga/Almw; (e) Mg/Alcv; (f) Mg/Almw. (\*NaNO<sub>3</sub>)

the intermetallic distances determined from the (110) diffraction line,  $a = 2d_{001}$ , increase (Table 1) owing to the larger ionic radius of Mg<sup>2+</sup> (0.66 nm) compared with Al<sup>3+</sup> (0.53 nm) or Ga<sup>3+</sup> (0.62 nm). The larger ionic size of Ga<sup>3+</sup> with respect to Al<sup>3+</sup> also explains why the unit cell  $a$  parameter increases with increasing Ga : (Ga + Al) molar ratios (Fig. 2).

The slightly higher lattice  $a$  parameters for the conventionally than for the microwave prepared samples should be noted. This can be attributed to the systematic difference in the (Al + Ga) : (Mg + Al + Ga) molar ratios of the layers between the two families of samples in spite of their similar global chemical compositions previously reported. This is an apparent discrepancy that arises because the lattice  $a$  parameter is related to the true composition of the layers, whereas chemical analysis is not able to discriminate between the cations belonging to the LDH layers and to eventual additional phases. Actually very low amounts of additional phases cannot be detected by XRD. These differences between conventionally prepared and microwave irradiated samples show that weak modifications in the chemical compositions of the LDH phases take place during the crystallisation steps. We finally note that an additional peak due to NaNO<sub>3</sub> appears at  $2\theta = 29.5^\circ$  in the microwave irradiated samples, and in the Mg/Ga sample conventionally prepared. This salt was not eliminated in spite of repeated washings and is perhaps occluded in the structure.

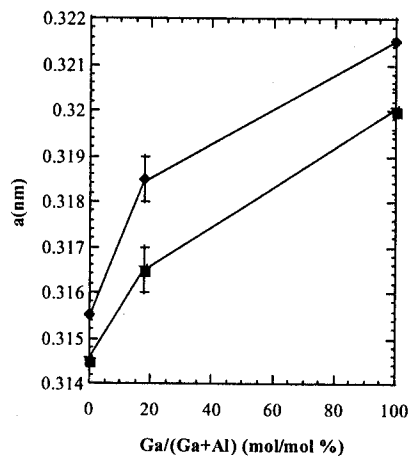


Fig. 2 Lattice  $a$  parameter as a function of Ga : (Ga + Al) ratio (mol/mol %) for cv (◆) and mw (■) samples.

The specific surface areas of the calcined samples remained almost constant or slightly increased (in the case of mw samples) on going from Mg/Al to Mg/Ga/Al samples, *i.e.* when about 18% of Al is replaced by Ga (Fig. 3). Conversely, they dramatically decreased for Mg/Ga samples, in agreement with the high crystallinity of Mg/Ga LDH's. Interestingly, the decrease in the surface area observed on going from Mg/Al to Mg/Ga samples was more marked for conventionally prepared samples (from 203 to 90 m<sup>2</sup> g<sup>-1</sup>) than for the microwave irradiated ones (from 160 to 120 m<sup>2</sup> g<sup>-1</sup>). It should be noted that conventionally prepared Mg/Al and Mg/Ga/Al samples exhibited higher specific surface areas than the microwave irradiated ones, in spite of the fact that prolonged reflux of the gels can increase the mean particle sizes of the samples. In contrast, the Mg/Gacv sample showed a lower mean particle size than Mg/Gamw.

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the Mg/Alcv and Mg/Gacv samples are shown in Fig. 4a. They are representative of both conventionally prepared and microwave irradiated samples because no significant differences due to the preparation method were evident. Three weight loss domains were identified with complex phenomena shown to take place above 500 K in the DTG profiles. More details concerning this behaviour were obtained by coupling the TG-DTG experiments with MS analysis of the gases released. The masses 18 (H<sub>2</sub>O), 44 (CO<sub>2</sub>) and 30 (NO) have been monitored, owing to the compositions of the LDH's. The MS profiles of Mg/Alcv and

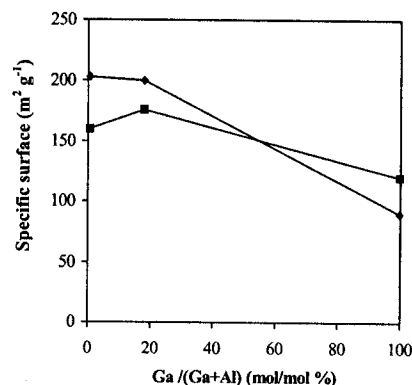


Fig. 3 Specific surface areas of cv (◆) and mw (■) samples calcined at 723 K as a function of Ga : (Ga + Al) ratio (mol/mol%).

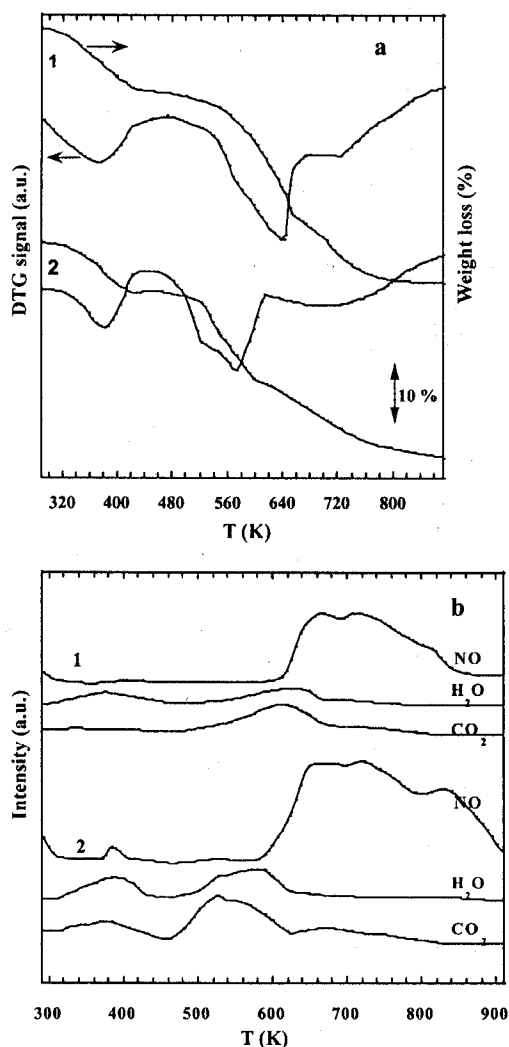


Fig. 4 TG-DTG profiles (a) and temperature-programmed desorption followed by mass spectrometry (b) of Mg/Alcv (curves 1), and Mg/Gacv (curves 2).

Mg/Gacv are given in Fig. 4b. Temperatures for the maximum rates of emission of the different gases are reported for all samples in Table 2, as well as the total weight losses at 873 K.

The low temperature domain, corresponding to elimination of the intercalated water molecules, is characterised by a broad peak with a maximum at 373–383 K. In addition, in Mg/Ga samples there is a concurrent release of CO<sub>2</sub> not observed in the case of Mg/Al samples. Consequently the amount of hydration water in samples of Mg/Gacv and Mg/Gamw could not be determined from the first weight loss in the TG analysis (see the formula of Table 1).

In the temperature range above 500 K, MS analysis clearly

Table 2 Temperature (K) of the peaks of emission of CO<sub>2</sub>, H<sub>2</sub>O and NO in MS analysis and total weight losses in TG.

Sample	CO <sub>2</sub>	H <sub>2</sub> O	NO	Total -Δm(%)
Mg/Alcv	610	385–620	660–740–790	48
Mg/Almw	585	370–585	685–753–860	49
Mg/Ga/Alcv	610	370–629	650–705–790	46.5
Mg/Ga/Almw	600	370–600	660–710–805	47.5
Mg/Gacv	380–530	380–590	670–720–840	43
Mg/Gamw	380–550	380–580	650–710–840	43

shows that decarbonation and dehydroxylation of the layers are strictly concomitant in Mg/Al LDH's, while decarbonation occurs at least 30 K before dehydroxylation of the layers in Mg/Ga LDH's. Moreover decomposition of the nitrate species occurs in several steps when the previous events are complete and without significant elimination of water. According to these assignments, dehydroxylation and decarbonation on one hand, and decomposition of the nitrate species on the other hand, account for the intense and very broad peaks respectively observed in the DTG profiles above 500 K.

#### Investigation of the surface acid–base properties

The number and strength of basic sites of the different mixed oxides obtained upon calcination of the samples at 723 K were firstly examined by microcalorimetric adsorption of CO<sub>2</sub>. They were affected both by the nature of the trivalent cation and by the preparation method. All samples exhibited heats of adsorption in the range of 70–85 kJ mol<sup>-1</sup>, consistent with those previously found for these types of materials (Fig. 5a).<sup>15</sup> It is noteworthy that the heats of adsorption for conventionally prepared samples increased significantly on increasing the Ga content (from 71 kJ mol<sup>-1</sup> for Mg/Alcv to 85 kJ mol<sup>-1</sup> for Mg/Gacv), whereas all the microwave irradiated samples exhibited values of around 80 kJ mol<sup>-1</sup>. Note that the Mg/Almw sample showed higher basic strength than Mg/Alcv, whereas the Mg/Gamw sample showed slightly lower basic strength than Mg/Gacv. To account for the different specific surface areas of the samples, the density of basic sites were compared (Fig. 5b). In this regard, the very different behaviour of conventionally prepared and microwave irradiated samples is immediately noted. In the former, the density of the basic

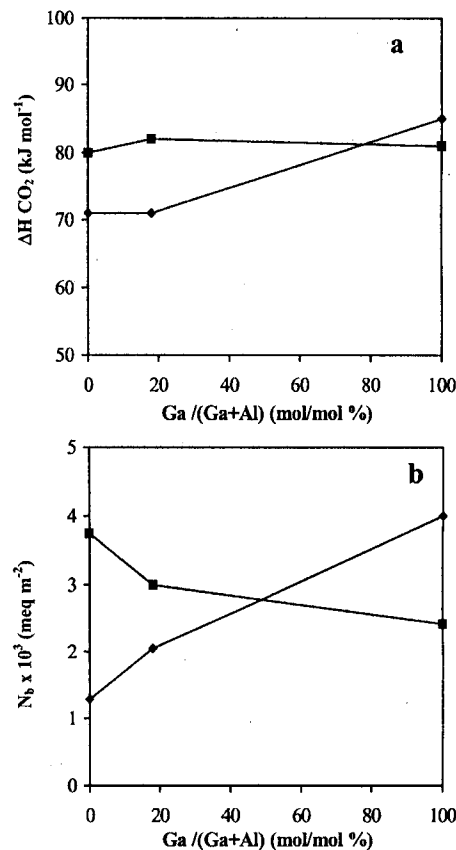
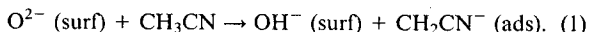


Fig. 5 Differential heat of adsorption (a) and density of basic sites (b) determined by microcalorimetric adsorption of CO<sub>2</sub> on cv (◆), and mw (■) LDH samples activated at 723 K as a function of Ga : (Ga+Al) ratio (mol/mol %).

sites markedly increased on increasing the Ga content, whereas in the mw samples it decreased. Moreover, the density of the basic sites on the Mg/Alcv sample was markedly lower than on Mg/Almw, while the opposite was found for the Mg/Ga samples. Also these results pointed out the necessity to characterise more extensively the surface properties of the samples by studying both their acidity and basicity. Indeed, it has been previously shown that LDH derived mixed oxides possess contemporaneously strongly basic sites, along with Lewis acid sites of medium-high strength.<sup>26</sup> In this work, we used acetonitrile as a probe, followed by FT-IR spectroscopy, this amphoteric molecule being particularly suitable to obtain information concerning the nature, strength and relative number of surface acid-base sites. For our purposes, here we just examined the C≡N stretching mode region, where the surface species formed either on acid or basic sites can be examined distinctly (Fig. 6). On Lewis acid sites acetonitrile is co-ordinated giving N-bonded complexes, exhibiting a couple of bands in the range 2350–2250 cm<sup>-1</sup> due to the ν(CN) fundamental mode split by coupling with the ν(CC) + δ<sub>sym</sub>(CH<sub>3</sub>) combination. The blue shift of these bands with respect to liquid acetonitrile (2292, 2254 cm<sup>-1</sup>) depends on the electron-withdrawing power of the cationic site and can be taken as a measure of the strength of the Lewis acid sites.<sup>27,28</sup> On strongly basic O<sup>2-</sup> sites acetonitrile forms CH<sub>2</sub>CN<sup>-</sup> carbanions which are thereafter stabilized onto the adjacent cationic sites, according to the following reaction:<sup>29</sup>



The anionic species show characteristic ν(CN) modes in the range 2200–2000 cm<sup>-1</sup>, the position depending on the acid-base character of the M<sup>n+</sup>-O<sup>2-</sup> adsorption pair. Moreover, CH<sub>2</sub>CN<sup>-</sup> anions can be solvated by CH<sub>3</sub>CN and lead to the formation of polymeric anionic forms such as

[CH<sub>3</sub>C(NH)CHCN]<sup>-</sup>. These species generally exhibit ν(CN) modes at a higher frequency than the monomer, but always in the same spectral range.

In Fig. 6a and b the spectra of adsorption of increasing doses of CH<sub>3</sub>CN on conventionally prepared Mg/Al and Mg/Ga samples, taken as examples, are displayed. The dotted lines correspond to the subsequent evacuation at RT, which removes physisorbed, weakly chemisorbed and hydrogen bonded acetonitrile species. In Fig. 6c we reported the spectra (for the sake of brevity only at the maximum CH<sub>3</sub>CN coverage and subsequent evacuation at RT) of microwave irradiated Mg/Al and Mg/Ga samples (curves 1 and 2, respectively) while in Fig. 6d, for the purpose of comparison, those of the reference oxides, Al<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and MgO (curves 1, 2 and 3, respectively).

The spectral features are mainly affected by the nature of the trivalent cation, and to a minor extent by the preparation method. In the 2350–2250 cm<sup>-1</sup> region, *i.e.* the region characteristic of acetonitrile co-ordinated on Lewis acid sites, two complex bands with maxima at 2300 and 2263 cm<sup>-1</sup> and shoulders at 2310 and 2280 cm<sup>-1</sup> were observed for the Mg/Alcv sample (Fig. 6a). They are ascribed to acetonitrile co-ordinated on Al<sup>3+</sup> sites with a different environment or coordination, thus with slightly different acidic strength. Interestingly, in the case of Mg/Almw sample (Fig. 6c, curve 1) Al<sup>3+</sup> sites with the highest strength (associated with the components at 2310, 2280 cm<sup>-1</sup>) were absent. The lower frequencies of the above bands with respect to those on alumina (2330 and 2300 cm<sup>-1</sup>, Fig. 6d, curve 1) shows that Al<sup>3+</sup> sites in the Mg/Al mixed oxides (and particularly in the Mg/Almw sample) are by far less acidic than in alumina, thus suffering the effects of the surrounding MgO-type lattice. Finally, note that Mg<sup>2+</sup> sites do not participate in the co-ordination of neutral acetonitrile species due to their very weak Lewis acidity, as shown by the comparison with the spectrum of pure MgO (Fig. 6d, curve 3).

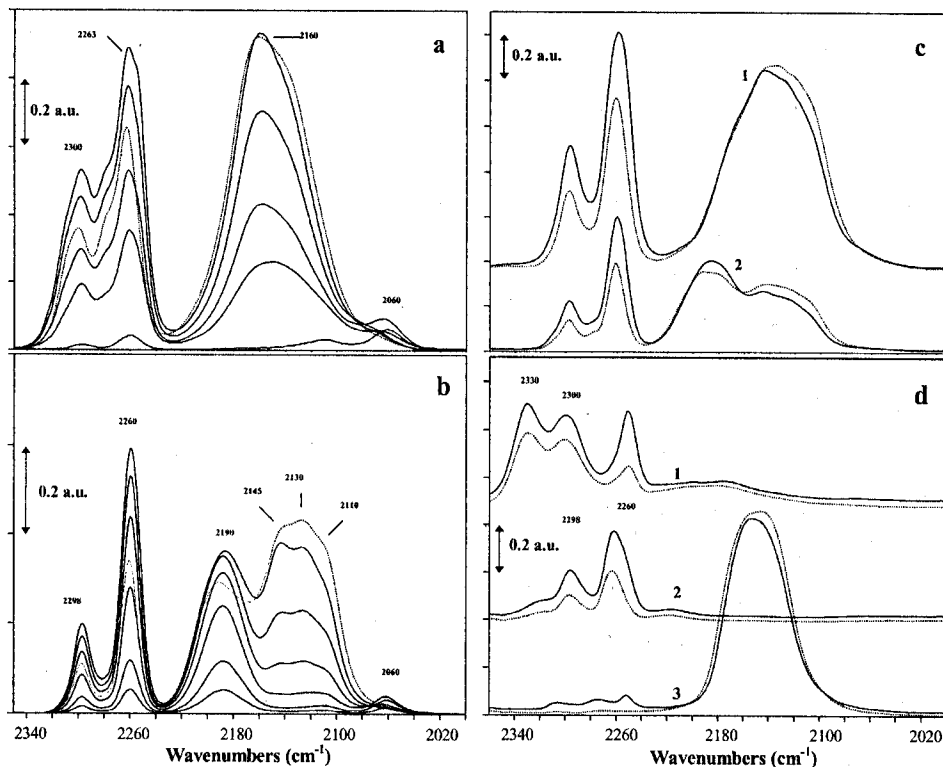


Fig. 6 FT-IR spectra in the ν(C≡N) region upon CH<sub>3</sub>CN adsorption on LDH samples activated at 723 K. Admission of increasing doses of CH<sub>3</sub>CN (from 0.1 to 200 Pa) on Mg/Alcv (a) and Mg/Gacv (b) samples. (c) Admission of 200 Pa of CH<sub>3</sub>CN on Mg/Almw (curve 1) and Mg/Gamw (curve 2). (d) Admission of 200 Pa of CH<sub>3</sub>CN on Al<sub>2</sub>O<sub>3</sub> (curve 1); Ga<sub>2</sub>O<sub>3</sub> (curve 2); MgO (curve 3). Dotted lines: subsequent evacuation at RT. Spectra have been reported after subtraction of the spectrum before CH<sub>3</sub>CN admission and translated along the y axis for the sake of clarity in sections (c) and (d).

For the Mg/Gacv sample (Fig. 6b) the bands due to adsorbed CH<sub>3</sub>CN were more symmetrical and were centered at 2298 and 2260 cm<sup>-1</sup>, thus revealing on one hand a lower heterogeneity, and on the other hand a lower acidic strength of Ga<sup>3+</sup> sites compared with Al-containing samples. The latter feature accounts for the scarce intrinsic Lewis acidity of Ga<sup>3+</sup> cations. In fact, Ga<sup>3+</sup> sites in Ga<sub>2</sub>O<sub>3</sub> show poor acidity, exhibiting bands at 2298 and 2260 cm<sup>-1</sup>, *i.e.* only slightly blue-shifted with respect to those of liquid CH<sub>3</sub>CN (Fig. 6d, curve 2). Similar features were observed for microwave irradiated Mg/Ga sample (Fig. 6c, curve 2).

The spectral region characteristic of anionic species formed on basic sites was next examined. For the Mg/Alcv sample a weak band at around 2060 cm<sup>-1</sup> was detected at a CH<sub>3</sub>CN equilibrium pressure below 10 Pa and disappeared on increasing the CH<sub>3</sub>CN coverage. Contemporaneously, a broad envelope with a maximum at around 2160 cm<sup>-1</sup> developed and slightly increased in intensity upon subsequent evacuation at RT. Similar behaviour was shown by MgO upon increasing the CH<sub>3</sub>CN coverage. Therefore, these bands were assigned to the monomeric and polymeric anionic species, respectively, formed on the strongly basic oxygen ions of Mg<sup>2+</sup>O<sup>2-</sup> pairs and co-ordinated to Mg<sup>2+</sup> cations. The higher complexity of the band at around 2160 cm<sup>-1</sup> in the Mg/Al sample than in MgO could reflect a higher heterogeneity of Mg<sup>2+</sup> adsorption sites in the mixed oxide (*e.g.* different coordination). Note that anionic species are not formed on alumina (Fig. 6d, curve 1) owing to the poor basicity of Al<sup>3+</sup>O<sup>2-</sup> pairs.

On changing from Mg/Alcv to the Mg/Almw sample the absorption due to anionic species showed a more complex shape, owing to the higher surface heterogeneity induced by the microwave treatment. Moreover, the maximum of this absorption was shifted from 2160 to 2150 cm<sup>-1</sup>, in agreement with the higher basic strength measured by microcalorimetry of CO<sub>2</sub> in the microwave irradiated sample.

In the case of the Mg/Gacv sample the monomeric anionic species adsorbed on Mg<sup>2+</sup> was again detected at low CH<sub>3</sub>CN coverage at 2060 cm<sup>-1</sup>, while the broad band associated with polymeric species of Mg<sup>2+</sup> was better resolved (components at 2145, 2130 and 2110 cm<sup>-1</sup>) and shifted to a lower frequency than in the Mg/Al sample. This is likely to account for the presence of Mg<sup>2+</sup>O<sup>2-</sup> pairs of higher basicity. Moreover, a further intense component was observed at 2190 cm<sup>-1</sup>. On the basis of its position, this band should be ascribed to anionic species formed on M<sup>n+</sup>O<sup>2-</sup> pairs with lower basicity than Mg<sup>2+</sup>O<sup>2-</sup>. However, it should be noted that Ga<sup>3+</sup>O<sup>2-</sup> pairs in pure Ga<sub>2</sub>O<sub>3</sub> (Fig. 6d, curve 2) are not sufficiently basic to give anionic species. So we suggest that a large fraction of the anionic species are formed on Mg<sup>2+</sup>O<sup>2-</sup> pairs, but adsorbed thereafter on adjacent Ga<sup>3+</sup> cations, isolated or belonging to small surface Ga oxide islands. Neutral and anionic species would thus compete for Ga<sup>3+</sup> adsorption sites. It should also be noted that the band at 2190 cm<sup>-1</sup> shows quite a different behaviour with respect to those at lower frequencies, being less pressure-dependent and its intensity slightly decreases upon evacuation at RT. These findings suggest that this absorption is more likely to be associated with monomeric rather than with polymeric anionic species.

Similar features were observed in the case of the Mg/Gamw sample, but for a slight intensity increase of the component at 2190 cm<sup>-1</sup> relative to the lower frequency ones. This could be attributed to a higher surface concentration of Ga<sup>3+</sup> (thus a lower surface concentration of Mg<sup>2+</sup>) in the case of the microwave irradiated mixed oxide. This datum is consistent with the slight increase in the lattice *a* parameter on going from Mg/Gacv to Mg/Gamw samples. It is also in agreement with the slightly lower basic strength shown by microcalorimetric measurements of the Mg/Gamw sample compared with

Mg/Gacv. However, IR results also point out the necessity to handle with prudence the microcalorimetric data, which give average values, in the case of systems presenting high surface heterogeneity. In particular, for Mg/Ga mixed oxides IR data have shown the presence of two main families of basic sites of strength, respectively, higher and lower than in the Mg/Al samples. Thus, the higher (for cv samples) or similar (for mw samples) basic strength determined by microcalorimetry of Mg/Ga samples in comparison to Mg/Al ones can be attributed to the different relative amounts of these sites.

Intermediate properties between those of Mg/Al and Mg/Ga mixed oxides were observed in the case of Mg/Ga/Al samples (spectra not reported). Actually in this case the analysis of the spectra in the region characteristic of acid sites is complicated by the strong superposition of the bands due to CH<sub>3</sub>CN co-ordinated to Al<sup>3+</sup> and Ga<sup>3+</sup> sites.

Information concerning the numbers of acid and basic sites can be obtained from the integrated intensity of the absorptions associated with acid and basic sites, *I<sub>a</sub>* and *I<sub>b</sub>*, respectively, assuming similar molar absorption coefficients for the different surface species observed. In order to eliminate the contribution of physisorbed and hydrogen bonded species, *I<sub>a</sub>* and *I<sub>b</sub>* have been evaluated from the spectra of samples upon acetonitrile admission and subsequent evacuation at RT. Moreover, owing to the different specific surface areas of the samples, they have been normalized per surface area unit (m<sup>2</sup>) (Fig. 7).

One observation concerns the decrease in the amount of acid sites (*I<sub>a</sub>*) on going from Mg/Al to Mg/Ga samples, which is more marked for microwave irradiated samples. This can be attributed on one hand to the lower number of M(III) cations relative to Mg<sup>2+</sup> in Mg/Ga samples compared with the Mg/Al ones. On the other hand it could be due to the higher basicity of Ga<sup>3+</sup> cations as previously evidenced. Accordingly, in the

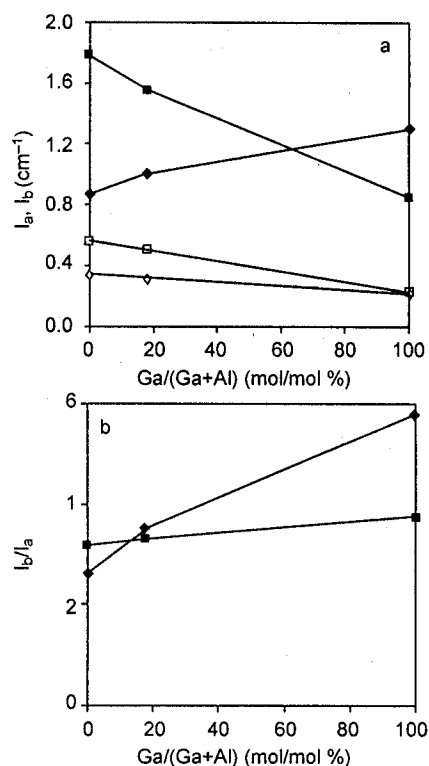


Fig. 7 (a) Integrated intensities (cm<sup>-1</sup>) of the IR bands associated with the species formed on acid and basic sites, *I<sub>a</sub>* and *I<sub>b</sub>*, respectively, normalized per surface area unit (m<sup>2</sup>) and per pellet density (mg cm<sup>-2</sup>) as a function of Ga : (Ga+Al) ratio (mol/mol %). *I<sub>a</sub>* (◇) and *I<sub>b</sub>* (◆) for cv samples; *I<sub>a</sub>* (□) and *I<sub>b</sub>* (■) for mw samples. (b) *I<sub>b</sub>*/*I<sub>a</sub>* ratios for cv (◆) and mw (■) samples as a function of Ga : (Ga+Al) ratio (mol/mol %).

case of conventionally prepared samples, the number of basic sites increased on increasing the Ga molar fraction and conversely, it decreased greatly for microwave irradiated samples. The lower amount of basic sites in Mg/Gamw mixed oxide with respect to Mg/Gacv is consistent with the higher surface enrichment in Ga<sup>3+</sup> as evidenced by IR results for this sample. It is worth noting that this increased coverage decreases the concentration of O<sup>2-</sup> basic sites on the surface, and therefore the adsorption of CO<sub>2</sub>. This feature accounts for the decrease in the density of basic sites in the microwave irradiated samples (Fig. 5b).

Therefore, due to the reverse behaviour of cv and mw samples on increasing the Ga content, the Mg/Almw sample has higher numbers of basic sites than Mg/Alcv, while the opposite is observed for Mg/Ga mixed oxides. Actually, in the case of Mg/Al mixed oxides both the amounts of basic and acid sites increased on changing from Mg/Alcv to Mg/Almw sample, so the I<sub>b</sub>/I<sub>a</sub> ratios for these samples were similar (Fig. 7b). These findings indicate that the microwave treatment probably induces higher amounts of surface defective sites.

In the case of Mg/Ga samples, the microwave treatment has a negative influence on the density of basic sites. However, when the relative amounts of basic and acid sites are considered (Fig. 7b), it is noted that both cv and mw Mg/Ga samples exhibit a more basic character than Mg/Al ones, although the differences are much more significant in the case of conventionally prepared materials.

## Conclusions

LDH compounds containing Mg<sup>2+</sup> as divalent and Al<sup>3+</sup> and/or Ga<sup>3+</sup> as trivalent cations have been prepared by microwave irradiation of the co-precipitated gels and their properties compared to those of samples conventionally obtained by prolonged reflux of the gels. Remarkably, the use of the microwave technique allows the duration of the synthesis to be significantly reduced. No significant differences were observed in the structural and textural properties of the microwave irradiated samples compared with conventionally prepared ones of similar chemical composition. Only a systematic difference in the lattice *a* parameters between the two families of materials is noted, owing to a less homogeneous distribution of cations in the case of Ga-containing LDH's. At variance, crystallinity markedly increases when going from Al- to Ga-containing samples as has generally been reported. Microcalorimetric and spectroscopic measurements upon CO<sub>2</sub> and CH<sub>3</sub>CN adsorption show that mixed oxides obtained by calcination at 723 K of LDH compounds exhibit strongly basic sites, along with acid sites of medium strength. The numbers and strengths of the basic and acid sites depend on the nature and amount of the trivalent cation, as well as on the synthesis method. The tendency is toward an increase in the basic character when going from Al to Ga-containing mixed oxides.

The microwave irradiation technique allows Al-containing materials exhibiting higher amounts of surface defective sites to be obtained, while in the case of Ga-containing materials it induces a higher surface segregation of Ga<sup>3+</sup>.

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