Inorg. Chem. **2003**, *42*, 5621–5631

Inorganic Chemistry
Article

New Layered Double Hydroxides Containing Intercalated Manganese Oxide Species: Synthesis and Characterization

Josanlet C. Villegas,[†] Oscar H. Giraldo,[‡,§] Kate Laubernds,[‖] and Steven L. Suib*[,†,‖,⊥]

Institute of Materials Science, and Departments of Chemistry and Chemical Engineering,
University of Connecticut, Storrs, Connecticut 06269, and Departamento de Química,
Universidad Nacional de Colombia, Bogotá, Colombia

Received February 7, 2003

Manganese oxide species (MnO_x) have been intercalated within the gallery spaces of Mg–Al layered double hydroxides (LDHs). Synthesis of these materials was achieved by ion-exchange of the LDH-nitrate precursor with permanganate anion followed by reduction with organic reagents, such as glucose, ethanol, and ascorbic acid. Elemental analysis, X-ray diffraction, FT-IR spectroscopy, Raman spectroscopy, HR-TEM, and N_2 sorption analyses have been used to characterize these materials. TEM micrographs of LDH-MnO_x materials revealed platelike morphology, characteristic of hydrotalcite-like compounds. Chemical analysis results showed that permanganate anions exchanged with nitrate anions. FT-IR and Raman spectroscopy confirmed the reduction of the permanganate anions after treatment with the organic reagents. The XRD diffraction patterns of LDH-MnO_x revealed that the layer structure is maintained after all synthetic steps. The observed basal spacings of intercalates varied depending on the reducing agent; the largest expansion was 9.93Å, corresponding to the use of ascorbic acid. The specific surface areas were also affected according to the organic reagent used, indicating that the structural modifications in the interlayer domain observed by X-ray diffraction also influence the microtextural properties.

I. Introduction

Intercalation of guest molecules into layered double hydroxides (LDHs) has attracted considerable interest over the past few years for both scientific and practical reasons.[1–5] Through the incorporation of a guest species into a layered host, the chemical composition of the structure is modified, and novel solid materials may be engineered, exhibiting enhanced physical and chemical properties compared to the host lattice.

Layered double hydroxides, also known as "anionic clays", consist of stacked brucite-type [$Mg(OH)_2$] octahedral layers with water molecules and anions occupying the space between the layers, often called the gallery or interlayer region (Figure 1).[1,6] The role of the interlayer anions is to compensate the excess positive charge due to the partial substitution of trivalent cations for divalent ions. The general formula of the LDHs can be written as follows: $[M^{2+}{}_{(1-x)}M^{3+}{}_x(OH)_2]A^{n-}{}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} represent the divalent and trivalent cations, respectively, and A^{n-} designates the interlayer anion. The stability of the structure is provided by hydrogen bonds between the hydroxyl groups of the inorganic sheets and the intercalated species: anions and water molecules.[1] LDHs are a versatile class of compounds; it is possible to modulate their properties by changing the nature of the M^{2+} and M^{3+} cations, their molar ratio, and the size of the A^{n-} anion.[1–8] One of the most important properties of such compounds is their high anion-

---

* To whom correspondence should be addressed. E-mail: suib@uconnvm.uconn.edu. Phone: (860)-486-2797. Fax: (860)-486-2981.

[†] Institute of Materials Science, University of Connecticut.

[‡] Departamento de Química, Universidad Nacional de Colombia.

[§] Current address: Departamento de Física y Química, Universidad Nacional de Colombia, Manizales, Colombia.

[‖] Department of Chemistry, U-3060, University of Connecticut.

[⊥] Department of Chemical Engineering, University of Connecticut.

(1) Cavani, F.; Trifirò, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.
(2) Trifirò, F.; Vaccari, A. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., MacNicol, D. D., Davies, J. E. D., Vogtle, F., Eds.; Pergamon: Oxford, 1996; Vol 7, p 251.
(3) Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191.
(4) Choy, J. H.; Kwak, S. Y.; Park, J. S.; Jeong, Y. J.; Postier, J. *J. Am. Chem. Soc.* **1999**, *121*, 1399.
(5) Choy, J. H.; Kwak, S. Y.; Jeong, Y. J.; Park, J. S.; *Angew. Chem., Int. Ed.* **2000**, *39*, 4041.
(6) de Roy, A.; Forano, C.; El Malki, K.; Besse, J. P. In *Expanded Clays and Others Microporous Solids*; Ocelli, M. L., Robson, H., Eds.; Van Nostrand Reinhold: New York, 1992; Vol 2, p 108.
(7) Newman, S. P.; Jones, W. *New J. Chem.* **1998**, *22*, 105.
(8) Miyata, S. *Clays Clay Miner.* **1983**, *31*, 305.

10.1021/ic030054k CCC: $25.00

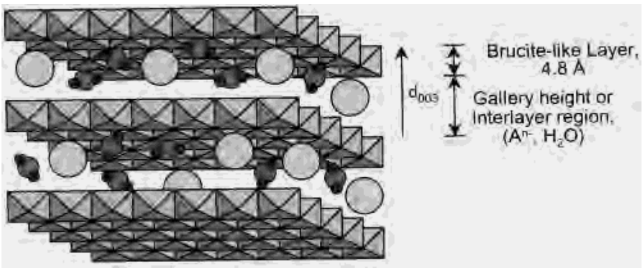

Figure 1. Schematic representation of a layered double hydroxide structure consisting of brucite-like hydroxide sheet with anions (A^{n-}) and water molecules in the interlayer region.

exchange capacities. The lamellar structure and the anion-exchange properties of the LDHs make them attractive for technological applications such as the following: ion-exchangers, adsorbents, optical memory, medicine stabilizers, ionic conductors, and precursors of new catalytic materials, and more recently, as host structures for nanocomposite materials.[1,9−13]

Due to the anion-exchange properties of these materials, a large number of organic and inorganic anions have been incorporated in the LDHs using different methods. The only limitation with regard to choice of the anions is that it must not form strong complexes with the present cations. Simple inorganic anions such as halides, OH^-, CO_3^{2-}, NO_3^-, and SO_4^{2-}, as well as silicates, terephthalates, benzoates, and a range of polyoxometalates, have been intercalated via ion-exchange, coprecipitation, and reconstruction methods.[1,14−18] An alternative route based on delamination and restacking of the LDH structure has also been used to prepare a novel generation of LDHs with a wide range of versatile materials.[19] Related manganese oxide layered materials with intercalated poly(diallyldimethylammonium chloride), PDDA, have been prepared by this method.[20]

Recently, the preparation of well ordered LDH materials containing intercalated transition metal anions, such as tungstate,[10,21] molybdate,[21] vanadate,[16,22] and also transition metal complexes,[18,23] using different synthetic routes has been investigated with the aim of developing new classes of selective catalysts. The incorporation of manganese into the LDH structures has also been reported.[24−27] However, despite the very interesting catalytic properties of manganese, relatively few studies have appeared in comparison to those devoted to other transition metals. Mn-containing LDHs have been synthesized using either ion-exchange or reconstruction methods. Mansuy et al.[27] have reported the preparation and catalytic properties of Mn(III) porphyrins intercalated into LDHs by ion-exchange. Other authors have used potassium permanganate as an intercalating solution.[24−26] In those cases, a partial replacement of the interlayer anions for permanganate ions has been observed. Therefore, MnO_4^- anions and Mn(III) porphyrins with Mn^{7+} present are the only Mn species that have been intercalated in LDH materials.

In the present study, we report the novel synthesis and characterization of layered double hydroxides containing intercalated manganese oxide species. The new LDH materials are prepared by an in-situ reaction between permanganate, MnO_4^-, anions and organic reducing agents, including glucose, ethanol, and ascorbic acid. The MnO_4^- anions were previously incorporated into the MgAl nitrate LDH via anion-exchange. The reduction of permanganate with organic agents has been successfully used before as a method to synthesize amorphous manganese oxide colloids, as well as microporous and layered manganese oxides materials.[28,29] The ability to incorporate manganese species into layered host materials opens new opportunities for the further synthesis of manganese oxide materials in confined environments, and for their use in catalytic applications. The new method described in this work is a simple approach for the synthesis of manganese species in layered double hydroxide materials.

II. Experimental Section

Synthesis. Pillared MnO_x-MgAl LDHs were prepared by a three-step method: synthesis of LDH-nitrate material, intercalation of MnO_4^- via anion-exchange, and finally, reduction of the MnO_4^- anions by organic reagents. In order to prevent contamination by carbonate from atmospheric CO_2, all the procedures were carried out with freshly decarbonated, deionized water under a constant nitrogen flow.

LDH-Nitrate Precursor. Mg/Al LDHs were prepared by a coprecipitation method similar to that already reported.[14,30] First, an aqueous solution containing a mixture of $Mg(NO_3)_2{\cdot}6H_2O$ (0.5 M) and $Al(NO_3)_3{\cdot}9H_2O$ (0.25 M) salts was prepared. Next, 200 mL of the aqueous solution was added dropwise with stirring to 100 mL of water preadjusted with NaOH to pH 10. The reaction pH was maintained at 10 ± 0.2 during the precipitation by the continuous addition of 2 M of NaOH solution. The white precipitate obtained was collected by centrifugation, washed several times, and stored to be used later in an anion-exchange reaction.

---

(9) Vaccari, A. *Catal. Today* **1998**, *41*, 53.
(10) Sels, B.; De Vos, D.; Buntinx, M.; Pierard, F.; Mesmaeker, K. D.; Jacobs, P. *Nature* **1999**, *400*, 855.
(11) Carrado, K. A.; Kostapapas, A.; Suib, S. L. *Solid State Ionics* **1988**, *26*, 77.
(12) Newman, S. P.; Jones, W. In *Supramolecular Organization and Materials Design*; Rao, C. N. R., Jones, W., Eds.; Cambridge University Press: Cambridge, U.K., 2001; p 295.
(13) Constantino, U.; Nochetti, M. In *Layered Double Hydroxides: Present and Future*; Rives, V., Ed.; Nova Science Publishers: New York, 2001, p 383.
(14) Miyata, S. *Clays Clay Miner.* **1975**, *23*, 369.
(15) Yun, S. K.; Pinnavaia, T. J. *Inorg. Chem.* **1996**, *35*, 6853.
(16) Drezdzon, M. A. *Inorg. Chem.* **1988**, *27*, 4628.
(17) Kooli, F.; Chisem, I. C.; Vucelic, M.; Jones, W. *Chem. Mater.* **1996**, *8*, 1969.
(18) Rives, V.; Ulibarri, M. A. *Coord. Chem. Rev.* **1999**, *181*, 61.
(19) Leroux, F.; Adachi-Pagano, M.; Intissar, M.; Chauvière, S.; Forano, C.; Besse, J. P. *J. Mater. Chem.* **2001**, *11*, 105.
(20) Liu, Z. H.; Yang, X.; Makita, Y.; Ooi, K. *Chem. Mater.* **2002**, *14*, 4800.
(21) Sels, B. F.; De Vos, D. E.; Grobet, J. P.; Pierard, F.; Mesmaeker, F. K. D.; Jacobs, P. A. *J. Phys. Chem. B* **1999**, *103*, 11114.
(22) Ulibarri, M. A.; Labajos, F. M.; Rives, V.; Trujillano, R.; Kagunya, W.; Jones, W. *Inorg. Chem.* **1994**, *33*, 2592.
(23) Inacio, J.; Taviot-Guebo, C.; Morlat-Therias, S.; de Roy, M. E.; Besse, J. P. *J. Mater. Chem.* **2001**, *11*, 640.
(24) Turney, T. W.; Christie, G. B.; Hardin, S. G.; Corrigan, P. A. PCT Int. Appl., WO 9118835, Dec. 12, 1991.
(25) Sato, T.; Wakabayashi, T.; Shimada, M. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 89.
(26) Shimada, H.; Saito, K. *Nippon Kagaku Kaishi* **1997**, *5*, 335.
(27) Barloy, L.; Lallier, J. P.; Battioni, P.; Mansuy, D.; Piffard, Y.; Tournoux, M.; Valim, J. B.; Jones, W. *New J. Chem.* **1992**, *16*, 71.
(28) Witzemann, E. J. *J. Am. Chem. Soc.* **1915**, *37*, 1079.
(29) Brock, S. L.; Duan, N.; Tian, Z. R.; Giraldo, O.; Zhou, H.; Suib, S. L. *Chem. Mater.* **1998**, *10*, 2619.
(30) Constantino, V. R. L.; Pinnavaia, T. J. *Inorg. Chem.* **1995**, *34*, 883.

MnO_4^--Containing LDHs. Permanganate-exchanged LDH (LDH-Mn) was prepared starting from the freshly synthesized LDH-nitrate without a drying step. The wet LDH-NO$_3$ was suspended in 200 mL of an aqueous solution of $KMnO_4$ (0.2 M). An anion-exchange reaction was performed while stirring at room temperature for 24 h. The resulting purple product was separated by centrifugation, and extensively washed. LDH-Mn was divided in four portions; one was air-dried at room temperature, and the other portions were used in the next step of the synthesis.

Reduction Process. This step was performed in order to produce manganese oxides between the hydroxyl layers, through the reaction of the wet LDH-Mn with one of the following organic compounds: glucose, ethanol, and ascorbic acid.

LDH-MOG. Manganese-oxide-pillared LDH reduced with glucose was prepared by redispersing wet LDH-Mn in 100 mL of water. Aqueous glucose solution (5 mL, 0.85 M) was added, and the suspension was stirred for an hour at room temperature under N_2 flow. The resulting product, a dark yellow powder, was centrifuged, washed extensively, and dried at room temperature.

LDH-MOEt. The preparation of the reduced form of permanganate-exchanged LDH was done following a procedure analogous to the LDH-MOG described previously. In this case, 30 mL of ethanol was used as a reducing agent. A yellow powder was obtained after centrifuging, washing, and drying the product of the reaction.

LDH-MOAA. The derivative LDH was prepared by reacting wet LDH-Mn with 5 mL of aqueous solution of ascorbic acid (0.85 M). The conditions of this reaction were similar to those already described. A tanlike powder was obtained after washing and drying.

Characterization. Elemental Analyses. An inductively coupled plasma atomic emission spectrometer (ICP-AES), Perkin-Elmer model 140, was employed for elemental analyses. Solutions were prepared by digesting approximately 30 mg of solid sample in concentrated HCl/HNO$_3$ (3:1) solution. Then, the volume was readjusted with distilled, deionized water to 100 mL. The carbon and nitrogen contents in the samples were determined using a Perkin-Elmer model 2400 CHN element analyzer.

X-ray Diffraction. X-ray diffraction patterns of the samples were recorded with a Scintag XDS-2000 diffractometer using Cu Kα radiation. The data were collected in the 2θ range 5−70° with a step scan rate of 0.02 deg/min. Samples were prepared by pipetting the LDH suspensions onto glass slides and allowing the water to evaporate at 40 °C. The beam voltage was 45 kV, and the beam current was 40 mA.

Fourier Transform Infrared (FTIR) Spectra. FTIR experiments were recorded on a Nicolet Magna 750 FT-IR spectrometer in the range 4000−400 cm^{-1} using a DTGS detector. The samples were diluted in KBr.

Raman Spectroscopy. The Raman spectra were taken at room temperature in the spectral range 100−2000 cm^{-1} using a Renishaw 2000 Raman microscope system, which includes an optical microscope and a CCD camera for multichannel detection. The spectra were recorded using a 514 nm argon ion laser.

Average Oxidation State Determinations. Standard potentiometric titration measurements were used to determine the AOS of manganese in the reduced LDH samples.[31]

Transmission Electron Microscopy. TEM images were obtained with a JEOL 2010 FasTEM at an accelerating voltage of 200 kV. Powder samples were ultrasonically dispersed in acetone, and the suspension was deposited on a copper grid coated with a holey carbon film.

Table 1. Composition, Interlayer Distances, and Manganese Average Oxidation States of the As-Synthesized LDHs

sample	Al (%)[a]	Mg (%)[a]	Mn (%)[a]	N (%)[a]	C (%)[a]	Mg/Al[b]	H_2O (%)[c]	interlayer distance (Å)	AOS of Mn
LDH-NO$_3$	9.3	17.7	nd[d]	3.7	0.5	2.11	13.7	8.66	na[e]
LDH-Mn	9.2	17.1	6.5	1.3	0.9	2.05	9.4	8.42	na[e]
LDH-MOEt	9.2	17.0	4.0	1.2	1.8	2.05	13.9	8.50	3.5
LDH-MOG	9.7	16.6	6.1	0.5	3.0	1.91	14.3	8.89	3.1
LDH-MOAA	9.5	15.3	1.6	0.2	6.7	1.79	14.7	9.93	[f]

[a] Weight percent. [b] Molar ratio. [c] Weight loss determined by TGA during heating at 150 °C for 1 h. [d] nd = not detected. [e] na = not applicable. [f] Further analysis is needed.

Specific Surface Area and Pore Size Distribution Measurements. Nitrogen sorption experiments were performed at 77 K with a Micromeritics ASAP 2010 accelerated surface and porosimetry system. The samples were previously degassed at 150 °C for 12 h. The specific surface area of the samples was measured using the Brunauer−Emmett−Teller (BET) method. The pore size distribution was determined using the model by Horvath and Kawazoe.

III. Results

Elemental Analysis. Chemical composition and water content of the synthesized MgAl LDHs are given in Table 1. The Mg/Al molar ratio in the solid samples is similar to the ratio in the parent solution except for samples LDH-MOG and LDH-MOAA where the corresponding ratios are slightly lower than the initial value. Deviations in the molar ratio of the metal cations in the product are attributed to the dissolution of the hydroxyl layers during the synthesis. This will be discussed elsewhere.

Elemental composition of the LDH-NO$_3$ sample shows that nitrates are the main counteranions in the intergallery region. Mn-incorporated LDH (LDH-Mn) shows 6.5 wt % Mn and a decrease of nitrogen from 3.7 to 1.3 wt % after Mn exchange. A small carbon content is observed for both LDH-Mn and the precursor (LDH-NO$_3$), suggesting the presence of carbonate ions in the interlayer. This carbon contamination is believed to occur during the washing/centrifuging cycles.

The manganese analysis data for the LDH-Mn sample reduced with glucose, ethanol, and ascorbic acid show that the Mn weight percentage in the samples decreases from 6.5 in LDH-Mn to 6.1, 4.0, and 1.6, respectively, in LDH-MnO$_x$, after the reduction process. The results of nitrogen analyses show similar behavior; hence, nitrate ions are removed from the interlayer during the reaction of the LDH samples with organic compounds. These data suggest that ion-exchange occurs during the reduction process. Whereas the N and Mn content diminish after the reduction process, Table 1 shows that the carbon content in LDH-MOEt, LDH-MOG, and LDH-MOAA samples increases, and that the C content is higher than that due to carbon contamination from the atmosphere observed previously for LDH-NO$_3$, and LDH-Mn.

X-ray Diffraction. The XRD patterns of the precursor LDH-NO$_3$ and the derivative LDH materials are shown in Figure 2. All the materials have a similar XRD pattern typical of layered compounds, with maximum intensity for the (00*l*) reflections at low values of 2θ.[6] The LDH-NO$_3$ pattern shows an intense diffraction peak at a *d* spacing of 8.66 Å, which

---

(31) *Handbook of Manganese Dioxides Battery Grade*; Glover, D., Schumn, B., Jr., Kazowa, A., Eds.; International Battery Materials: Cleveland, OH, 1989.

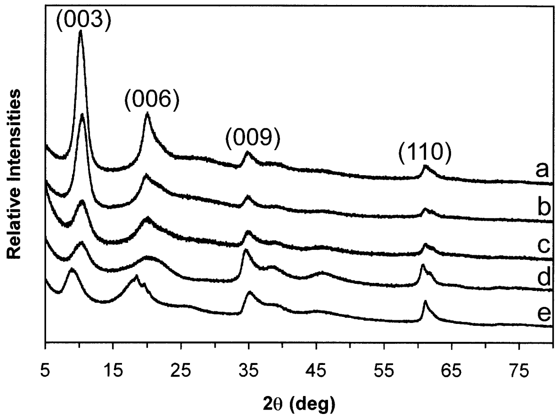

Figure 2. X-ray diffraction patterns of thin film as-synthesized samples: (a) LDH-NO_3, (b) LDH-Mn, (c) LDH-MOEt, (d) LDH-MOG, and (e) LDH-MOAA.

is similar to the interlayer distance reported in the literature for LDH nitrate.[1] The interlayer distances (d_{003}'s) for all the synthesized LDH materials are shown in Table 1. For LDH-NO_3, this distance corresponds to an intergallery height of 3.86 Å, assuming 4.8 Å as the thickness of the brucite-like layer, which is larger than the diameter of NO_3^-.[14] Given that the size of the NO_3^- anion is known to be 3.78 Å, this value of intergallery height has previously been attributed to the presence of the nitrate anion adopting a “tilted” position within the gallery, due to the higher net positive charge of the layers (Mg/Al 2.1:1), and the larger number of nitrate anions required for charge balancing.[32,33] Upon ion-exchange of MnO_4^- for NO_3^-, a slight decrease in the basal spacing of the sample LDH-Mn is observed. The presence of permanganate in the interlayer also causes a loss in the intensity of the main diffraction peak, as illustrated in Figure 2. However, a significant decrease in the intensity of the 003 peak is observed when the permanganate ions are reduced with ethanol, glucose, and ascorbic acid (Figure 2c–e). The XRD patterns for LDH-MOEt, LDH-MOG, and LDH-MOAA also show that the 003 diffraction peak shifts to lower 2θ values; consequently, the basal spacing for all of the samples increases compared to the d_{003} observed in Table 1 for LDH-Mn. Interlayer distances of 8.50 and 8.89 Å are observed for LDH-MnO_x reduced with ethanol and glucose, respectively, whereas an interlayer distance of 9.93 Å is found when ascorbic acid is used.

Infrared Study. The presence and nature of the charge-compensating anions were investigated with IR spectroscopy. The FTIRs for the nitrate precursor LDH together with permanganate intercalated LDH and the pillared derivatives are illustrated in Figure 3. In all the spectra, an intense and broad adsorption band located at 3480 cm^{-1} and a band close to 1640 cm^{-1} are observed. The strong band corresponds to the stretching vibration of the hydroxyl group (OH) from both the hydroxide layers and the interlayer water. The broadening of this band is due to hydrogen bond formation.[34]

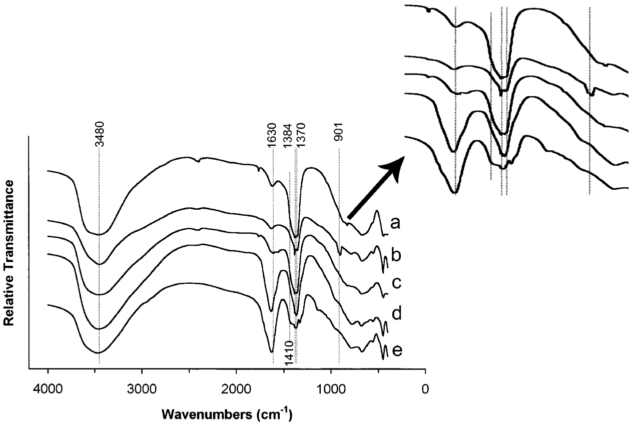

Figure 3. FTIR spectra of as-synthesized LDH samples: (a) LDH-NO_3, (b) LDH-Mn, (c) LDH-MOEt, (d) LDH-MOG, and (e) LDH-MOAA.

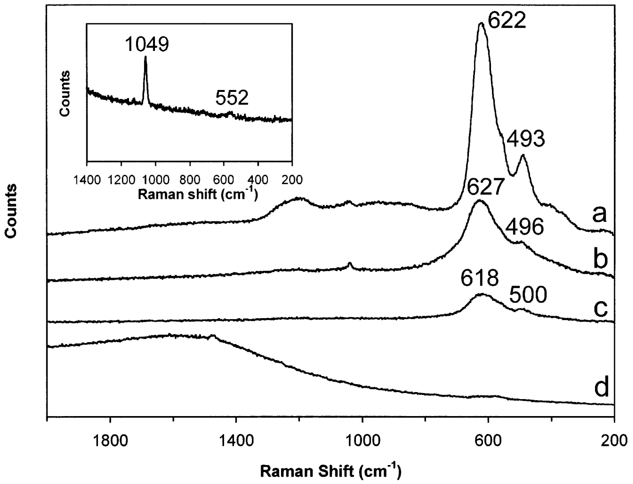

Figure 4. Raman spectra of the precursor LDH and its derivatives: (a) LDH-Mn, (b) LDH-MOEt, (c) LDH-MOG, (d) LDH-MOAA (inset: LDH-NO_3).

The second band corresponds to the deformation mode (δ H_2O) of water molecules. The intensity of this peak varies from medium to weak, depending on the amount of water in the samples.

The intense band at 1384 cm^{-1} in spectrum of Figure 3a (LDH-NO_3) corresponds to the ν_3 mode of the nitrate species.[35] Bands recorded below 800 cm^{-1} are due to the vibration of the metal–oxygen bonds in the brucite-like lattice. Upon ion-exchange, the ν_3 vibration of NO_3^- becomes weak, and an additional IR adsorption band at 901 cm^{-1}, assigned to the antisymmetric stretching vibration ν_3 of the tetrahedral MnO_4^-, appears.[35] After the reduction of MnO_4^- with organic reagents, the ν_3 stretching vibration of MnO_4^- was no longer detected. This suggests the transformation of MnO_4^- to some other form of manganese oxide (Figure 3c–e). However, no bands associated with the vibration of the manganese oxide groups were observed in these spectra.

For LDH-MOG, in addition to the ν_3 NO_3^- band at 1384 cm^{-1}, a band is also observed at 1370 cm^{-1} which corre-

---

(32) Kruissink, E. C.; Van Reijen, L. L.; Ross, J. R. H. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 649.

(33) del Arco, M.; Gutiérrez, S.; Martín, C.; Rives, V.; Rocha, J. *J. Solid State Chem.* **2000**, *151*, 272.

(34) Labajos, F. M.; Rives, V.; Ulibarri, M. A. *J. Mater. Sci.* **1992**, *27*, 1546.

(35) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

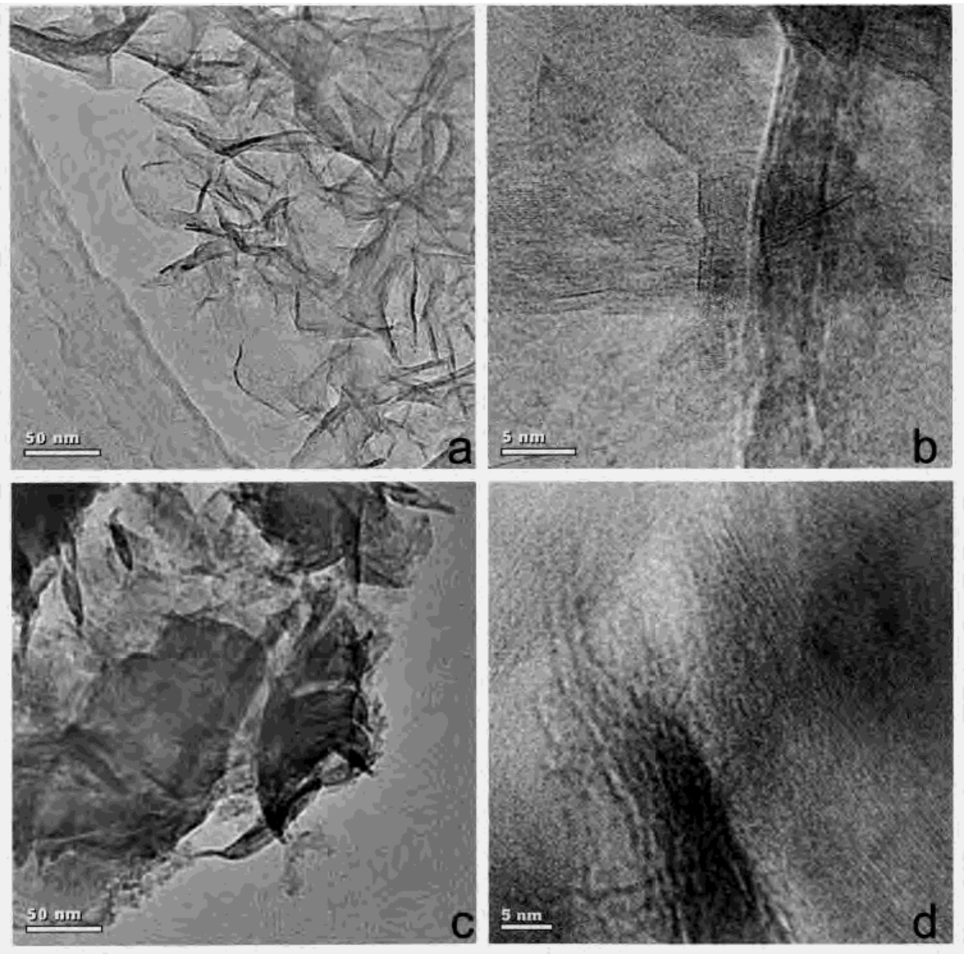

Figure 5. TEM micrographs of (a, b) LDH-NO_3, (c, d) LDH-Mn. (b) High magnification view of an area of part a showing lattice fringes. (d) High magnification view of an area of part c.

sponds to the ν_3 mode of carbonate species. These two bands are also present in the LDH-MOEt spectrum (Figure 3c). For LDH-MOAA, the spectrum shows a shoulder around 1410 cm^{-1} and a strong adsorption band at 1636 cm^{-1}, corresponding to the presence of organic species in the LDH structure. This band obscures the band arising from the bending mode δ H_2O.

Raman Spectroscopy and Average Oxidation State Determination. Raman spectroscopy was used to identify the nature and the state of the manganese species formed after the reduction step. Raman data are particularly useful to distinguish between such species as Mn_3O_4, Mn_2O_3, MnO_2, and MnO.[36-38] The Raman spectra of all of the synthesized LDH materials are depicted in Figure 4. The LDH-NO_3 sample has a simple spectrum consisting of two bands at 552 and 1049 cm^{-1} (Figure 4, inset). The first band is due to the lattice vibration of the hydroxyl layers, similar to those observed in the infrared spectrum, while the strong band at 1049 cm^{-1} is assigned to the symmetric stretching vibration of NO_3^-.[21,35] Anion-exchanging of the NO_3^- for MnO_4^- produces changes in the Raman spectrum (Figure 4a), a sharp new peak at 622 cm^{-1}, and a significant decrease in intensity of the peak at 1049 cm^{-1}. The peak at 622 cm^{-1} is accompanied by a smaller band at 493 cm^{-1}. The Raman spectra of LDH-MOEt and LDH-MOG (Figure 4b,c) reveal qualitatively the same behavior. However, they differ in the position of the main Raman band. This band is located at 627 and 618 cm^{-1} for LDH-MOET and LDH-MOG, respectively. A weaker shoulder at 496−500 cm^{-1} is observed in both samples. Finally, the LDH-MOAA sample (Figure 4d) is not Raman active. As will be discussed, the peaks located in the range 480−630 cm^{-1} in the LDH-Mn, LDH-MOG, and LDH-MOEt samples correspond to manganese oxide species. The absence of vibrational frequencies in the Raman region where the bands due to manganese oxides appear for the LDH-MOAA sample will also be discussed.

Average oxidation state (AOS) measurements for the reduced LDH samples were performed to complement the Raman results. As observed in Table 1, the AOS values of manganese for the LDH-MOG and LDH-MOEt materials are 3.1 and 3.5, respectively, while no reasonable value was measurable for LDH-MOAA.

Morphology. TEM and HRTEM images of the precursor LDHs and the organic-reduced LDHs are shown in Figures 5 and 6, respectively. Electron micrographs reveal that the

---

(36) Buciuman, F.; Patcas, F.; Cracium, R.; Zahn, D. R. T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 185.

(37) Li, W.; Gibbs, G. V.; Oyama, S. T. *J. Am. Chem. Soc.* **1998**, *120*, 9041.

(38) Radhakrishnan, R.; Oyama, S. T.; Chen, J. G.; Asakura, K. *J. Phys. Chem. B* **2001**, *105*, 4245.

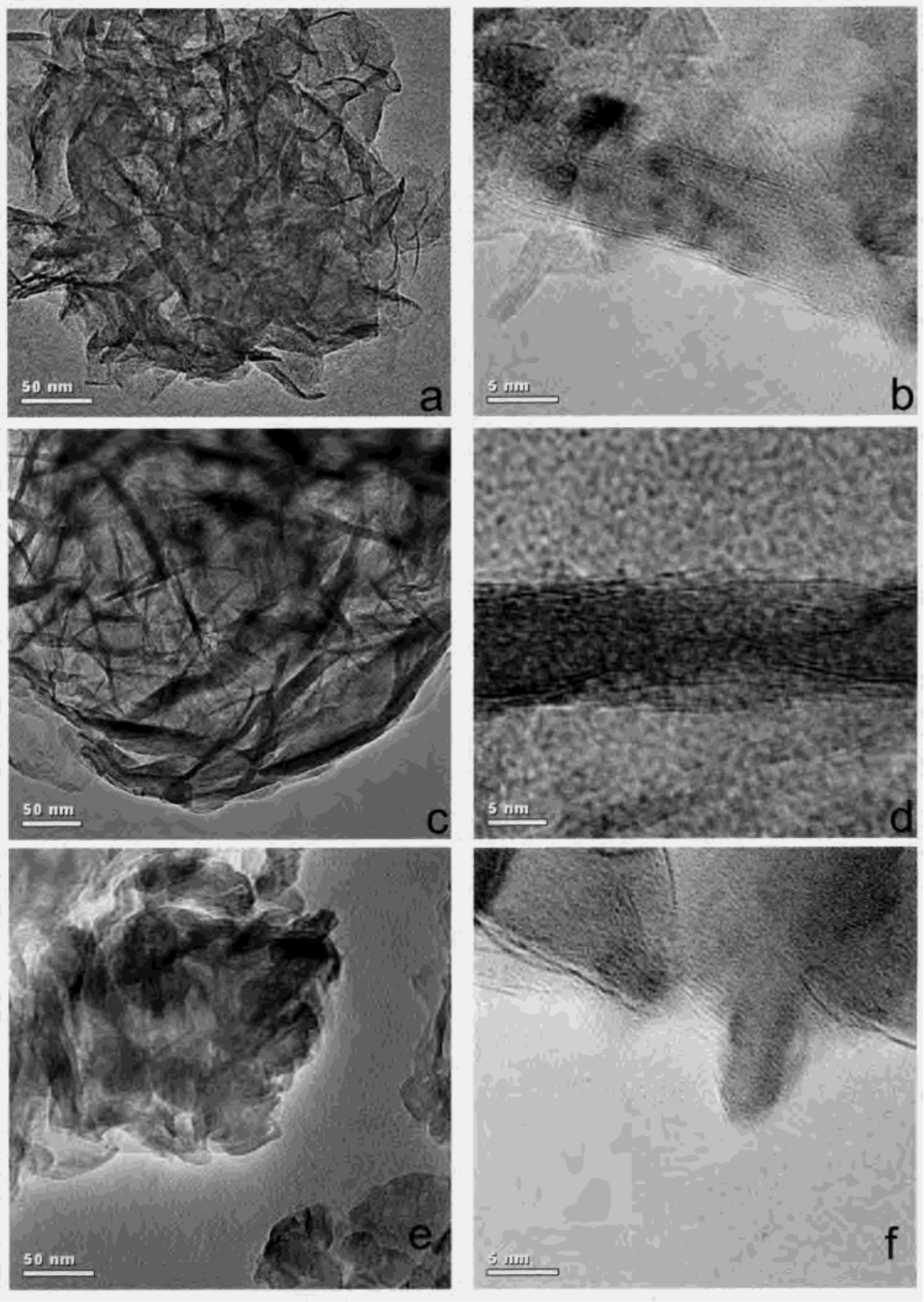

Figure 6. TEM micrographs of (a, b) LDH-MOEt, (c, d) LDH-MOG, and (e, f) LDH-MOAA. Images b, d, and f are high magnification views of an area of images a, c, and e, respectively.

general morphology of the LDHs is conserved throughout the synthesis. Low-resolution images of the materials show the aggregation of platelike particles. Layering within the samples was evident from high-resolution TEM micrographs (Figures 5b,d and 6b,d,f). While samples LDH-NO_3, LDH-Mn, and LDH-MOEt exhibited regular periodicity in the lattice fringes, disturbance in the layer stacking sequences was observed for LDH-MOG and LDH-MOAA materials (Figure 6d,f). These results are consistent with the behavior of these samples, with a low Mg/Al ratio (Table 1) and weak XRD peaks (see Figure 2).

Surface Area and Porosity Study. The textural properties of the derivative LDH materials have been studied by the nitrogen adsorption−desorption isotherms. The isotherms recorded for LDH-NO_3 and LDH-Mn are similar and correspond to reversible type II (IUPAC classification)[39] characteristic of nonporous materials. LDH samples reduced with organic reagents also exhibit a type II isotherm, although a type H3 hysteresis loop is shown. This type of hysteresis is characteristic of aggregates of platelike particles leading to slit-shaped pores,[39] which is in agreement with the microtexture of the hydrotalcite. The BET surface areas, S_{BET}, and pore volumes are summarized in Table 2.

---

(39) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A. Rouquérol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

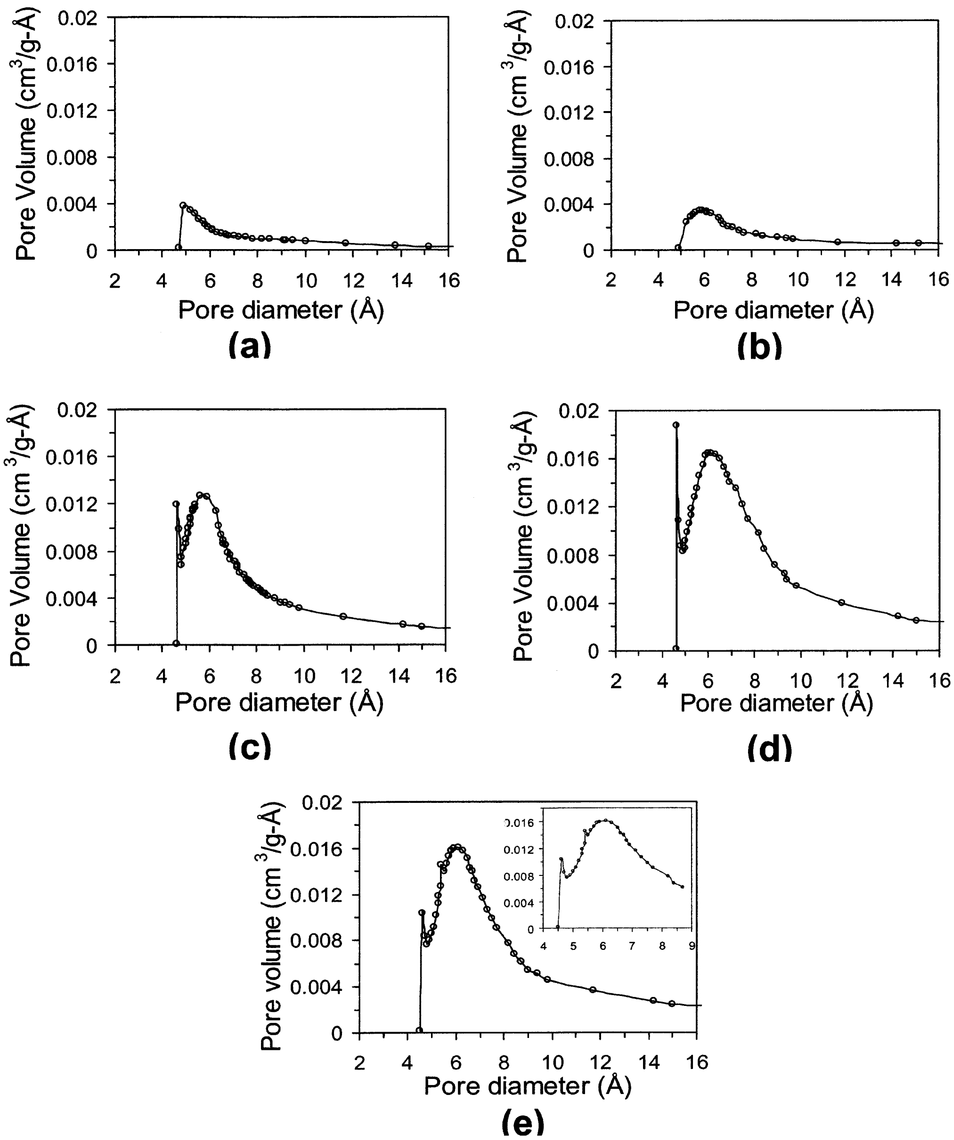

Figure 7. Horvath–Kawazoe pore size distribution curves of (a) LDH–NO_3, (b) LDH–Mn, (c) LDH-MOEt, (d) LDH-MOG, and (e) LDH-MOAA. The inset in figure e shows the details in the pore distribution of the sample LDH-MOAA in the 5–7 Å range of pore diameter.

Table 2. BET Surface Area (S_{BET}) and Pore Volume (V_p) of MgAl LDHs

sample	S_{BET} (m^2/g)	$V_p{}^a$ (cm^3/g)
LDH-NO_3	45	0.359
LDH-Mn	40	0.324
LDH-MOEt	134	0.670
LDH-MOG	211	0.941
LDH-MOAA	196	0.837

[a] Single point total pore volume at $P/P_0 = 0.99$.

According to Table 2, LDH-NO_3 and LDH-Mn materials are nonporous and have surface areas of around 40–45 m^2/g. The BET surface area of the synthesized LDH-NO_3 decreases after the incorporation of permanganate ions into the interlayer region. However, when LDH-Mn is reduced by an organic compound, the resultant LDH materials (LDH-MOG, LDH-MOEt, and LDH-MOAA) have higher surface areas and pore volumes (130–215 m^2/g).

Pore size distribution curves for all the materials are depicted in Figure 7. LDH-NO_3 and LDH-Mn samples (Figure 7a,b) show a broad distribution of pores with a maximum diameter close to 5–6 Å. On the other hand, LDH-MOEt, LDH-MOG, and LDH-MOAA materials exhibit bimodal micropore size distribution curves, as shown in Figure 7c–e, respectively. In the specific case of the LDH-MOAA sample (Figure 7e), a narrow peak is also observed between the two pore sizes corresponding to the bimodal distribution.

IV. Discussion

Ion-Exchange, Reduction, and Composition. The incorporation of Mn in the interlayer space of the LDH structure was evaluated by comparing the chemical analyses of Mn-containing materials with that of the parent LDH-NO_3. Nitrogen analysis data showed a reduction of the N weight percentages in LDH-Mn after the reduction step. The presence of manganese in the LDH-Mn sample and the large variation in nitrogen content from LDH-NO_3 to LDH-Mn confirm that permanganate anions are successfully incorporated in the structure of MgAl LDH through ion-exchange, occupying the interlayer anion sites in replacement of some nitrate anions. Permanganate incorporation is also evidenced from the FTIR results, where the band corresponding to the vibration of NO_3^- decreases with the introduction of permanganate, and a new band is observed in the spectrum. This new band located at 901 cm^{-1} confirmed that the exchanged Mn is present in the structure of the LDH as tetrahedral permanganate.

Intercalating permanganate ions in the intergallery region of MgAl LDH nitrate was the intermediate step in the further synthesis of manganese oxide species in this layered host. LDH materials containing manganese species as counteranions were prepared by adding a solution of the organic compounds to LDH-Mn slurry at room temperature and stirring for an hour. Elemental analysis of the LDH-MOEt, LDH-MOG, and LDH-MOAA products showed that Mn weight percentages decreased as carbon weight percentage increased after the reduction process. Chemical analysis results suggest that ion-exchange is occurring simultaneously during the reduction reaction. The organic compounds in addition to reducing MnO_4^- ions are also partly exchanging with some of the counteranions from the interlayer. The amount of carbon observed in Table 1 is consistent with the presence of carbon-containing species in the interlayer space of LDH-MOEt, LDH-MOG, and LDH-MOAA.

The incorporation of carbon species in the structure seems to depend on the nature of the organic compound used to reduce permanganate to manganese oxide. When ascorbic acid is used as a reducing agent, most of the NO_3^-, and MnO_4^- ions are removed from the interlayer, while incorporating ascorbate as the main anion. The introduction of ascorbate was confirmed by preparing ascorbate-intercalated MgAl LDH. The properties of this material were similar to those of LDH-MOAA. The use of ascorbic acid as a reducing agent not only causes an ion-exchange in the sample but also a deviation in the Mg/Al ratio from the initial ratio, as observed in Table 1. This behavior was also observed in ascorbate LDH, where the Mg/Al ratio was 1.3. The deviation of the molar ratios from the theoretical value in LDH-MOAA, and also LDH-MOG, indicates there is a high density of Al in the brucite-like layer. This suggests that the composition of the hydroxyl layers in LDH-Mn is being influenced during the reduction process with ascorbic acid and glucose. Partial dissolution of the brucite-like layers takes place during the exchange process when carried out at neutral or acidic pH.[22,40] Therefore, the difference in Mg/Al ratio in the LDH-MOAA sample can be attributed to the acidic functionality of the ascorbic acid. The nature of the ascorbic acid is also believed to be the reason for the larger loss of Mn due to ion-exchange observed for LDH-MOAA compared to LDH-MOG and LDH-MOEt.

The existence of carbon species in the interlayer of the reduced LDH materials was also evidenced from infrared results. The FTIR spectra of the LDH-MOG and LDH-MOEt suggested the presence of carbonate ions in these samples, due to the appearance of a peak at 1370 cm^{-1}. The presence of these species in the structure is due to the decomposition of the organic compounds to CO_2 during the reaction rather than atmospheric carbonate, since the experimental conditions were chosen to prevent the formation of carbonates. CO_2 can lead to the formation of interlayer carbonate species due to the basic medium of the layered host.

In the case of LDH-MOAA, the most significant features observed in the spectrum are a strong adsorption band at 1636 cm^{-1} and a shoulder around 1410 cm^{-1}. These bands were compared with literature data for ascorbic acid and metal complexes of sodium ascorbate,[41-43] and with our result for MgAl LDH ascorbate. This comparison demonstrates that the band at 1636 cm^{-1} corresponds to the stretching vibration of C=C, which shifts to lower wavenumbers in ascorbate-type compounds. The broadening of this band is attributed to the overlapping of the carbonyl (C=O) stretch band, which is observed as a medium band at 1720 cm^{-1} for LDH ascorbate. The difference in intensity can be explained by the fact that more ascorbate is retained in the interlayer of LDH ascorbate than in the ascorbic acid reduced LDH-MOAA. The changes observed for these absorption frequencies can also be due to the participation of the carbonyl group in Mn–ascorbate complexation. The shoulder at 1410 cm^{-1} is related to CH and OH stretching vibrations.[43] The presence of the characteristic vibrations of C=O and C=C functional groups in the spectrum of LDH-MOAA and the similarities of this spectrum with the one for LDH ascorbate are in agreement with the retention of ascorbate between the hydroxide layers after the reduction process.

Effects of Mn Incorporation on the Properties of LDH Nitrate. The stability of the LDH structure upon anion intercalation and the reduction process was evaluated by comparing the XRD patterns of Mn-containing materials with that of the parent LDH nitrate. XRD patterns confirmed that Mn-containing materials have a layered structure, characteristic of hydrotalcite-like compounds. The XRD results showed a decrease in the intensity of the main reflection peaks in all the Mn-containing LDH samples. The intensity decrease in the X-ray reflections of LDH after an anionic exchange has been attributed to a disturbance in the stacking sequence of the layers due to the adsorption of anions on the surface.[44] TEM results showed that the reducing agent affected the degree of order of the LDH materials. The most ordered product was obtained when ethanol was used as a reducing agent, whereas ascorbic acid produced the least ordered structure. The lattice fringes highlighted in Figures 5b,d and 6b,d,f) correspond to the intergallery height, supporting the XRD results that will be described. The fact that the loss in intensity of the X-ray reflections is significant in the reduced LDHs could be attributed to the pillaring of the materials. In many instances, the first-order peak of pillared LDH materials is not very intense, and in some cases, the peaks are absent.[45] The presence of pillars in LDH-MOEt,

---

[40] Kooli, F.; Rives, V.; Ulibarri, M. A. *Inorg. Chem.* **1995**, *34*, 5114.

[41] Lohmann, W.; Pagel, D.; Penka, V. *Eur. J. Biochem.* **1984**, *138*, 479.

[42] Obaleye, J. A.; Orjiekwe, C. L. *J. Sci. Islamic Repub. Iran* **1998**, *9*, 148.

[43] Hvoslef, J.; Klaeboe, P. *Acta Chem. Scand.* **1971**, *25*, 3043.

[44] Miyata, S.; Okada, A. *Clays Clay Miner.* **1977**, *25*, 14.

[45] Nijs, H.; De Bock, M.; Vansant, E. F. *J. Porous Mater.* **1999**, *6*, 101.

LDH-MOG, and LDH-MOAA is also evidenced from the N_2 adsorption results where micropores are formed in the interlayer space of the LDH-Mn due to the reduction of permanganate with organic agents. As reported by other authors, the presence of microporosity in LDHs correlates with the formation of pillars in the intergallery space.[46,47]

The structural modification occurred in the interlayer domain upon permanganate reduction can be followed by the evolution of the basal spacing. XRD results show that the interlayer distances of the reduced LDH materials shift to higher values compared to that of their predecessor LDH-Mn. The increasing of the basal spacings is attributed to both the formation of manganese oxide species, and the intercalation of organic species between the LDH layers during the reduction process, which is in agreement with elemental analysis and infrared results. The largest shift is observed upon the reaction of LDH-Mn with ascorbic acid. A gallery height of 5.1 Å was obtained after subtracting the brucite thickness (4.8 Å). This value is in good agreement with the data reported by Hwang et al. for ascorbic acid intercalated ZnAl-LDH[48] and with the interlayer distance of 5.3 Å obtained for our MgAl-LDH ascorbate.

The presence of ascorbic acid in the interlayer region coexisting with the nitrate and manganese species is also evidenced by the shape of the first and the second diffraction peaks. By examining the XRD pattern, the first peak is asymmetric, which suggests the presence of an overlapped peak. The second reflection peak corroborates this observation. This peak consists of one peak located at 18.4° (2θ) followed by a shoulder at ~20°. The d spacing of this reflection peak is approximately half of the value of d_{003}, while the d spacing of the shoulder is also half of the d spacing value of the overlapped peak. Thus, the resulting LDH-MOAA material would consist of stacks containing the organic group and nonsubstituted layer. This characteristic behavior was confirmed with N_2 sorption results, as will be discussed. Even though the gallery height, the XRD pattern, and the porosity are considerably changed by the MnO_4^- reduction, HR-TEM micrographs show that this process does not cause significant alteration in the morphologies of LDH-MOEt, LDH-MOG, and LDH-MOAA materials.

The modifications which occurred in the interlayer domain of the LDH-Mn after the reduction process are not limited to the expansion of the basal spacing observed in the reduced LDH materials. The nature of the bond between the interlayer manganese species and the host hydroxylated sheets is also influenced by the selection of the reducing organic chemicals. Back-exchange reaction with NaCl and Na_2CO_3 for 3 days was unsuccessful for LDH-MOG and LDH-MOAA samples. No significant amounts of Cl^- and CO_3^{2-} were exchanged for Mn species. The lack of back-exchange indicates that there is an interaction between the interlayer manganese species and the LDH layers. This could be due to the grafting of anionic species to the host. Contrary to the case of LDH-MOG and LDH-MOAA, manganese species were exchanged by Cl^- in sample LDH-MOEt. The manganese weight percentage decreased 26% and the basal spacing decreased from 8.5 to 7.9 Å, being close to that (7.86 Å) of LDH chloride, after 3 h of reaction. This suggests that the interlayer manganese species formed when permanganate ions are reduced with ethanol are not chemically bonded to the host matrix.

The process of reducing permanganate ions with organics and the selection of these reagents influence not only the structural properties of the synthesized LDHs but also the textural properties of these materials. The full nitrogen adsorption isotherms showed that the reduction process produces porous materials containing micropores. The presence of microporosity in the reduced LDH samples is also confirmed by the higher microporous volume obtained in comparison to those obtained for LDH-NO_3, and LDH-Mn. BET surface areas of LDH-NO_3 and LDH-Mn (45 and 40 m^2/g, respectively) are also significantly different from those of the reduced LDH samples (130−215 m^2/g). These surface areas for the precursor LDHs are created by the external surface of the different layers due to the high density of monovalent ions between the layers of both LDH-NO_3 and LDH-Mn, which leaves less empty space or limits the diffusion of the nitrogen molecules through the interlayer space. The inaccessibility of the interlamellar space of MgAl LDH nitrate to molecules as small as nitrogen has been ascribed to the nature of the interlayer anion.[49]

The large increase in surface area after reducing permanganate suggests that the pores in LDH-MOEt, LDH-MOG, and LDH-MOAA materials arise mainly from the gallery surface rather than from the interparticle voids, as was observed for LDH-Mn. The accessibility of the nitrogen molecules to the interlayer space of an LDH material is related to the void region. This is determined by the basal spacing of the layered material, and by the size and charge of the intercalating anions.[47,49] Therefore, one should expect a higher surface area in LDH-MOAA than in the other two reduced LDH materials. However, the N_2 sorption results did not show this to be true. Surface areas of the organic-reduced LDHs increase in the following order: LDH-MOG > LDH-MOAA > LDH-MOEt. The difference in surfaces areas of LDH-MOEt and LDH-MOG is believed to be associated with the presence of carbonate in the interlayer. LDH-MOG has more carbonate species than LDH-MOEt, as indicated by FTIR results. The presence of divalent ions in interlayer space reduces the density of the anions, which increases the distances between the anionic species and leaves a large free space in this region for the diffusion of the absorbate. LDH-MOG also presents a large gallery height, which provides access to the interlamellar region more easily than LDH-MOEt. The nature of the manganese species can also influence the surface areas of these materials. In the case of LDH-MOAA, the lower surface area observed

---

(46) Kwon, T.; Tsigdinos, G. A.; Pinnavaia, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 3653.

(47) Nijs, H.; De Bock, M.; Vansant, E. F. *Microporous Mesoporous Mater.* **1999**, *30*, 243.

(48) Hwang, S. H.; Han, Y. S.; Choy, J. H. *Bull. Korean Chem. Soc.* **2001**, *22*, 1019.

(49) Cavalcanti, F. A. P.; Schutz, A.; Biloen, P. In *Preparation of Catalyst IV.;* Delmon, P., Grange, P., Jacobs, P. A., Poncelet, G., Eds.; Elsevier: Amsterdam, 1987; p 165.

compared to LDH-MOG is believed to be related to the presence of the two different stacks. Even though ascorbate is retained in the interlayer of LDH-MOAA, opening the gallery height of the structure, nonsubstituted layers are also observed for this material. This results in a reduction of the access of the nitrogen molecules to the interlamellar region of these stacks, which could account for the negative impact on the surface properties of this material. The variation of the S_{BET} of the resultant solids with the organic agent used to reduce permanganate suggests that the nature of the organic compounds has an influence in the porosity of the materials. Therefore, it is possible to synthesize manganese-containing hydrotalcite-like compounds with different surface areas by simply changing the reducing agent.

The pore size distribution of the LDH is also affected by the reduction process. Whereas LDH-NO_3 and LDH-Mn show a broad distribution of pores, LDH-MOEt, LDH-MOG, and LDH-MOAA materials exhibit bimodal micropore size distribution curves. This finding has previously been reported by several authors for both cationic[50−52] and anionic[22] pillared clays. The first peak of the bimodal distribution is narrow for all the three samples and is related to the longitudinal pore size (gallery height), while the broader peak at higher values represents the lateral pore size or interparticle void. The different behavior in the pore distribution curve of LDH-MOAA compared to that for samples LDH-MOEt and LDH-MOG is due to the presence of two stacking sequences in the LDH, as concluded from the asymmetric shape of the first main diffraction peak in the X-ray diffraction pattern. The first peak of the pore size distribution curves is related to the interlayer distance of the LDH stack containing small anions, while the peak located at a pore diameter of around 5.4 Å corresponds to the longitudinal pore size of an expanded layered structure. These results confirm the presence of stacking of two types of interlayers in the material, when ascorbic acid is used as a reducing agent, as was proposed previously from the XRD data.

Mn Species Formed. Raman spectroscopy was used to evaluate the manganese oxide species in the layered material. A Raman study was also performed for LDH-Mn as a complement to the infrared study. The main features observed in the Raman spectrum of the LDH-Mn sample were two peaks at 622 and 493 cm^{-1}. A typical vibrational band for permanganate ions is located at 834 cm^{-1}, corresponding to the symmetric stretching vibration of this group.[35,53] Thus, the presence of bands other than the one corresponding to the vibration of the permanganate ion in the spectrum could be attributed to the reduction of permanganate during the spectrum acquisition because of local heating of the sample. Therefore, the peaks observed can be due to various forms of manganese oxide.

Numerous spectroscopic studies have been performed on manganese oxide species.[36,54−57] Buciuman et al.[36] found vibrational frequencies at 650 cm^{-1} and a weaker signal at 485 cm^{-1} for Mn_3O_4 species. They also observed frequencies close to 680 cm^{-1} corresponding to α-Mn_2O_3 and at 630 cm^{-1} characteristic of γ-Mn_2O_3. Raman peaks were also observed by Kapteijn et al.[54] in the range 637−648 cm^{-1} for samples of alumina-supported manganese oxides. These signals were attributed to a highly dispersed oxidic phase with Mn_2O_3 as an average stoichiometry. Although Kapteijn et al. did not observe any vibrational features for MnO_2, other authors have observed weak characteristic bands for this phase at 510 and 580 cm^{-1}.[36,55,56] Ludvigsson et al.[55] observed vibrational frequencies at 630 and 498 cm^{-1} for the λ-MnO_2 phase. On the basis of the literature, the Raman data for LDH-Mn in the region 480−630 cm^{-1} confirm the presence of manganese oxide species and also suggest that the LDH-Mn material does not contain a single manganese oxide phase, but a mixture of oxides coexisting in the sample.

For LDH-MOG and LDH-MOEt, Raman qualitatively revealed the same information. These samples showed peaks in the range 495−630 cm^{-1}, which is consistent with mixed-valent Mn in the manganese oxide system. However, a shift in the position of the peaks with respect to LDH-Mn and also between the reduced LDH samples was observed. This fact suggests that the choice of the reducing agent influences the formation of the manganese oxide species. The manganese average oxidation state measurements for LDH-MOG and LDH-MOEt samples give values of 3.1 and 3.5, respectively, which confirmed that a mixture of manganese oxide species with different oxidation states coexist in each sample. In the case of sample LDH-MOAA, no coherent value of AOS was obtained after several determinations, which indicates that either MnO_x is not present in the sample or the method used to determine AOS is not applicable in this case. Raman results suggested that manganese oxide species are not formed when the reduction is performed with ascorbic acid. However, it is possible that MnO_x is present in the sample but absent in the spectrum due to the low percentage of Mn (1.6 wt %) in the sample, which is close to the detection limit ($\geq$1 wt %) of the instrument. Another possibility is that the Mn is formed as a complex with the ascorbate retained in the layer, which may not be Raman active. Clearly, a detailed structural study is needed to confirm the local environment of the Mn species in the reduced LDH materials, although the confirmation is often difficult because of the small amount of Mn contained in the materials. Structural characterization methods, such as electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), and extended X-ray adsorption fine structure (EXAFS) measurements, may provide information on the environment where Mn is located.

---

(50) Gil, A.; Montes, M. *Langmuir* **1994**, *10*, 291.
(51) Gil, A.; Guiu, G.; Grange, P.; Montes, M. *J. Phys. Chem.* **1995**, *99*, 301.
(52) Ge, Z.; Li, D.; Pinnavaia, T. J. *Microporous Mater.* **1994**, *3*, 165.
(53) Gonzalez-Vilchez, F.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1972**, *16*, 1416.
(54) Kapteijn, F.; van Langeveld, A. D.; Moulijn, J. A.; Andreini, A.; Vuurman, M. A.; Turek, A. M.; Jehng, J. M.; Wachs, I. E. *J. Catal.* **1994**, *150*, 94.
(55) Ludvigsson, M.; Lindgren, J.; Tegenfeldt, J. *J. Mater. Chem.* **2001**, *11*, 1269.
(56) Ammundsen, B.; Burns, G. R.; Islam, M. S.; Kanoh, H.; Rozière, J. *J. Phys. Chem. B* **1999**, *103*, 5175.
(57) Julien, C.; Massot, M.; Rangan, S.; Lemal, M.; Guyomard, D. *J. Raman Spectrosc.* **2002**, *33*, 223.

V. Conclusions

A new series of LDH materials containing intercalated manganese oxide, not yet reported in the literature, has been prepared by a simple two-step method starting from a nitrate LDH. The synthetic route, involving exchange with permanganate ions and reduction reactions, offers the advantage that the manganese oxide species, rather than be incorporated by direct coprecipitation or ion-exchange, are readily synthesized inside the LDH structure. This method allows a simple control of the reaction and permits both a rapid and easy process. The in-situ reduction also gives the possibility of modulating the physicochemical properties of the material by choosing the reducing agent. The use of organic compounds in the reduction process appears to substantially modify the composition, structural parameters, and textural behavior of the synthesized LDHs. The Mn-containing LDHs obtained using glucose and ethanol show manganese oxides in the gallery domain coexisting with other anionic species. However, the manganese oxide species obtained by using glucose are different than those obtained using ethanol as determined by AOS measurements. These materials also exhibit different basal spacings. When ascorbic acid is used as reducing agent, carboxylate groups are incorporated in the interlayer space, and an expansion of the basal spacing occurs, as demonstrated by XRD studies. The presence of manganese oxide was not observed when ascorbic acid was used as a reducing agent. Studies are in progress in order to elucidate the nature of the manganese species formed as products of the organic reduction of permanganate, which are believed to be forming a complex with the organic group.

In terms of surface area and porosity, the organic compound used in the preparative route seems to be particularly important. Higher surface area results from the sample prepared using glucose. Therefore, a wide range of Mn-intercalated LDHs can be synthesized by simply changing the reducing agent. This feature of the Mn-containing LDHs will be an important parameter in catalyst preparation.

Overall, this work provides the first study of inorganic derivative LDHs containing intercalated manganese oxide species. These new materials have a bright prospect for developing novel selective catalysts, due to the fact that manganese oxides are confined in a constrained medium. Thus, this new method is promising for the synthesis of different kinds of manganese oxide nanocomposites.

Acknowledgment. The authors acknowledge support by the Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. We also thank to Dr. Mark Aindow for use of the JEOL 2010 TEM in the Institute of Materials Science, UConn. Special thanks are given to Dr. Francis Galasso for helpful suggestions.

IC030054K