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Microwave-Assisted Homogeneous Precipitation of Hydrotalcites by Urea Hydrolysis

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The use of urea as a precipitating agent in the synthesis of Ni−Al and Zn−Al layered double hydroxides having a hydrotalcite-like structure via a microwave−hydrothermal method is reported. For comparison purposes, the samples were also prepared by a conventional hydrothermal method. Ni−Al compounds with the hydrotalcite-like structure were obtained in shorter periods of time by the microwave method than by the conventional method, whereas when zinc cations were involved, no successful synthesis was achieved regardless of the method used. In order to find the best synthesis conditions for the Ni−Al solids, samples were submitted to microwave−hydrothermal treatment at different temperatures for increasing periods of time, and the structural, thermal, and textural properties of the synthesized materials were evaluated. All of the solids were fully characterized by chemical elemental analysis, powder X-ray diffraction (PXRD), FT-IR spectroscopy, and transmission and scanning electron microscopy as well as by N_2 adsorption/desorption at −196 °C for assessment of specific surface area and porosity. The PXRD patterns showed that the layered structure appeared after merely 10 min when the synthesis was carried out at 125 °C; however, the FT-IR spectra showed the presence of some cyanate groups that were formed during urea hydrolysis and were quite difficult to remove completely. When the conventional hydrothermal treatment was used, longer periods of time were required in order to develop the hydrotalcite-like structure, but increasing the aging time improved the crystallinity of the compounds and yielded large particles.

1. Introduction

Layered double hydroxides (LDHs) or hydrotalcite-like compounds (HTlcs) are layered materials consisting of positively charged layers having the brucite-like structure, in which divalent cations have been partially replaced by trivalent ones; solids with monovalent and tetravalent cations have been also prepared. In order to balance the excess positive charge, anions coexisting with water molecules are located in the interlayer region.[1,2] Although these solids are easily synthesized by coprecipitation,[3] reproducible, fast, and inexpensive synthesis procedures are still needed in order to control some of the properties, such as crystallinity, particle-size distribution, and specific surface area. In this sense, homogeneous precipitation in the presence of urea leads to solids of high quality in terms of morphology, size uniformity, and crystallinity, which are much better than those of solids prepared by the conventional coprecipitation method.[4] The high crystallinity of these solids has led to the possibility of determining the cationic order by AFM microscopy[5,6] and performing some Rietveld[7,8] and Diffax[8] studies.

In the homogeneous precipitation process during urea hydrolysis, massive supersaturation is avoided by slow in situ generation of the basic medium via thermal decomposi-

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tion of urea in aqueous solution.[9] Urea hydrolysis proceeds in two steps: formation of ammonium cyanate (NH_4CNO), which is the rate-determining step, and subsequent hydrolysis of NH_4CNO to ammonium carbonate. Because of the low-supersaturation conditions, the number of nuclei formed is small, therefore leading to large, well-crystallized particles.[10] The parameters affecting the properties of the materials, such as phase purity and particle size, are the total concentration of metal (M) cations, the $M^{2+}/(M^{2+} + M^{3+})$ molar fraction, the urea/$(M^{2+} + M^{3+})$ molar fraction in solution, and the temperature,[7,11–13] since altering some of these modifies the extent of supersaturation as well. Among all of these parameters, temperature seems to be the most important one for yielding well-crystallized samples, since urea decomposition is thermally activated and the decomposition kinetics can be greatly enhanced by increasing the temperature.

Thermal activation of urea decomposition at ambient pressure requires long reaction times. Several modifications of this thermal decomposition procedure have been proposed. For instance, use of hydrothermal conditions leads to faster precipitation of the compounds than during thermal activation at ambient pressure and reduces the time required to yield the pure hydrotalcite phase.[14,15] Another modification is the use of microwave radiation as a heating source. In a previous paper,[16] we reported the synthesis of Mg−Al LDH compounds using microwave-assisted urea hydrolysis, showing that the formation of the LDH phase depends on the temperature and irradiation time and that the microwave−hydrothermal treatment reduces the time required for the synthesis. Also, Jobbágy and co-workers[17] recently proposed the synthesis of Ni−Cr samples by a similar method but using higher temperatures.

In this work, we studied the influence of the cations on the microwave-assisted homogeneous precipitation using urea. For this reason, we extended the method to the synthesis of nickel- and zinc-containing LDHs in order to assess whether the method can be validated for other systems. The starting solutions containing the metallic salts and urea were submitted to microwave−hydrothermal treatment at different temperatures for increasing periods of time, and the structural, thermal, and textural properties of the synthesized materials were evaluated. For comparison purposes, the conventional hydrothermal treatment was also applied.

2. Experimental Section

2.1. Preparation of the Solids. The solids were prepared by a method modified from that proposed by Costantino and co-workers[7] and similar to that previously reported.[16] One liter of a 0.5 M solution containing 0.333 mol of $NiCl_2 \cdot 6H_2O$ or $ZnCl_2$ and 0.165 mol of $AlCl_3 \cdot 6H_2O$ was mixed with 1.65 mol of urea to give a urea/$(M^{2+} + M^{3+})$ ratio of 3.3 (smaller values of this ratio yielded poorer results and incomplete precipitation), and the mixture was stirred until the solids were totally dissolved. The solution was heated at 100, 125, 150, or 175 °C for times ranging from 5 to 300 min, depending on the layer composition, in a Milestone ETHOS PLUS microwave oven. The times required in order to reach the desired temperatures were 2.5, 5.0, 7.5, and 10 min for 100, 125, 150, and 175 °C, respectively. The temperature during irradiation was measured using a thermocouple introduced into the reference vessel. The software dynamically controlled the temperature profile, adjusting the delivered power at every moment. The feedback mechanism optimized the effects of too-high temperatures and pressures and at the same time prevented thermal runaways. However, the formation of hot spots within the vessel as a result of selective microwave absorption by some particles could not be ruled out. For comparison purposes and in order to study the exclusive effect of the microwave radiation during the treatment, the samples were compared to another set prepared using conventional hydrothermal treatment, which was carried out at autogenous pressure in a Teflon-lined, stainless steel Phaxe 2000 bomb placed in a static oven at 150 °C for 2, 3, 5, 12, or 24 h. A volume of 50 mL of solution per vessel was used in both the microwave and conventional procedures. After the sample was cooled to room temperature, the pH was measured, and then the precipitate was centrifuged and washed with distilled water until chloride anions and products of the urea decomposition were completely removed. Finally, the solids were dried in an oven at 40 °C in air.

The solids prepared under microwave irradiation are named as XAW-*T*-*t*, where X = N or Z (for Ni or Zn, respectively), *T* represents the heating temperature in degrees Celsius, and *t* refers to the heating time in minutes. The samples produced under conventional hydrothermal conditions are named as XAHT-150-*t*, where *t* stands for the heating time in hours.

2.2. Characterization of the Solids. Chemical elemental analysis for Ni and Al was accomplished via atomic absorption using a Mark 2 ELL-240 apparatus by the Servicio General de Análisis Químico Aplicado (University of Salamanca). CHN elemental analyses were performed using a LECO CHNS-932 elemental analyzer by the Servicio Interdepartamental de Investigacion (University Autonoma of Madrid).

Powder X-ray powder diffraction (PXRD) patterns were recorded on a Siemens D-500 instrument using Cu Kα radiation ($\lambda = 1.54050$ Å) and equipped with Diffrac AT software. The crystalline phases were identified by comparison with JCPDS files.[18] Unit cell parameters were obtained by refining the peak positions of the PXRD pattern with a least-squares method using the CELREF unit-cell refinement program,[19] assuming a hexagonal unit cell and space group $R\bar{3}m$. Average sizes of crystallites were calculated using the

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Scherrer equation: $D = K\lambda/(\beta \cos \theta)$, where D is the average crystallite size, K is the shape factor for the average crystallite (the expected shape factor is 0.9), λ is the X-ray wavelength (1.54056 Å for Cu Kα_1), θ is the Bragg angle, and β is the full width at half-maximum (FWHM) in radians [$\beta = (B^2 - b^2)^{1/2}$, where B is the measured FWHM and b is the instrumental broadening, which was determined by collecting the diffraction pattern of a NIST-traceable LaB_6 line-width standard (SRM660a)].

FT-IR spectra were recorded on a PerkinElmer FT1730 instrument using KBr pellets; 100 spectra (recorded with a nominal resolution of 4 cm^{-1}) were averaged in order to improve the signal-to-noise ratio.

Transmission electron microscopy (TEM) photographs were taken by the Servicio General de Microscopía Electrónica (University of Salamanca) using a ZEISS-902 microscope. Each sample was dispersed in acetone by ultrasound, and a few drops of the dispersion was deposited on a copper grid previously impregnated with an amorphous carbon film using a voltaic arc. Scanning electron microscopy (SEM) images were recorded using a JEOL 6300 instrument at 25 kV at the University of Córdoba.

Assessment of specific surface area was carried out using a Gemini instrument from Micromeritics. Before each measurement, the sample (80−100 mg) was degassed in flowing nitrogen at 110 °C for 2 h in a Micromeritics FlowPrep 060 apparatus in order to remove physisorbed water; the data were analyzed using published software.[20] Values of pore volumes were obtained from saturation adsorption capacities; nitrogen uptake at $P/P_0 = 0.95$ was converted into adsorbed volume by assuming that the adsorbate had the normal liquid density at the operational temperature.

Thermogravimetric analysis and differential thermal analysis (DTA) were performed using PerkinElmer TG-7 and DTA-7 instruments, respectively, in flowing oxygen and/or nitrogen (L'Air−Liquide) at a heating rate of 10 °C min^{-1}.

3. Results

3.1. Ni−Al LDHs. 3.1.1. Powder X-ray Diffraction. PXRD patterns for Ni−Al samples prepared at 150 °C in the microwave oven and a conventional furnace are displayed in panels a and b, respectively, of Figure 1. The patterns show diffraction lines characteristic of the hydrotalcite-like structure, with nonuniform broadening of the lines that points to some structural disorder. No secondary crystalline phases are identified by PXRD, even at low synthesis times. This is contrary to the behavior showed by Mg−Al−CO_3 compounds synthesized using the urea method under both hydrothermal (conventional and microwave)[16] and refluxing[4] conditions, where an aluminum hydroxide phase is formed during the first stages of the synthesis and then incorporation of the divalent cations takes place, leading finally to the formation of the LDH structure. However, the absence of an amorphous secondary phase cannot be completely ruled out on the basis of PXRD only.

Although an enhancement in the degree of crystallinity (broadly defined as the sharpness of the diffraction peaks) with increasing irradiation time is expected, a first exploration of the patterns in Figure 1a does not show any appreciable effect of the irradiation time for either short or long treatment times. It can be concluded that extending the duration of the microwave treatment does not lead to an appreciable enhancement of the crystallinity of the Ni−Al LDH compounds once their structures have been formed. Very recently, Liu et al.[21] have also claimed that refluxing Ni−Al compounds in the presence of urea achieved no improvement in the crystallinity and that hydrothermal treatment for 2 days was necessary in order to improve the crystallinity of the solids. To obtain a more accurate analysis of the evolution of crystallinity during the synthesis process, FWHM values for the 003 lines were used in the Scherrer equation to calculate average crystallite sizes in the stacking direction, taking into account the instrumental contribution to the broadness of the lines; the results are included in Table 1. It should be noted that the line broadening can be also caused by structural disorder, which must be discounted before estimating the crystallite size;[22] however, for comparison purposes in the present work, the results give useful qualitative information concerning crystal growth in the stacking direction for samples submitted to different treatments. The values of the crystallite sizes are very close to each other and support the qualitative information obtained from the analysis of the PXRD patterns, i.e., the sizes do not change as much as for Mg−Al LDHs.[16]

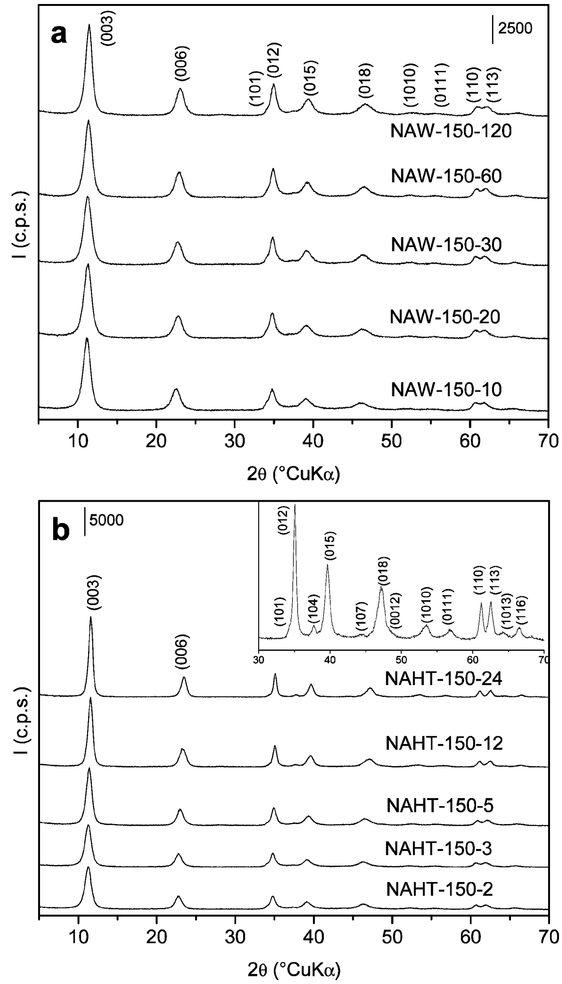

Figure 1. PXRD patterns for Ni−Al solids obtained at 150 °C by (a) microwave and (b) conventional methods.

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Table 1. Cell Parameters *a* and *c* (Å) and Crystallite Sizes D_{003} (nm) of Ni−Al−CO_3 Compounds Obtained by Microwave-Assisted and Hydrothermal Precipitation at 150 °C

sample	*c*	*a*	D_{003}
NAW-150-10	23.59(2)	3.05(3)	8
NAW-150-20	23.37(5)	3.05(9)	7
NAW-150-30	23.47(2)	3.05(6)	7
NAW-150-60	23.26(6)	3.05(2)	8
NAW-150-120	23.28(3)	3.04(3)	9
NAW-175-60	22.85(9)	3.03(3)	9
NAW-175-120	22.76(6)	3.03(3)	9
NAHT-150-2	23.38(9)	3.05(3)	9
NAHT-150-3	23.32(8)	3.05(7)	9
NAHT-150-5	23.24(5)	3.04(1)	10
NAHT-150-12	22.74(3)	3.03(6)	13
NAHT-150-24	22.64(8)	3.03(1)	15

In regard to the conventional hydrothermal procedure, increasing the treatment time leads to more intense and symmetric diffraction lines without development of nondesired side phases (Figure 1b). It should be remarked that the PXRD pattern for NAHT-150-24 also shows well-resolved (110) and (113) diffraction lines, which are features not observed for the microwave-irradiated solids. Comparison of the values obtained for samples synthesized by the microwave and conventional hydrothermal treatments at the same temperature (150 °C) for 2, 3, and 5 h reveals that the microwave treatment leads to particles with similar crystallite sizes regardless of the irradiation times, while larger crystallites are obtained when the conventional treatment is prolonged.

Refined values of the lattice parameters *a* and *c* are summarized in Table 1. The values depend on the synthesis time, and both parameters show a general decrease when the aging time is prolonged. For example, the *c* values for the NAW-150 series range from 23.59(2) to 23.28(3) Å for the samples aged for 10 and 120 min, respectively. The basal spacing for sample NAW-150-10 is significantly larger than the value reported for carbonate-containing LDHs[23] but in agreement with values previously reported for Ni−Al compounds obtained by the urea method.[15,24] Moreover, the *c* values for the samples prepared following the conventional hydrothermal method are smaller and closer to those reported for LDHs having carbonate in the interlayers. Several authors have related an increase in basal spacing to the location of CNO^- anions (intermediate species formed in the decomposition of urea)[25,26] in the interlayer; however, such a large value could be also ascribed to weakness of the electrostatic interactions between the cationic layers and the interlamellar anions[27] or to the presence of different amounts of interlayer water.[28] The amount of water has been calculated from thermogravimetric analyses and found to depend on the synthesis conditions (Table 2). However, it should be stressed that the calculated amount of water includes both physisorbed and interlayer water and that the former could also be modified during the synthesis steps. In the NAW-150 series, for instance, a slight increase in the water content takes place between the samples aged for 10 and 30 min, after which the water content decreases as the irradiation time is extended, reaching a value as low as 0.30. Finally, in samples prepared by the conventional hydrothermal method, the water content increases with the treatment time. Taking into account these results, it cannot be stated that the only factor in determining the value of the parameter *c* is the water content; other factors, such as stronger interactions between layer and interlayer domains and the type and arrangement of the anions, can determine this value as well. On the other hand, the variation of the cell parameter *a* suggests a slight modification of the layer composition, since this parameter corresponds to the average closest-cation distance. The *a* values for the solids obtained after the shortest synthesis times are 3.05(3) Å, and these decrease to 3.04(3) Å for the NAW-150 series and 3.03(1) Å for the NAHT-150 series. In view of the ionic radii of Ni^{2+} (0.83 Å) and Al^{3+} (0.68 Å) in octahedral coordination,[29] the decrease in the value of *a* suggests the removal of nickel cations at long synthesis times in both synthesis procedures.

In summary, nickel−aluminum layered double hydroxides are formed at 150 °C under microwave irradiation at shorter times than are the corresponding magnesium−aluminum compounds, but no remarkable improvement in the ordering of the solid is attained by using microwave radiation as a heating source. In order to complete the study, the synthesis was carried out at longer treatment times at 150 °C and at lower (125 °C) and higher (175 °C) temperatures. The synthesis at lower temperature was performed in order to obtain some clues about the precipitation process taking place in the vessels, whereas prolonging the treatment time and increasing the temperature were aimed at achieving an improved degree of crystallinity.

When heating is performed at 125 °C (see Figure 1 in the Supporting Information), the single hydrotalcite phase is formed after a very short time (i.e., 10 min), and the degree of crystallinity is quite similar to that reported above for samples prepared at 150 °C. No fast enhancement of the ordering is observed on prolonging the irradiation time, as the crystallite sizes range between 8 and 9 nm for samples NAW-125-10 through NAW-125-120. However, the lattice parameter *a* remains almost constant at 3.05(2) Å for all of the synthesis times, whereas the *c* values show a slight increase from 23.68(7) to 23.98(5) Å in the first 20 min and then a decrease to 23.76(4) Å for sample NAW-125-120. When the synthesis is carried out at 150 °C, it is necessary to prolong the synthesis up to 300 min to observe just a small enhancement in crystallinity. Finally, when the reaction temperature is set at 175 °C, it is possible to obtain a solid with a higher degree of crystallinity and smaller *c* and *a* values [22.85(9) and 3.03(3) Å, respectively] than in NAW-

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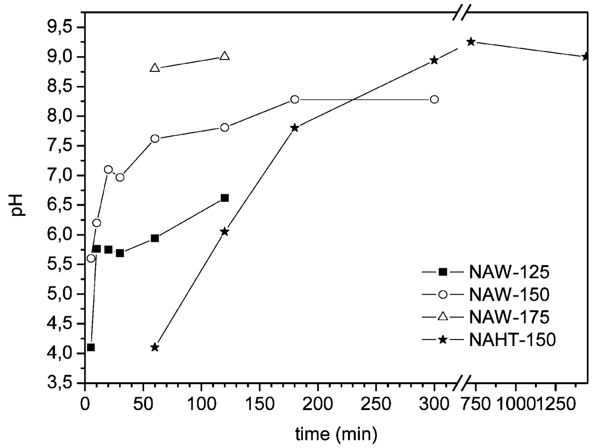

Figure 2. Evolution of the pH during syntheses in the microwave oven at 125 °C (NAW-125), 150 °C (NAW-150), and 175 °C (NAW-175) and in the conventional oven under hydrothermal conditions at 150 °C (NAHT-150).

150-300 in 60 min. Heating the mixture for 120 min (NAW-175-120) yields only a decrease in the *c* value [to 22.76(6) Å].

The differences observed between the synthesis processes for the Ni−Al−CO_3 and Mg−Al−CO_3 samples must be related to their titration curves obtained by titration of solutions containing divalent and trivalent metal chlorides with NaOH to yield LDHs.[30] The pH of the second plateau is observed at lower pH values for the nickel-containing compounds than for the magnesium LDHs. Consequently, the pH needed to form the LDH structure is more rapidly attained in the urea hydrolysis. The general shape of the pH curves shown in Figure 2 (measured after the cooling of the vessels) is quite similar to that for the Mg−Al−CO_3 compounds.[16] Only small differences are detected in the temperatures at which the same pH values are reached. The pH increases very rapidly at 125 °C: a steady increase of the basicity takes place during the first 20 min, followed by a plateau that is maintained until an irradiation time of 60 min and then by another increase, to a pH value close to 6.5. This behavior is similar to that observed during the synthesis of the Mg−Al−CO_3 samples. No important differences are observed when the temperature is set to 150 °C, where both the initial pH rise and the posterior plateau are observed, as well as an increase to a maximum pH followed by a small decrease as the irradiation time is further prolonged. The same differences reported between the two treatments are observed, but the pH rises more slowly here. Finally, it should be noticed that an increase of the reaction temperature to 175 °C leads to the most rapid pH increase.

3.1.2. FT-IR Spectra. FT-IR spectra of the samples prepared in the microwave oven at 150 and 175 °C and by the conventional hydrothermal treatment are displayed in Figures 3 and 4, respectively.

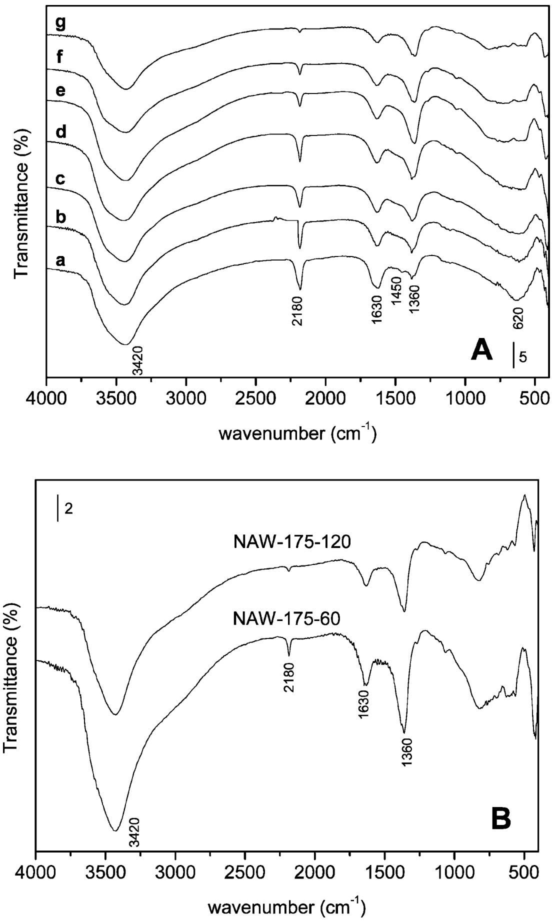

Figure 3. FT-IR spectra of Ni−Al LDHs obtained in the microwave oven at (A) 150 and (B) 175 °C. In (A), samples were aged for (a) 10, (b) 20, (c) 30, (d) 60, (e) 180, (f) 240, and (g) 300 min.

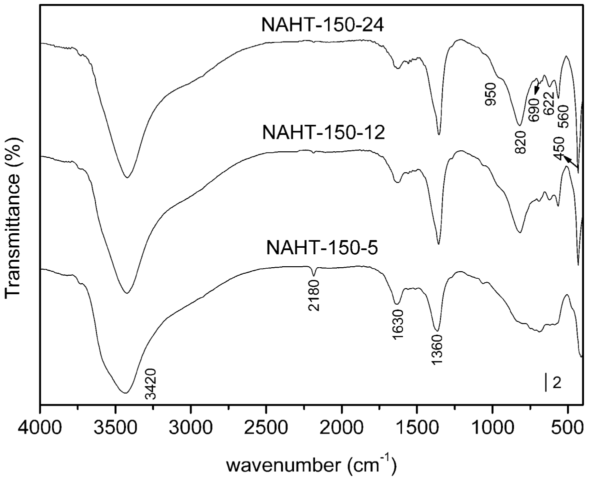

Figure 4. FT-IR spectra of Ni−Al LDHs obtained by the conventional hydrothermal method using a temperature of 150 °C and reaction times of 5, 12, and 24 h.

The characteristic bands related to the hydrotalcite structure are observed in all cases.[31] The broad and intense band at 3420 cm^{-1} is ascribed to the stretching vibrations of OH groups in the layers and in water molecules. The weak band at 1630 cm^{-1} is due to the water deformation mode and that close to 1500−1360 cm^{-1} to the ν_3 mode of carbonate anions released during urea hydrolysis. The sharp but not very intense band observed at 2180 cm^{-1} is related to the presence

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Table 2. Chemical Analyses and Chemical Formulas for Selected Samples

sample	Ni^{2+}[a]	Al^{3+}[a]	Ni^{2+}/Al^{3+}[b]	N[a]	C[a]	N/C[b]	formula
NAW-150-10	35.40	8.40	1.94	2.11	1.64	1.09	$[Ni_{0.660}Al_{0.340}(OH)_2](OCN)_{0.164}(CO_3)_{0.000}\cdot 0.45H_2O$
NAW-150-30	36.41	8.28	2.00	1.12	1.75	0.53	$[Ni_{0.669}Al_{0.331}(OH)_2](OCN)_{0.084}(CO_3)_{0.073}\cdot 0.51H_2O$
NAW-150-60	36.10	8.28	2.00	0.30	1.80	0.13	$[Ni_{0.667}Al_{0.333}(OH)_2](OCN)_{0.022}(CO_3)_{0.141}\cdot 0.39H_2O$
NAW-150-180	35.47	8.28	1.97	0.18	1.78	0.09	$[Ni_{0.663}Al_{0.337}(OH)_2](OCN)_{0.014}(CO_3)_{0.148}\cdot 0.35H_2O$
NAW-150-300	34.94	8.52	1.88	0.16	1.82	0.07	$[Ni_{0.653}Al_{0.347}(OH)_2](OCN)_{0.012}(CO_3)_{0.155}\cdot 0.30H_2O$
NAW-175-60	35.21	8.55	1.77	0.14	1.76	0.07	$[Ni_{0.654}Al_{0.346}(OH)_2](OCN)_{0.011}(CO_3)_{0.155}\cdot 0.32H_2O$
NAW-175-120	33.99	8.78	1.78	0.10	1.83	0.05	$[Ni_{0.640}Al_{0.360}(OH)_2](OCN)_{0.008}(CO_3)_{0.162}\cdot 0.34\ H_2O$
NAHT-150-5	34.71	8.63	1.85	0.10	1.73	0.05	$[Ni_{0.649}Al_{0.351}(OH)_2](OCN)_{0.008}(CO_3)_{0.150}\cdot 0.34H_2O$
NAHT-150-12	33.58	8.72	1.77	0.06	1.80	0.03	$[Ni_{0.639}Al_{0.361}(OH)_2](OCN)_{0.004}(CO_3)_{0.163}\cdot 0.37H_2O$
NAHT-150-24	34.06	8.71	1.80	0.04	1.83	0.01	$[Ni_{0.642}Al_{0.358}(OH)_2](OCN)_{0.002}(CO_3)_{0.167}\cdot 0.54H_2O$

[a] Weight percent. [b] Molar ratio.

of products formed during urea decomposition;[25,26,32,33] for example, it may be the C−N stretching mode of cyanate anions in the interlayer region[25,26,33] or adsorbed on the surface.[33] On the basis of Raman and FT-IR spectra, Kloprogge and co-workers[15] have recently ascribed this band to the presence of intercalated $(NH_2)COO^-$ species formed during urea decomposition. It is worth noting that this band is not observed in the FT-IR spectra of Mg−Al LDHs.

The intensity of the $\nu_3(CO_3^{2-})$ band increases as the irradiation time at 150 °C increases, while the band at 2180 cm^{-1} becomes less intense (Figure 3A). These features suggest a steady intercalation of CO_3^{2-} with a simultaneous release of the urea-derived anions, although some species still persist after treatment for 300 min at 150 °C. Increasing the temperature to 175 °C does not completely remove the band at 2180 cm^{-1} (Figure 3B). However, conventional hydrothermal treatment for 12 and 24 h is enough to almost remove this species (Figure 4).

In regard to the low-wavenumber region (where bands due to M−O modes and other bands of the interlayer anions usually appear), a broad band with a minimum at 620 cm^{-1} is observed for the solids prepared at 150 °C for short periods of time; this feature is attributed to the nitrogen-bonded cyanate deformation of OCN^- species $[\delta(OCN^-)]$.[33] As the exposure time increases, this band steadily disappears and the bands corresponding to LDHs start to appear, but no resolution of this region is achieved even when the exposure time is prolonged to 300 min. However, a well-resolved spectrum containing merely the vibrational modes due to the brucite-like layers and the carbonate species is observed for the hydrothermally synthesized samples, from which the cyanate species are almost completely removed.

It should also be mentioned that the supernatant liquids of the samples whose FTIR spectra do not display the 2180 cm^{-1} band are blue, typical of $[Ni(NH_3)_6]^{2+}$ species. Kloprogge and co-workers[15] pointed out that upon hydrothermal treatment, the $(NH_2)COO^-$ species decomposes through reaction with interlayer water, resulting in the formation of CO_3^{2-} and NH_4^+; the strongly basic medium also gives rise to liberation of ammonia, which coordinates unprecipitated Ni^{2+} cations to form $[Ni(NH_3)_6]^{2+}$. In order to confirm that the blue color of the supernatant liquids was due to the presence of $[Ni(NH_3)_6]^{2+}$, the UV−vis spectrum of the supernatant liquid of the NAHT-150-24 sample was recorded (see Figure 2 in the Supporting Information). The spectrum shows two bands centered at 368 and 598 nm (27 170 and 16 720 cm^{-1}, respectively), which are ascribed to the $^3T_{2g} \leftarrow {}^3A_g$ (ν_3) and $^3T_{1g} \leftarrow {}^3A_g$ (ν_2) transitions, respectively, of Ni^{2+} cations in an octahedral environment.[34] The values calculated for the parameters Dq and B using the Dou equations[35] are 1045 and 836 cm^{-1}, respectively. The Dq value agrees with that reported for $[Ni(NH_3)_6]^{2+}$, so it can be concluded that upon hydrothermal treatment, nitrogen-containing species are removed as an ammonia complex.

3.1.3. Chemical Elemental Analyses. Elemental analysis data for metal cations in selected samples are summarized in Table 2, together with the chemical formulas for the compounds synthesized. In regard to the NAW-150 samples, the one synthesized in 10 min shows a slightly lower Ni^{2+}/Al^{3+} ratio than expected, probably because nickel precipitation was not completed in such a short period of time; nevertheless, the Ni^{2+}/Al^{3+} molar ratios are very close to that in the starting solutions for the solids obtained in short periods of time (30, 60, and 180 min), and a small release of Ni^{2+} cations is observed with increasing irradiation time (sample NAW-150-300). Increasing the temperature to 175 °C gives slightly smaller Ni^{2+}/Al^{3+} molar ratio values, suggesting decreased incorporation of Ni^{2+} cations into the lattice. For the conventional hydrothermally treated samples, a solid with a ratio of 1.85 is obtained in 5 h, and increasing the treatment time leads to a decrease in this value as well. The decrease observed in the Ni^{2+}/Al^{3+} molar ratio is in agreement with the smaller value of lattice parameter a. Therefore, a release of Ni^{2+} cations takes place under hydrothermal conditions, in agreement with the observed formation of $[Ni(NH_3)_6]^{2+}$ explained above.

The chemical analyses also show that the nitrogen content decreases with increasing aging time (microwave and hydrothermal) and temperature, becoming almost negligible for the NAHT-150-12 and NAHT-150-24 samples, as suggested by FT-IR spectroscopy.

3.1.4. Thermal Analyses. DTA curves for representative solids prepared by the microwave-assisted method at 150 and 175 °C and by the conventional hydrothermal treatment

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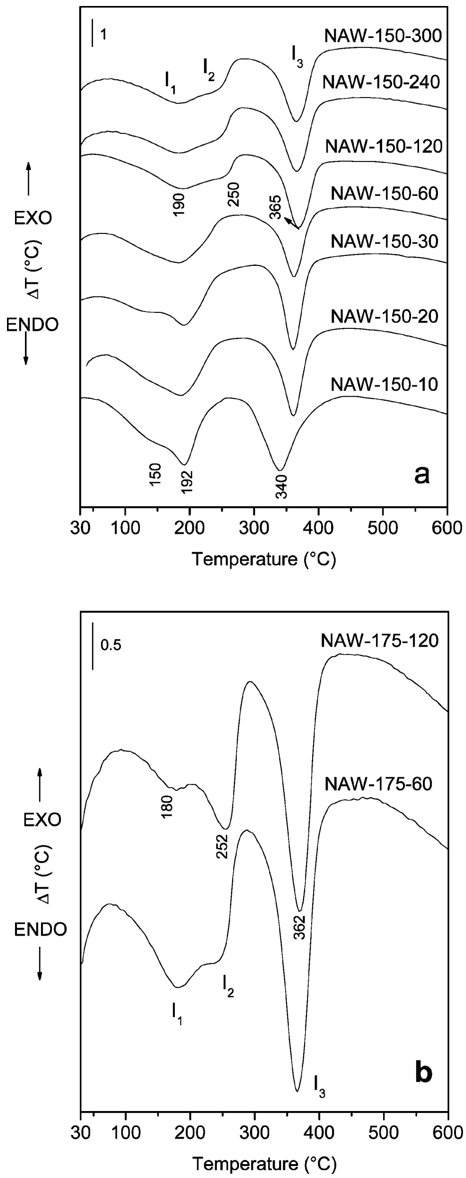

Figure 5. DTA curves for microwave-irradiated Ni−Al samples at (a) 150 and (b) 175 °C.

at 150 °C are shown in Figures 5a,b and 6, respectively. Changes in the shapes and positions of the effects are observed as both the time and the temperature of the treatment are increased.

In regard to the first endothermic effect, which is related to water release,[36] a broad peak I_1 displaying a low-temperature shoulder is observed for the samples aged for short periods of time at 150 °C (i.e., samples NAW-150-10, NAW-150-20, and NAW-150-30). As the microwave−hydrothermal treatment is prolonged, the shoulder disappears and the peak becomes broader and splits into two overlapped peaks (I_1 and I_2). No differences are found in the DTA profiles upon further exposure to the microwave field. Finally, in the sample treated for 120 min at 175 °C (NAW-175-120), the second peak (I_2) becomes more intense and shifts toward higher temperatures. The curves recorded for the samples submitted to conventional hydrothermal treatment (Figure 6) follow the same evolution as those for the microwave-assisted solids, but it should be noticed that sample NAHT-150-24 has a rather sharp I_2 peak with the I_1 peak appearing as a weak shoulder. The second endothermic effect (I_3) is due to structural collapse with simultaneous elimination of the interlamellar anions.[36] This feature is sharp and intense with a minimum at 365 °C for all of the solids, regardless of the treatment to which the samples are submitted, with the exception of compound NAW-150-10, where the minimum occurs at a lower temperature, and compounds NAHT-150-12 and NAHT-150-24, where it occurs at higher temperatures.

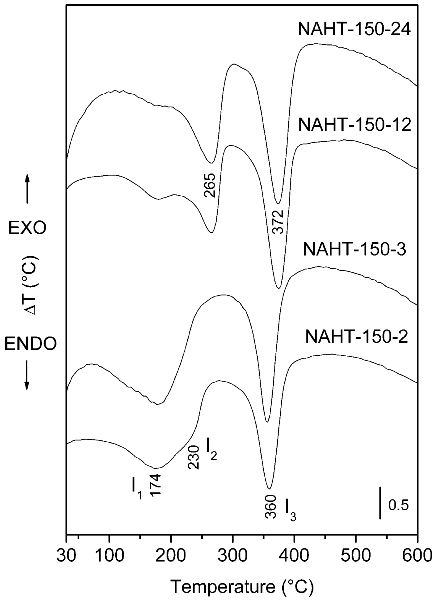

Figure 6. DTA curves for Ni−Al samples conventionally heated at 150 °C.

In the present work, the strength with which surface-adsorbed and interlayer water molecules (whose removal accounts for the first two endothermic effects) are held seems to depend on the synthesis time, while the lamellar stability is only slightly improved when the most drastic synthesis conditions [i.e., 175 °C for 2 h (NAW-150-120) or 150 °C for 12 h (NAHT-150-12)] are applied. However, the shift of the second endothermic peak toward higher temperatures observed for samples submitted to conventional treatment could be also attributed to the slight modification of the Ni/Al ratio.

3.1.5. N_2 Adsorption/Desorption at −196 °C. Regardless of the microwave irradiation time or temperature conditions used, the adsorption/desorption isotherms were type-IIb isotherms,[37] having nearly parallel adsorption and desorption branches in spite of the relatively low crystallinities of some of the samples. The hysteresis shape is related to the pore structure: the mesoporosity of LDHs arises from interparticle pores, since the nitrogen molecules are unable to enter

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(36) Rives, V. In *Layered Double Hydroxides: Present and Future*; Rives, V., Ed.; Nova Science Publishers: New York, 2001; Chapter 4, p 115.
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Table 3. Values of Specific Surface Areas (S_{BET}) and Pore Volumes (V_p) for the Microwave-Assisted and Hydrothermal Samples

sample	S_{BET} (m^2 g^{-1})	V_p (mm^3 g^{-1})
NAW-150-10	54	135
NAW-150-20	85	199
NAW-150-30	74	163
NAW-150-60	87	196
NAW-150-120	80	186
NAW-150-180	85	241
NAW-150-240	85	237
NAW-150-300	85	220
NAW-175-60	81	216
NAW-175-120	80	247
NAHT-150-2	34	84
NAHT-150-3	69	152
NAHT-150-5	73	183
NAHT-150-12	64	168
NAHT-150-24	56	84

the interlayer space. As the urea hydrolysis is supposed to give rise to uniformly sized particles, the particle−particle interactions, which in the end determine the pore structure, might be better defined, giving rise to a narrow hysteresis loop. The only differences are found for the samples obtained by conventional heating, for which broader hysteresis loops were recorded.

The values of the specific surface area (S_{BET}) are given in Table 3. An increase in S_{BET} is observed in going from sample NAW-150-10 to sample NAW-150-20.[38] However, in contrast to what would be expected, extending the irradiation time further does not modify the S_{BET} values during the treatment: a value of 85 m^2 g^{-1} is always observed. The almost constant S_{BET} values agree with the slight increase in the degree of crystallinity concluded from the PXRD patterns. Changes in the pore volumes (V_p) run parallel with changes in the specific surface areas. The samples prepared by the conventional hydrothermal method show similar textural properties; the initial surface-area development is observed on increasing the time from 2 to 3 h; however, a cancellation of the surface area is observed under conventional hydrothermal conditions as the treatment is prolonged.

3.1.6. SEM and TEM Images. Representative SEM and TEM micrographs are shown in Figures 7 and 8, respectively. The SEM micrograph, Figure 7, shows very small primary particles with disklike shapes and rather uniform sizes that adopt a sand-rose morphology upon aggregation.[39] Increasing the irradiation time and the temperature causes larger particles to form.

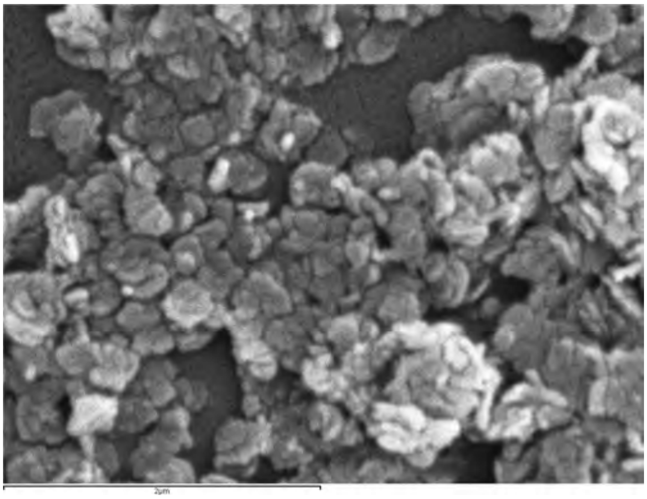

Figure 7. SEM micrograph of sample NAW-150-120.

The TEM images in Figure 8 show formation of very thin particles in some cases (e.g., NAW-150-180), and even at long irradiation times, small particles without a well-defined shape are obtained (not shown). However, the samples prepared by conventional hydrothermal treatment (e.g., NAHT-150-12) form larger particles. It should be noticed that the darkness of these hexagonal particles is not homogeneous, suggesting that some agglomeration takes place. These results agree with those recently reported by Okamoto et al.[13] for the formation of LDHs by the urea method; these authors observed imperfect particles beside the perfect hexagonal ones. They explained this behavior by assuming that formation of LDHs took place in circles around aluminum hydroxide seeds: if a circle became closed, hexagonal particles were observed, but if the growth was not complete, imperfect particles shaped as semihexagons or hexagonal platelets with a hole in the center were formed.

3.2. Zn−Al LDHs. It is well-known that the coprecipitation method usually followed to prepare various LDHs fails when Zn-containing solids are pursued if the precipitation parameters are not carefully controlled;[40] actually, the best method for preparing Zn-containing hydrotalcites is the so-called oxide-salt method.[41] Here we report several attempts to prepare Zn-containing hydrotalcites via the urea hydrolysis method using both conventional hydrothermal conditions and microwave irradiation.

PXRD patterns of the solids prepared at 150 °C by both microwave and conventional hydrothermal treatments (Figure 9) indicate that a pure hydrotalcite-like phase was not ever formed. Precise identification of the phases is very difficult because of the large number of diffraction lines recorded, but at least the following phases can be identified for sample ZAW-150-10 (i.e., the one formed after only 10 min of microwave irradiation): (i) hydrozincite and hydrozincite-like compounds [$Zn_5(CO_3)_2(OH)_6$ and $Zn_5Cl_2(OH)_6$, respectively], since both carbonate and chloride anions exist in the reaction mixture, the former as a product of urea hydrolysis and the latter as a constituent of the starting metallic salts; (ii) ZnO; (iii) several aluminum oxide phases, such as Al_2O_3, although the presence of an amorphous alumina phase not detectable by X-ray diffraction cannot be ruled out; and (iv) a Zn−Al hydrotalcite-type phase that produces a weak diffraction line. Increasing the irradiation time enhances all of the diffraction lines due to the hydrotalcite-like structure,

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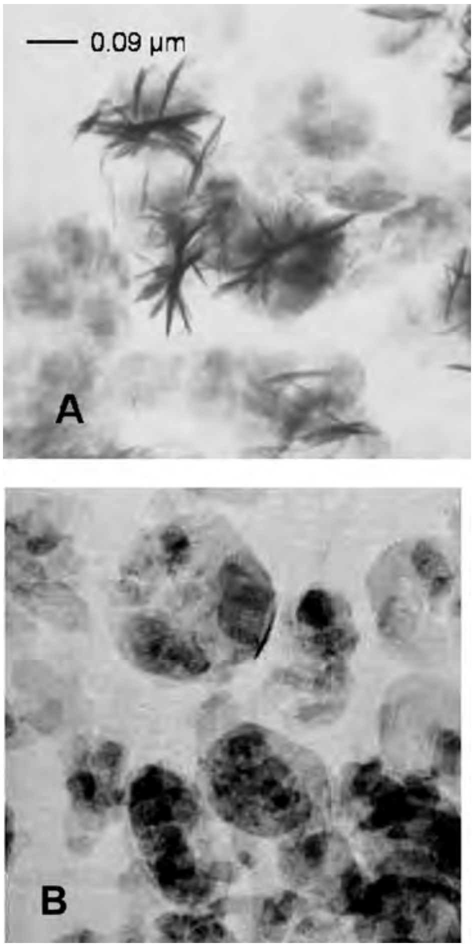

Figure 8. TEM micrographs of samples (A) NAW-150-180 and (B) NAHT-150-12 [with the same bar scale as in (A)].

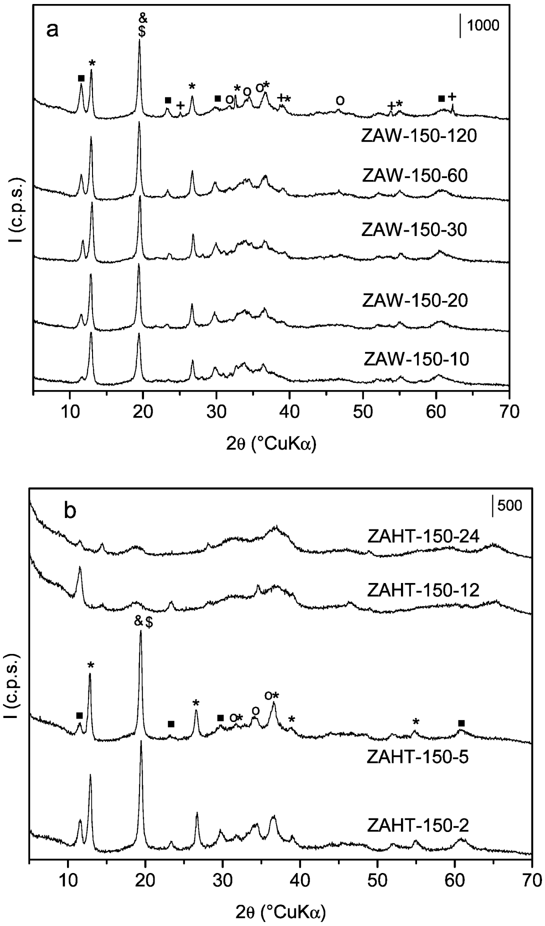

Figure 9. PXRD patterns of Zn−Al compounds prepared at 150 °C (a) in the microwave oven and (b) by the conventional process: (■) hydrotalcite, (*) hydrozincite, (+) $ZnCO_3$, (o) ZnO, (&) $Al(OH)_3$, ($) $Zn(OH)_2$.

but the side products are not completely removed. In an attempt to prepare pure Zn−Al compounds, the synthesis temperature in the microwave oven was decreased to 100 or 125 °C without success (see Figure 3 in the Supporting Information).

The same phases as those recorded for the microwave-assisted solids are observed when using the conventional hydrothermal synthesis (Figure 9b) for the compounds obtained after treatment for 2 and 5 h; however, when the synthesis time was prolonged to 12 h, the only intense diffraction line recorded was that corresponding to $d_{(003)}$ planes of the hydrotalcite phase. After 24 h of treatment, the structure is destroyed and only broad, poorly resolved diffraction peaks are observed. The same negative results were obtained when the microwave treatment was carried out at 100 or 125 °C.

4. Discussion

On the basis of the results reported here for the synthesis of Ni−Al LDHs, it can be stated that urea decomposition is greatly enhanced using microwave irradiation, under which the coprecipitation conditions for LDH formation are achieved in times that are similar to those for Mg−Al compounds and shorter than those for the conventional hydrothermal process and the ones reported previously for the syntheses performed under refluxing conditions.[7,21] This behavior must be related to the different sort of heating that initiates urea decomposition using the microwave-assited method rather than the conventional hydrothermal method and to the severe temperature and pressure conditions operating in hydrothermal treatments in comparison with the mild conditions under reflux. Very short treatment times in the conventional hydrothermal treatment are probably not enough to achieve the set temperature within the reactor, and temperature gradients are generated inside the autoclave bomb. The microwave radiation, which is directly transmitted to the solution inside the reactor (rather than to the container) and converted into heat, enables the established temperature to be achieved rapidly. It is well-known that the size of the particles prepared by the urea method depends on several factors, such as temperature, the concentrations of the metal salts, and the urea concentration. All of these factors affect the extent of supersaturation of the solution, which is responsible for the formation of nuclei that serve as precursors of the final particles. In our case, it can be assumed that microwave radiation increases the supersaturation within the whole volume of solution in the reaction vessel because of a rapid and homogeneous decomposition of the urea. This should lead to a decrease in the nucleation rate, yielding a higher number of nuclei and thus smaller particles. Consequently, increasing the irradiation time should lead to formation of larger particles with a lower free energy in the growing step.

However, despite the decrease in the precipitation time, no enhancement of the degree of crystallinity was achieved. Once the hydrotalcite phase appears, crystallization of Ni−Al compounds seems to be unaffected by the irradiation time, as no enhancement of the crystallization degree was achieved and no decrease in the S_{BET} values observed. However, hydrothermal treatment for longer periods of time (24 h) yielded a better-crystallized compound. Mavis and Akinc[42] observed that although the particles grow up to several micrometers, primary crystallites remain nanosized; they related this behavior to an agglomerative growth mechanism. Liu et al.[21] reported that hydrothermal treatment at 190 °C for 2 days was necessary to improve cystallinity, but these authors did not report an explanation for this behavior. In order to explain all of these features, the presence of some nitrogen-containing species (i.e., cyanate), as confirmed by elemental analyses and FT-IR spectroscopy, should be noted. Cyanate is an intermediate product of the decomposition of urea, and its concentration reaches a maximum during the first hours of heating in conventional urea hydrolysis.[42] However, in the synthesis reported here, this maximum can be reached in shorter times, so for the samples prepared at short periods of time and lower temperature (150 °C), cyanate ions together with some carbonate anions and water molecules are incorporated into the interlayer region to balance the excess positive charge. Thus, an interstratified compound is formed, with cyanate in a given interlayer and carbonate in the next one (although a precise model cannot be proposed). This interstratification destroys the periodicity along the *c* axis, so the crystallinity cannot be improved until cyanate anions are removed and a carbonate-containing phase is formed. Increasing the synthesis time (microwave or hydrothermal) and temperature causes an Ostwald ripening mechanism (dissolution/reprecipitation) to occur. During this process, release of cyanate species, which are replaced by carbonates because of their high affinities for LDHs, can take place. Cyanate species are then further hydrolyzed to NH_3 and CO_2, the former of which binds to Ni^{2+} cations from the layers to form $[Ni(NH_3)_6]^{2+}$ complexes, which are removed in the supernatant liquid as observed using UV−vis spectroscopy. Removal of these species is accompanied by an improvement in the crystallinity observed when the sample is aged under conventional hydrothermal treatment for 24 h, which leads to smaller, better-defined particles having lower specific surface areas.

On the other hand, concerning Zn−Al samples, Costantino et al.,[7] Yang et al.,[43] and Liu et al.[21] have reported the preparation of well-crystallized Zn−Al−CO_3 hydrotalcite by urea hydrolysis. Different sources of zinc cations were used: while Costantino et al. used ZnO dissolved in HCl, Yang et al. and Liu et al. employed nitrates and chlorides, respectively. Therefore, it would seem that the source of Zn(II) does not influence the nature of the final products. An important point is that in all these reports, urea was decomposed under refluxing, i.e., under milder conditions than in our case. However, preparation of well-crystallized solids was achieved under different conditions: Costantino et al. reported that a very good crystallized material was obtained after 48 h at 90 °C but only good crystallinity was observed when the synthesis conditions were 100 °C for 36 h, suggesting that the crystallinity decreased when the temperature increased; Liu et al. claimed that highly crystalline Zn−Al LDHs required shorter reaction times (1 instead of 2 days) in order to avoid formation of a layered hydroxycarbonate impurity through dissolution of initially formed LDH and reprecipitation of Zn^{2+} into another phase. Consequently, our lack of success should be mainly attributed to the severe hydrothermal conditions used, which might have affected several aspects of the preparation procedure. If the LDH structure was ever formed, it could have been destroyed during the hydrothermal treatment, with Zn^{2+} cations leading to ZnO segregation, which is easily produced under hydrothermal conditions.[44] On the other hand, crystallization of pseudoboehmite also could have taken place under such conditions. Titration curves of Zn−Al mixtures with NaOH in an aqueous medium reveal that the plateau corresponding to precipitation of a Zn/Al phase is poorly defined and close to those for precipitation of $Zn(OH)_2$ and $Al(OH)_3$.[30,45] When studying the synthesis of sol−gel Zn−Al LDHs, Tichit et al.[46] concluded that Zn^{2+} and Al^{3+} cations are more likely to be involved in the formation of pure hydroxides or oxides rather than a coprecipitated Zn−Al LDH structure when the synthesis is performed at high temperatures. Under these conditions, the kinetically stable product is formed. During synthesis by the sol−gel method, the pure hydroxides are preferentially formed, leading to a mixture of ZnO [formed by dehydration of $Zn(OH)_2$] and alumina. In the present work, the kinetics of urea decomposition is enhanced either by the microwave-assisted or the conventional hydrothermal synthesis, a fact that could account for the rapid formation of the kinetically favored products. Actually, when the treatment time is increased, the thermodynamically favored product, i.e., the Zn−Al layered double hydroxide, is formed in a small amount, but the nondesired side products remain in the final solid.

5. Conclusions

Ni−Al hydrotalcite-like compounds can be synthesized quickly using microwave-assisted urea decomposition. A pure hydrotalcite-type phase is obtained in very short periods of time; however, some CNO^- species were detected, and it was necessary to increase both the temperature and the irradiation time in order to remove them under these conditions. By this method, small particles having a filamentous shape are obtained in the first stages, and the shape

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becomes hexagonal in samples irradiated for long times; specific surface area values of 80 m^2 g^{-1} are obtained. On the other hand, when the urea decomposition was carried out under conventional hydrothermal conditions, the hydrotalcite-type structure is formed after longer reaction times, and larger particles with smaller specific surface areas are formed. Finally, no successful results were obtained from attempts to synthesize Zn−Al compounds, regardless of the hydrothermal treatment method (conventional or microwave-assisted).

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Supporting Information Available: PXRD patterns and UV−vis spectra for various samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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