Journal of Solid State Chemistry **168,** 156–161 (2002)
doi:10.1006/jssc.2002.9655

Comparative Study of Mg/*M*(III) (*M*=Al, Ga, In) Layered Double Hydroxides Obtained by Coprecipitation and the Sol–Gel Method

María A. Aramendía, Victoriano Borau, César Jiménez, José M. Marinas, José R. Ruiz,[1] and Francisco J. Urbano

Departamento de Química Orgánica, Universidad de Córdoba, Campus de Rabanales, Edificio C-3, Ctra. Nacional IV-A, km 396, E-1404 Córdoba, Spain

Received October 8, 2001; in revised form May 8, 2002; accepted May 13, 2002

Various layered double hydroxides (LDHs) consisting of magnesium and a trivalent metal (Al, Ga or In) in an Mg/*M*(III) ratio of 3 were prepared by precipitation from the corresponding nitrates and also from magnesium ethoxide and the acetylacetonates of the trivalent metals using the sol–gel method. The six LDHs thus obtained were calcined at 500°C. All solids were characterized by XRD and IR spectroscopy prior to and after calcination. Their textural properties were determined from nitrogen adsorption measurements and their surface chemical properties by CO_2 chemisorption. © 2002 Elsevier Science (USA)

Key Words: **hydrotalcite; layered double hydroxides; mixed oxides; sol–gel method; coprecipitation.**

INTRODUCTION

Layered double hydroxides (LDHs) constitute a major class of materials of the anionic clay family. LDHs are structurally related to brucite [$Mg(OH)_2$]: magnesium cations are at the centers of octahedra the vertices of which are occupied by hydroxyl groups that are connected to one another forming layers. The layers in turn bind via hydrogen bonds between hydroxyl groups to form stacks. In LDHs, some Mg^{2+} ions are replaced with trivalent ions, which introduces a charge deficiency in the layers. In order to ensure electroneutrality in the overall structure, the positive charge is countered by anions present in a disorderly manner in the interlayer spacing, which also contains crystallization water (1).

The general formula of LDHs is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}A^{n-}_{x/n}\cdot mH_2O$, where *M*(II) and *M*(III) denote a divalent and a trivalent metal, respectively, and *A* is an anion. A wide variety of LDHs containing divalent and trivalent cations (Mg, Zn, Cr, Al, Fe, Ni, Co) in combination with different anions has been reported (2). Lately, our group has used Mg/Al, Mg/Ga, Mg/In and Ca/Al LDHs obtained by coprecipitation in various organic oxidation and reduction processes (3–6). LDHs and their calcination products are also widely used as catalysts for condensation (7–10) and hydrogenation reactions (11, 12). Finally, LDHs can also act as sorbents (13) and ion exchangers (14).

LDH are commonly prepared by coprecipitation method of metallic salts in alkaline media either at constant or increasing pH. The morphology and particle size distribution will thus depend on the supersaturation of the synthesis solutions (2, 15). The changes undergone by LDHs during calcination up to 500°C are well-documented (16, 17). Below 200°C, they only lose interlayer water; at 450–500°C, however, they undergo dehydroxylation and decomposition of all carbonate into carbon dioxide and the corresponding metal oxide. The mixed oxides obtained, exhibiting peculiar properties, such as high specific surface areas and narrow pore size distributions. In order to modify the textural properties of LDHs and their calcination products, different LDHs have been obtained using the sol–gel method. This includes the hydrolysis of alkoxide precursors and has been used to obtain solids of different nature, including TiO_2–MgO (18), MgO–Al_2O_3 (19) and Ga_2O_3–Al_2O_3 (20) systems.

This paper reports on the synthesis of Mg/Al, Mg/Ga and Mg/In LDH using the sol–gel method. The results are discussed in the light of those previously obtained with Mg/*M*(III) LDHs prepared by coprecipitation (21,22). All solids were characterized by using X-ray diffraction and IR spectroscopy. The textural properties of the LDHs and the surface basic properties of their calcination products at 500°C as determined by CO_2 chemisorption are also reported.

---

[1] To whom correspondence should be addressed. Fax: +34-957-21-86-06. E-mail: qo1ruarj@uco.es.

0022-4596/02 $35.00

EXPERIMENTAL

The Mg/Al, Mg/Ga and Mg/In LDHs obtained by coprecipitation were prepared from aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Ga(NO_3)_3 \cdot 6H_2O$ and $In(NO_3)_3 \cdot 5H_2O$ in an Mg(II)/*M*(III) ratio of 3 at pH 10 at 60°C. The solutions containing the metals were slowly added to a second aqueous solution containing Na_2CO_3 in a CO_3^{2-}/[Mg(II) + *M*(III)] ratio of 0.05. pH 10 was maintained by addition of aqueous 1 M NaOH. The resulting mixtures were allowed to stand at 80°C for 24 h, after which the solids were filtered, washed with 2 L of de-ionized water and dried in a stove at 110°C.

The procedure followed to synthesize the LDHs by the sol–gel method was as follows: an amount of 0.15 mol of magnesium ethoxide was dissolved in 200 mL of ethanol containing a small amount of 35% aqueous HCl (until pH = 3). The solution was refluxed for 3 h under continuous stirring. Then, a volume of 200 mL of acetone containing 0.05 mol of aluminum, gallium or indium acetylacetonate was added. The pH of the mixture was adjusted to 10 with aqueous ammonia (33% in water) and the solution was refluxed under continuous stirring until a gel was formed. The gel was isolated by filtration, washed several times with distilled water and dried at 110°C in a stove.

Once synthesized, the LDHs were ion-exchanged with carbonate to remove intercalated ions between layers. To this end, the six LDHs were suspended in solutions containing 0.345 g of Na_2CO_3 in 50 mL of bidistilled, de-ionized water per gram of LDH at 100°C for 2 h. Next, each solid was filtered off *in vacuo* and washed with 200 mL of bidistilled, de-ionized water. The products thus obtained were subjected to a second exchange operation under the same conditions, and the supernatant analyzed for nitrate, which gave a negative test. The resulting solids, named HT-A1, HT-G1 and HT-I1 (for aluminum, gallium and indium, respectively) were stored in a stove at 110°C and, finally, calcined at 500°C in a nitrogen atmosphere for 8 h. The calcination products thus obtained were given the same names as their precursors, followed by the digits 500 to state the calcination temperature.

The previous solids were characterized by X-ray diffraction, Fourier Transform IR spectroscopy and gas sorption.

X-ray diffraction patterns were obtained on a Siemens D-5000 diffractometer using Cu*Kα* radiation. Patterns were recorded over the 2θ range from 5° to 80°.

Fourier transform IR (FT-IR) spectra for the LDHs and diffuse reflection IR (DRIFT) spectra for their calcination products were recorded over the wavenumber range 400–4000 cm^{-1} on a Bomen MB-100 FT-IR spectrophotometer. Samples were prepared by mixing each powdered solid with KBr (the blank) in a 15:85 ratio. DRIFT spectra were recorded at 200°C and FT-IR spectra at room temperature.

Nitrogen adsorption–desorption isotherms were obtained on a Micromeritics ASAP-2010 analyser. BET surface areas were calculated from the isotherms, using the adsorption values at P/P_0 ratios of 0.05–0.30. The pore size distribution of each solid was determined with the classical BJH method.

The amount of CO_2 chemisorbed on each solid was measured on a Micromeritics 2900 TPD/TPR analyser. Prior to analysis, samples were heated at 500°C in a argon stream for 1 h. Measurements were made at room temperature by alternately passing argon and the same gas containing 5% CO_2 over the sample; the amount of chemisorbed CO_2 was calculated as the difference between the first adsorption peak (physisorbed plus chemisorbed CO_2) and the arithmetic mean of the adsorption and desorption peaks. Basicity was assessed under the assumption that one molecule of CO_2 would be adsorbed at one basic site. The number of basic sites obtained, n_b, was thus a measure of basicity.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the LDHs obtained using the coprecipitation and sol–gel methods. The sharp, symmetric lines at low 2θ values are consistent with the presence of an LDH phase. The diffraction peaks obtained throughout the 2θ range studied were sharp, so they allowed the lattice parameters and metal ratios for the LDHs shown in Table 1 to be determined. Parameter a represents the mean cation–cation distance in the brucite-like layer and was calculated from the expression $a =$

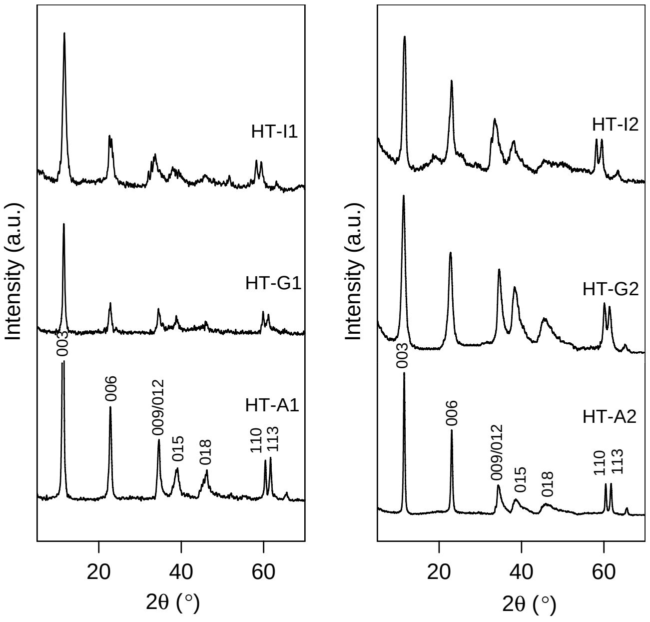

FIG. 1. XRD patterns for the uncalcined LDHs.

TABLE 1
Lattice Paramenters, Chemical Composition, and Parameters of the LDHs

LDH	Lattice parameters (A) *c*	*a*	Crystallite size (nm)	Mg/*M*(III) Atomic ratio[a]	Surface area (m^2/g^{-1})	Pore volume (cm^3/g^{-1})
HT-A1	23.153	3.060	928	3:1.01	50.0	0.23
HT-G1	23.237	3.086	644	3:0.84	68.6	0.43
HT-I1	23.184	3.164	395	3:0.81	85.4	0.26
HT-A2	23.245	3.070	752	3:1.02	151.0	0.57
HT-G2	23.172	3.090	411	3:0.97	173.9	0.83
HT-I2	23.169	3.182	341	3:0.91	97.4	0.86

[a] Determined by ICP.

$2d_{(110)}$; parameter *c* is related to the distance between brucite-like layers and was obtained from the equation $c/3 = \frac{1}{2}\{d_{(0\,0\,3)} + [2d_{(0\,06)}]\}$. As can be seen, *a* increased from Al to In, whichever the synthetic method used. This suggests that both Ga and In are effectively incorporated into the LDH lattice; in fact, an increase in ionic radius of the trivalent ion should result in an increased distance between the cations (the ionic radius for Al^{3+}, Ga^{3+} and In^{3+} is 0.51, 0.62 and 0.83 Å, respectively). On the other hand, *c* exhibits no clear-cut trend; in any case, it varies little among the LDHs, which is logical as replacing a cation with another of the same charge should have no significant effect on this parameter.

The XRD patterns also reveal that the height or width of all peaks decreases with increasing ionic radius of the isovalent ion, which is consistent with previous findings (23,24). Table 1 shows the crystallite size values of (003) and (006) diffractions for the LDHs as a measure of crystallinity along the direction of the *c*-axis. As can be seen crystallinity decreases with increasing ionic radius of the trivalent cation, both in the LDHs obtained by coprecipitation and in those prepared using the sol–gel method.

Figure 2 shows the FT-IR spectra for the solids. The six LDHs exhibit a broadband at 3400–3500 cm^{-1} corresponding to the OH stretching vibration. However, the shoulder at 3050–3100 cm^{-1} suggests the presence of a second type of OH stretching vibration (possibly due to hydrogen bonds in the interlayer spacings). The high water content of such spacings must result in especially strong hydrogen bonds. A shoulder at 1600–1650 cm^{-1} that can be ascribed to the bending motion of interlayer water is also observed in all spectra. This peak might also be due to HCO_3^-; however, because all LDHs were exchanged with carbonate, the presence of this species can be ruled out. The six spectra include bands for carbonate ion, which, in a symmetric environment, exhibits three close to those for the free ion (viz. $\nu_3 = 1445$, $\nu_2 = 880$ and $\nu_4 = 680\,\text{cm}^{-1}$). ν_3 is clearly observed at 1350–1390 cm^{-1} in all spectra, and so is ν_2, which appears around 870 cm^{-1}. The presence of a shoulder at ca. 1400 cm^{-1} can be ascribed to a decreased carbonate symmetry (25) that activates the vibrational mode ν_1; this mode, which is inactive in wholly symmetric carbonate appears as a shoulder at 1510–1520 cm^{-1} in the spectra. On the other hand, ν_4 is only seen in some of them. These results confirm the presence of interlayer carbonate in the LDHs.

Figure 3 shows the nitrogen adsorption/desorption isotherms. Table 1 shows the values of the textural properties, and, as can be seen, the synthetic method used has a decisive influence on the texture of the resulting LDHs. Thus, the six solids exhibit type IV isotherms, which are typical of mesoporous materials (26): at high partial pressures, beyond a certain point there is no further uptake of gas with increase in pressure and the desorption isotherm follows a different path to the adsorption isotherm down to a nitrogen partial pressure of ca. 0.45,

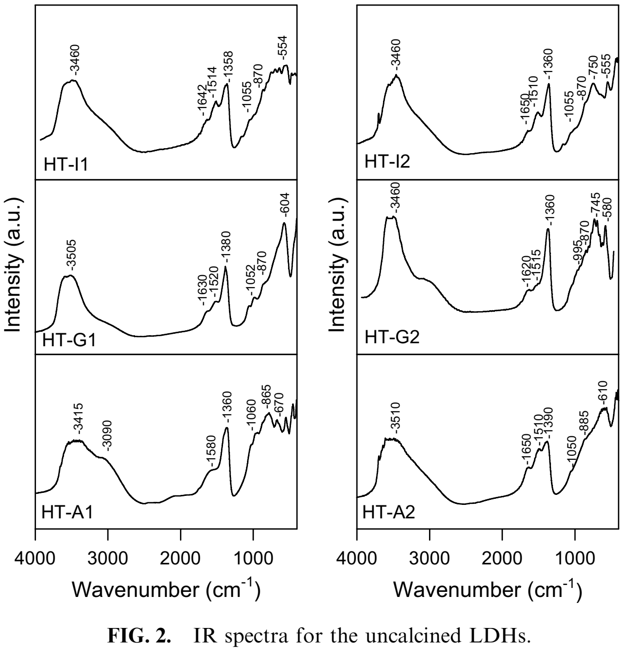

FIG. 2. IR spectra for the uncalcined LDHs.

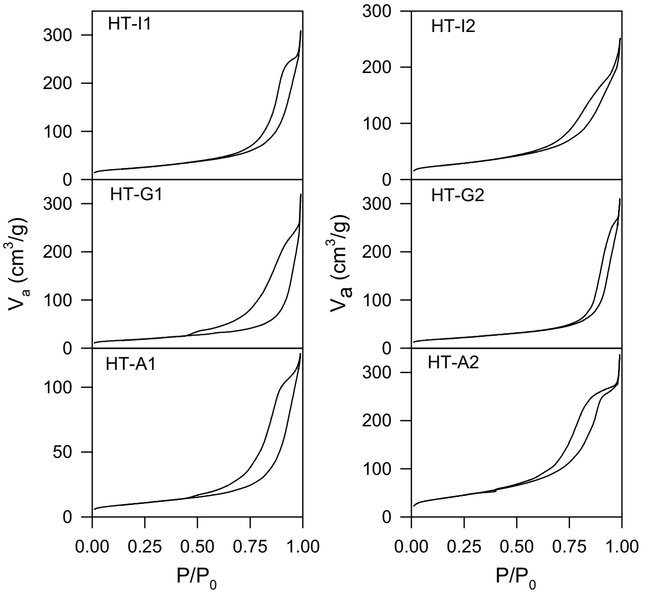

FIG. 3. Nitrogen adsorption–desorption isotherms for the uncalcined LDHs.

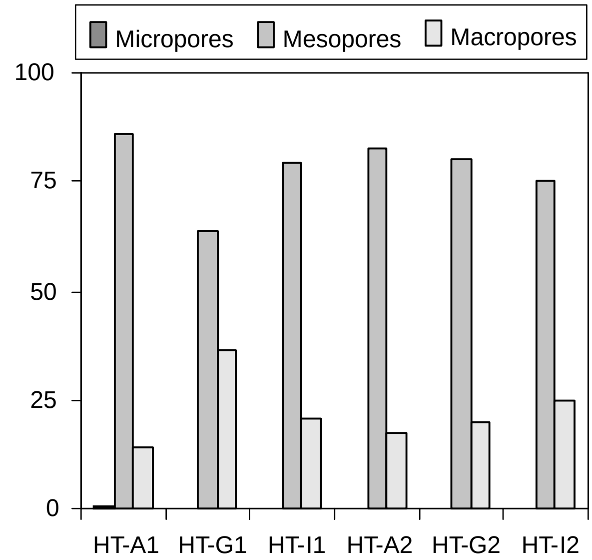

FIG. 4. Pore size distribution of the uncalcined LDHs.

the hysteresis loop being associated with capillary condensation in the mesopores. The shape of the hysteresis loop has frequently been interpreted in terms of the specific pore structure, although it can be affected by other factors including pore shape and non-uniformity in pore size. According to Sing (26), the type H3 hysteresis loop observed in all solids, which exhibits no limiting adsorption at high P/P_0 ratios, is observed with aggregates of plate-like particles giving rise to slit-shaped pores. This is particularly true for layered double hydroxides, which possess this type of microtexture.

Figure 4 shows the proportions of the different pore types present in the solids. As can be seen from Table 1, the solids obtained with the sol–gel method exhibit significantly increased specific surface areas relative to those prepared by coprecipitation. This can be ascribed mainly to the increased pore volumes of the former solids, which are virtually twice as large. As can be seen from Fig. 4, most of the pores fall in the meso size range ($2\,\mathrm{nm} < r_\mathrm{p} < 50\,\mathrm{nm}$), particularly in the solids obtained with the sol–gel method; this is consistent with their increased specific surface areas. Finally, neither synthetic method produces micropores.

Figure 5 shows the XRD patterns for the calcined solids and Table 2 the phases identified from them. As can be seen, calcination destroyed the layered structure in all cases, yielding a periclase MgO phase from all solids. The Mg/Al LDHs yielded a single periclase MgO phase, the aluminum forming an amorphous oxide phase. In previous work (22), we found calcining Mg/Al LDHs at temperatures of 500°C to produce no crystal phase other than periclase. The patterns for Mg/Ga containing samples exhibit a broad reflection at $2\theta = 30-33^\circ$ that does not belong to the MgO structure and overlaps the (111) reflection (denoted by ▼ in Fig. 5). These reflections may arise from the presence of a gallium-rich phase formed in addition to the MgO phase, as previously observed by Rebours et al. (27). Finally, the calcination products of the

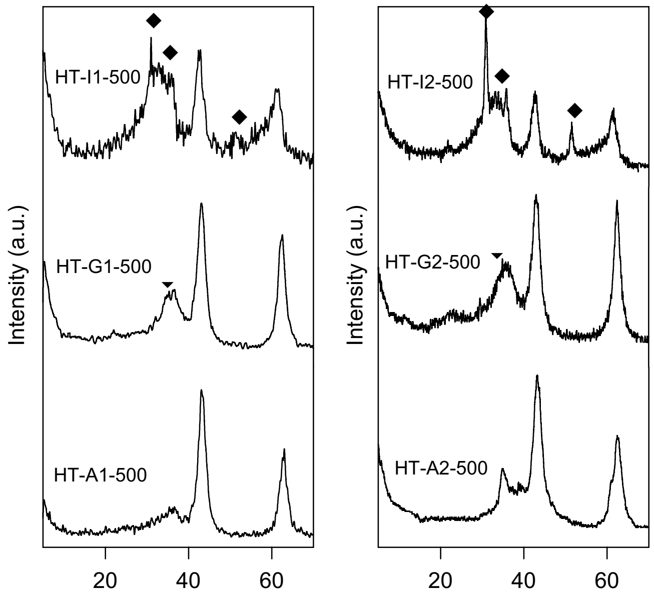

FIG. 5. XRD patterns for the calcined LDHs. Symbols denote phases other than periclase MgO. 2θ values for HT-A1-500 = 42.60, 62.97; HT-A2-500 = 43.24, 62.43; HT-G1-500 = 43.08, 62.53; HT-G2-500 = 42.97, 62.40; HT-I1-500 = 43.02, 61.68; HT-I2-500 = 42.95, 62.22.

TABLE 2
Phases Detected for the Surface and Chemical Surface Properties of the Calcined LDHs

LDH	Phase	S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Basicity (μmol $CO_2 g^{-1}$)
HT-A1-500	MgO	235.2	0.61	330
HT-G1-500	MgO	138.4	0.69	182
HT-I1-500	MgO + In_2O_3	80.9	0.55	193
HT-A2-500	MgO	224.6	0.72	296
HT-G2-500	MgO	141.9	0.61	170
HT-I2-500	MgO + In_2O_3	65.4	0.42	173

In containing LDHs exhibit a periclase MgO phase of decreased crystallinity relative to the other LDHs; however, it also exhibits a crystalline In_2O_3 phase (denoted by ♦ in Fig. 5) that is much more significant in the calcination product of the LDH obtained with the sol–gel method than in that of the LDH prepared by coprecipitation.

Figure 6 shows the DRIFT spectra for the solids calcined at 500°C. As can be seen, they are rather different from those for the precursor LDHs; in fact, they exhibit strong bands in the 450–650 cm^{-1} region corresponding to characteristic vibrations of the oxides (MgO, Al_2O_3, Ga_2O_3 and In_2O_3) (28). The particular synthetic method used introduces no significant differences in this respect. All spectra exhibit a broadband at 1400–1500 cm^{-1} that is typical not of interlayer carbonate, but of carbonate adsorbed on the oxide surface during calcination (29), in addition to carbonate and water reversibly adsorbed on the oxide surface. Finally, a band at 3500 cm^{-1} is also observed that corresponds to $OH\cdots OH_2$ and $H_2O\cdots OH_2$ groups (30).

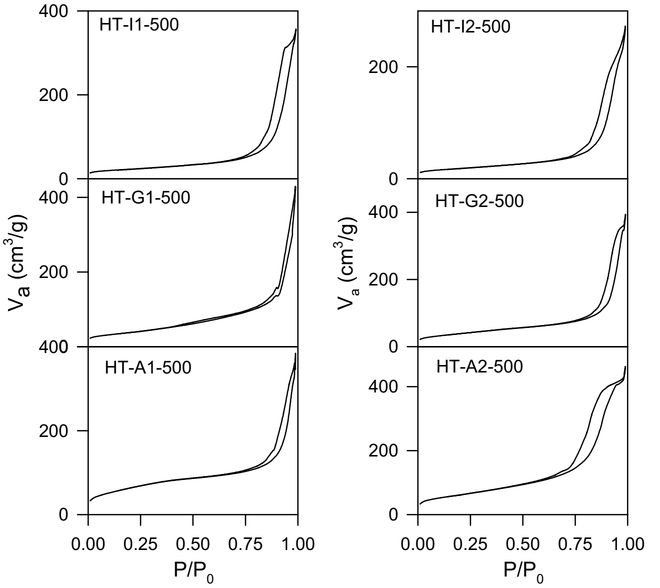

FIG. 7. Nitrogen adsorption–desorption isotherms for the calcined LDHs.

As regards the textural properties of the calcined solids, the corresponding nitrogen adsorption–desorption isotherms (Fig. 7) are similar to those for the precursor LDHs (viz. of type IV, with hysteresis cycles of type H3). The essential difference lies in the specific surface area, which is

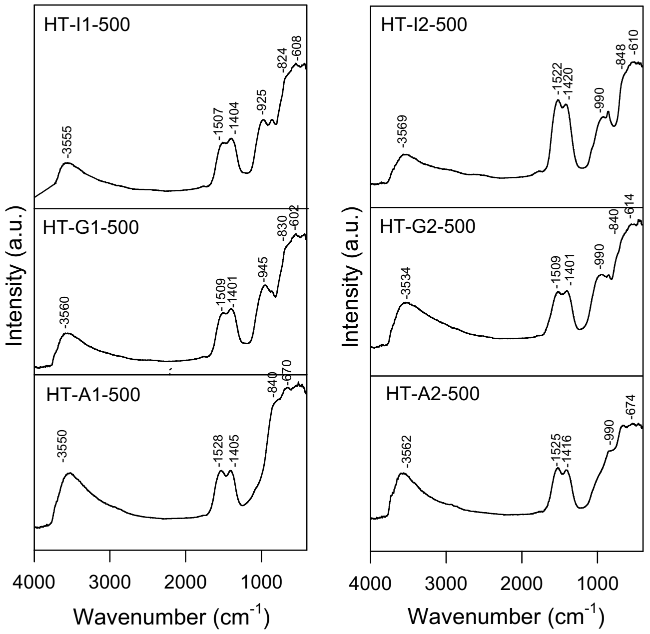

FIG. 6. DRIFT spectra for the calcined LDHs.

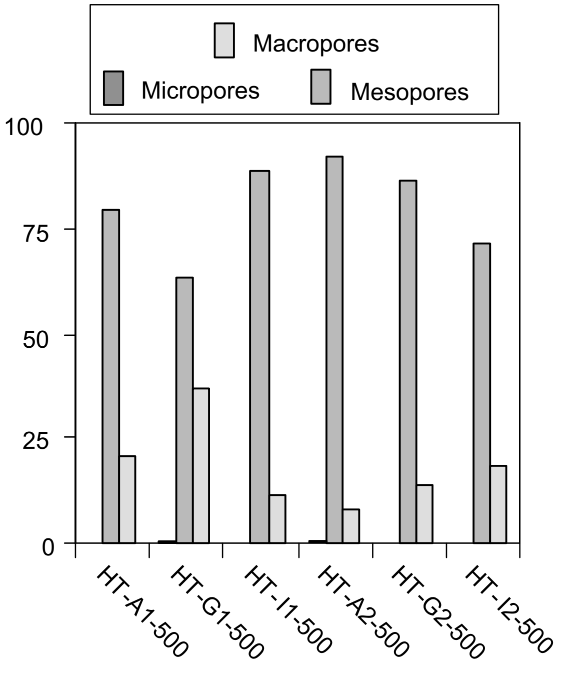

FIG. 8. Pore size distribution of the calcined LDHs.

much greater in the uncalcined solids obtained with the sol–gel method than in those prepared by coprecipitation but similar between the two types of calcined solids; this suggests that the synthetic method has no appreciable influence on the textural properties of the calcined products. It should be noted, however, that the specific surface area is maximal for the Mg/Al solids, followed by the Mg/Ga and Mg/In LDHs. Figure 8 shows the distribution of the pore populations in the solids—as noted earlier, all are predominantly mesoporous.

The present study was completed by determining the number of basic sites in each calcined solid. As can be seen from Table 2, the Mg/Al calcined product is more basic than the Mg/Ga and Mg/In ones—which are similar in this respect—whichever the synthetic method used. Finally, the solids provided by the sol–gel method are slightly less basic than those obtained by coprecipitation; the differences, however, are quite small (close to 10% in all cases).

CONCLUSIONS

Mg/*M*(III) LDHs with *M*(III) = Al, Ga and In were synthesized using both the traditional coprecipitation method and the sol–gel method. The particular synthetic method was found to strongly influence the crystallinity of the resulting LDHs, which was higher with the coprecipitation method. Also, crystallinity was found to decrease with increasing ionic radius of the tervalent method, i.e., in the sequence Mg/Al > Mg/Ga > Mg/In, whichever the synthetic method used. The synthetic method was also found to significantly affect the texture of the LDHs. Thus, the specific surface area of the solids obtained with the sol–gel method was up to three times greater than that achieved by coprecipitation. Calcining the solids at 500°C suppressed the above-described differences between both synthetic methods. It should be noted, however, that calcination at this temperature produced periclase from all solids, in addition to amorphous oxide phases—by exception, the Mg/In solid yielded crystalline In_2O_3 in addition to the periclase. Finally, the Mg/Al LDHs were found to be the most basic, the synthetic method used having no appreciable influence on the results.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding by the Spanish Ministry of Science and Technology and the Plan Nacional de Investigación, Desarrollo e Innovación Tecnológica (Project BQU-2001-2606), as well as by the Consejería de Educación y Ciencia de la Junta de Andalucía.

REFERENCES

1. H. F. W. Taylor, *Mineral. Mag.* **39,** 377 (1973).
2. F. Cavani, F. Trifiro, and A. Vacari, *Catal. Today* **11,** 173 (1991).
3. M. A. Aramendía, V. Borau, C. Jiménez, J. M. Marinas, J. R. Ruiz, and F. J. Urbano, *Appl. Catal. A: General* **206,** 95 (2001).
4. M. A. Aramendía, V. Borau, C. Jiménez, J. M. Luque, J. M. Marinas, F. J. Romero, J. R. Ruiz, and F. J. Urbano, *Stud. Surf. Sci. Catal.* **130,** 1667 (2000).
5. M. A. Aramendía, V. Borau, C. Jiménez, J. M. Luque, J. M. Marinas, J. R. Ruiz, and F. J. Urbano, *Mater. Lett.* **43,** 118 (2000).
6. M. A. Aramendía, V. Borau, C. Jiménez, J. M. Marinas, F. J. Romero, and J. R. Ruiz, *J. Solid State Chem.* **131,** 78 (1997).
7. F. Figueras, D. Tichit, M. B. Naciri, and J. R. Ruiz, *in* "Catalysis of Organic Reactions" F. E. Hercks, Ed.), p. 37. Marcel Dekker, Inc., New York, 1998.
8. A. Corma, V. Fornés, and F. Rey, *J. Catal.* **148,** 205 (1994).
9. M. J. Climent, A. Corma, S. Iborra, and J. Primo, *J. Catal.* **151,** 60 (1995).
10. H. Meyer, H. Gorzawski, and W. F. Holderich, *Catal. Lett.* **59,** 201 (1999).
11. S. Narayanan and K. Krishna, *Appl Catal. A: General* **198,** 13 (2000).
12. A. Monzón, E. Romeo, C. Royo, R. Trujillano, F. M. Labajos, and V. Rives, *Appl. Catal. A: General* **185,** 53 (1999).
13. M. J. Kang, K. S. Chun, S. W. Rhee, and Y. Do, *Radiochim. Acta* **85,** 57 (1999).
14. I. C. Chisem and W. Jones, *J. Mater. Chem.* **4,** 1737 (1994).
15. W. T. Reichle, *J. Catal.* **94,** 547 (1985).
16. W. T. Reichle, S. Y. Kang, and D. S. Everhardt, *J. Catal.* **101,** 352 (1986).
17. S. Miyata, *Clays Clay Miner.* **23,** 369 (1975).
18. T. López, J. Hernandez, R. Gomez, X. Bokhimi, J. L. Boldu, E. Muñoz, O. Novarro, and A. Garcia-Ruiz, *Langmuir* **15,** 5689 (1999).
19. J. A. Wang, A. Morales, X. Bokhimi, O. Novarro, T. Lopez, and R. Gomez, *Chem. Mater.* **11,** 308 (1999).
20. M. Haneda, Y. Kintaichi, H. Shimada, and H. Hamada, *J. Catal.* **192,** 137 (2000).
21. M. A. Aramendía, Y. Avilés, J. A. Benítez, V. Borau, C. Jiménez, J. M. Marinas, J. R. Ruiz, and F. J. Urbano, *Microp. Mesop. Mater.* **29,** 319 (1999).
22. M. A. Aramendía, Y. Avilés, V. Borau, J. M. Luque, J. M. Marinas, J. R. Ruiz, and F. J. Urbano, *J. Mater. Chem.* **9,** 1603 (1999).
23. J. T. Kloprogge and R. L. Frost, *Appl. Catal. A: General* **184,** 61 (1999).
24. S. Ribet, D. Tichit, B. Coq, B. Ducourant, and F. Morato, *J. Solid State Chem.* **142,** 382 (1999).
25. H. Miyata, W. Wakamiya, and I. Kibokawa, *J. Catal.* **34,** 117 (1974).
26. K. S. W. Sing and J. Rouquerol, *in* "Handbook of Heterogeneous Catalysis" (G. Ertl, H. Knözinger and J. Weitkamp, Eds.), Vol. 2, p. 427, Wiley-VCH, New York, 1997.
27. B. Rebours, J. B. D. De la Caillerie, and O. Clause, *J. Am. Chem. Soc.* **116,** 1707 (1994).
28. M. J. Hernández-Moreno, M. A. Ulibarri, J. L. Rendón, and C. J. Serna, *Phys. Chem. Miner.* **12,** 34 (1985).
29. J. Lercher, C. Colombier, H. Vinec, and H. Noller, *in* "Catalysis by Acids and Bases" (B. Imleik, C. Maccache, G. Carduvier, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 25, Elsevier, Amsterdam, 1985.
30. R. Allman, *Chimia* **24,** 99 (1970).