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Characterization of Intercalated Ni/Al Hydrotalcites Prepared by the Partial Decomposition of Urea

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ABSTRACT: Layered double hydroxides containing Ni^{2+} and Al^{3+} have been synthesized by homogeneous precipitation through urea hydrolysis. The nature of the interlayer species changes according to the treatment of the samples, formation of interlayer $(\text{NH}_2)\text{COO}^-$ species being observed immediately after precipitation, which undergo transformation to carbonate after hydrothermal treatment. Simultaneously, liberation of ammonia during decomposition under hydrothermal conditions gives rise to formation of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ species in solution.

Introduction

The synthesis of inorganic layered compounds with the hydrotalcite-like structure (HTIs), also known as layered double hydroxides (LDHs), their structure, properties, and evolution with the calcination temperature have been widely studied in the literature in recent years. The structure of hydrotalcite consists of brucite-like $-\text{Mg}(\text{OH})_2-$ layers, where one-fourth of the Mg^{2+} cations have been substituted for Al^{3+} and the positive charge is balanced by carbonate anions which, together with water molecules, are located between the layers. The nature of the divalent and the trivalent cations can be changed in a wide range, as well as the nature of the interlayer anion.¹ These solids can be prepared by direct synthesis, i.e., precipitation of the mixed metal hydroxide in a solution containing the anion to be located in the interlayer, also by anion exchange, and by the so-called “reconstruction” method, consisting of suspending the solid obtained by mild calcinations of a LDH in a solution containing the anion to be intercalated. In recent years new methods of preparation for these kinds of materials have been developed^{1–3} in order to obtain solids with the desired crystallite size and an homogeneous particle size distribution, etc. Precipitation of the layered compounds from homogeneous solutions gives rise to the formation of hydrotalcite-like materials with a good crystallinity. The hydrolysis of urea in a solution containing the M^{2+} and M^{3+} salts and the interlayer desired anion leads to much better crystallized solids than those prepared by coprecipitation, especially for Ni–Al hydrotalcites.^{3,4} The effects of the temperature of precipitation, the total metal cations concentration, the $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ molar fraction, and the concentration of urea, etc., on the composition and on the crystallinity of the samples have been widely studied.^{4–6} Studies aimed to compare the urea hydrolysis method and the use of other precipitating agents, such as aqueous basic solutions (e.g., NaOH and Na_2CO_3 , etc.) on the nucleation, crystal growth, and particle size and shape have been also reported.^{7,8} From these studies, it can be concluded that urea hydrolysis is one of the few methods available to produce LDHs with a rather narrow particle size distribution. Yao et al. have prepared Mg–Al–

CO_3 hydrotalcites by urea hydrolysis to study the redox processes of adsorbed $[\text{Fe}(\text{CN})_6]^{3-}$ on the hydrotalcite crystal.⁹ Zn–Al hydrotalcites prepared by the urea method have been chosen as precursors to obtain materials in which the dye is exchanged only on the surface of the microcrystals or is also incorporated into the interlayer region.¹⁰ Several catalytic reactions, such as the reduction of α,β -unsaturated aldehydes, the Knoevenagel condensation, or the oxidative methanol reforming reactions, have been tested by using LDHs prepared by urea hydrolysis.^{11–13} Recently, Mavis and Akinc have tested the stability and electrochemical performance of three-component LDHs with varying composition, produced by urea hydrolysis.¹⁴ However, despite these and other studies in the literature using this synthesis route, few studies have been dedicated to follow the changes in the samples along the synthesis steps, as usually the interest of the authors has been mostly addressed to the properties of the final solid. We here report the synthesis of two hydrotalcite-like compounds containing Ni^{2+} and Al^{3+} by the partial decomposition of urea and the effect of the hydrothermal treatment. Although this is not the first report on the synthesis of this particular LDH, we pay special attention to the nature of the intermediate species during the synthesis, i.e., before total hydrolysis of urea has taken place. A full characterization of the two solids obtained (with and without hydrothermal treatment) has been also carried out. The more remarkable differences as well as the processes involved in the formation of the hydrotalcite by this synthesis method have been thoroughly studied, mainly by infrared and Raman spectroscopic measurements.

Experimental Section

Synthesis. A solution containing 25.52 g (0.43 mol) of urea in 250 mL of bidistilled, decarbonated water was prepared. A 19.78 g (0.083 mol) amount of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 10.02 g (0.041 mol) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the solution. The pH of the resulting solution was 2.90.

The solution was heated under reflux at 100 °C for 25 h. After 5 h heating, turbidity appeared. The pH of the light green solution after this treatment was 7.6.

The solid formed was separated by centrifugation and divided in two portions. One portion (NiAl-HT) was submitted to hydrothermal treatment in a Teflon lined stainless steel bomb for 4 days at 130 °C. A second portion (NiAl-in) was washed with decarbonated water and dried at room temperature in a vacuum desiccator. After the hydrothermal treatment the pH of the solution had increased to 9.4. The solid

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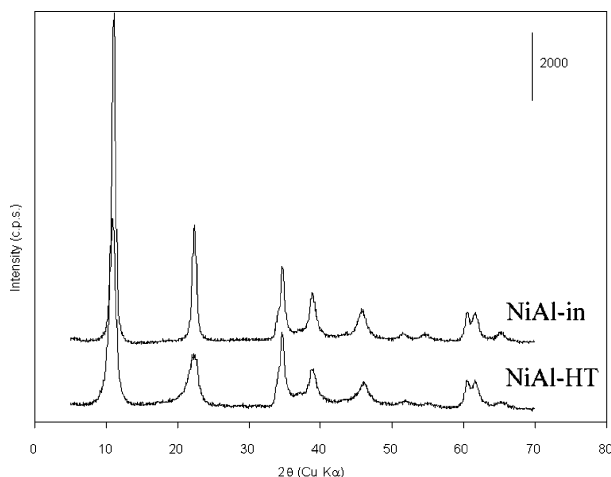


Figure 1. Powder X-ray diffraction diagrams of the NiAl layered double hydroxide before (NiAl-in) and after (NiAl-HT) hydrothermal treatment. The diagrams have been vertically displaced for clarity.

Table 1. Elemental Composition of NiAl-in and NiAl-HT Samples

	wt %			molar ratio	
	NiAl-in	NiAl-HT		NiAl-in	NiAl-HT
Ni	34.82	34.11	Ni/Al	2.31	2.02
Al	6.94	7.76	N/C	0.81	0.008
C	0.90	2.20			
N	0.85	0.02			

obtained was washed with decarbonated water, and the washing liquid had a light blue color.

Analytical Procedures. (a) Element Chemical Analysis. Element chemical analyses for Ni and Al were carried out by atomic absorption in a Mark-2 ELL-240 apparatus at Servicio General de Análisis Químico Aplicado (University of Salamanca, Spain) after dissolution of the samples in nitric acid aqueous solutions. The C and N contents were determined in a element analyzer from Leco, model CHNS-932.

(b) Powder X-ray Diffraction. The powder X-ray diffraction (PXRD) patterns were recorded using Cu K α radiation ($\lambda = 1.5405$ Å) in a Siemens D-500 diffractometer with a DACO-MP microprocessor. Diffractograms were evaluated by means of Diffract-AT software. The scan step was 0.05° (2θ) and collecting time 1.5 s, with a filament intensity of 30 mA and a voltage of 40 kV. The crystalline phases existing in the samples were identified by comparison with data in the Joint Committee for Powder Diffraction Standards database.

(c) Thermal Analyses. Differential thermal analyses (DTA) and thermogravimetric (TG) analyses for thermal stability were carried out in DTA-7 and TG-7 instruments from Perkin-Elmer, respectively. The analyses were carried out under oxygen gas flow (ca. 30 mL min^{-1} , from L'Air Liquide, Spain) atmosphere at a heating rate of $10^\circ \text{C min}^{-1}$.

(d) Mid-infrared Spectroscopy. The samples were finely ground for 1 min, combined with oven-dried spectroscopic grade KBr (containing approximately 1 wt % sample) and pressed into a disk under vacuum. The transmittance spectrum of the sample was recorded in triplicate by accumulating 512 scans at 4 cm^{-1} resolution between 400 and 4000 cm^{-1} using the Perkin-Elmer 1600 series Fourier transform mid-infrared spectrometer equipped with a LITA detector.

(e) Raman Spectroscopy. The samples were placed on a polished metal surface on the stage of an Olympus BHS microscope, which is equipped with $10\times$, $20\times$, and $50\times$ objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system, and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a resolution of 2 cm^{-1} and a precision of $\pm 1 \text{ cm}^{-1}$ in the range between 200 and 4000 cm^{-1} . Repeated acquisition on the crystals using the highest magnification ($50\times$) were accumulated to improve the signal-to-noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

(f) Spectral Manipulations. Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spec-

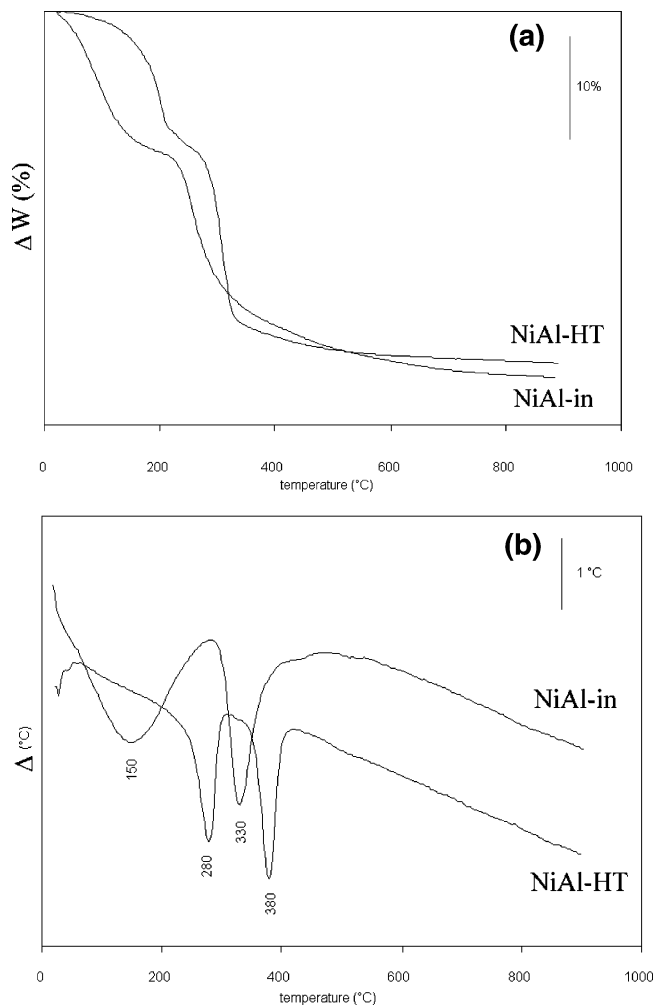


Figure 2. Thermogravimetric (a) and differential thermal (b) analyses of the NiAl layered double hydroxide before (NiAl-in) and after (NiAl-HT) hydrothermal treatment.

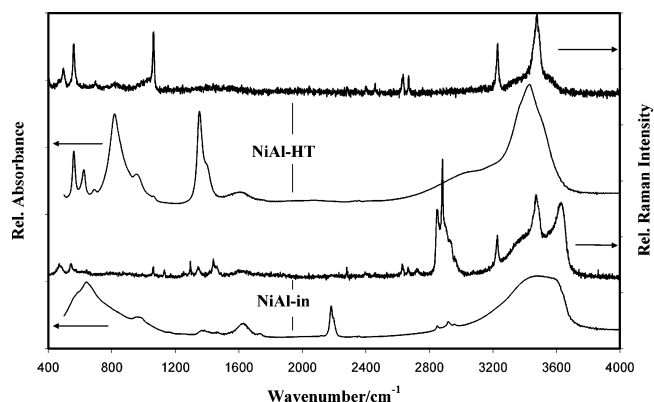


Figure 3. Infrared and Raman spectra in the region between 400 and 4000 cm^{-1} of the NiAl layered double hydroxide before (NiAl-in) and after (NiAl-HT) hydrothermal treatment.

tracalc software package GRAMS (Galactic Industries Corp., NH). Band component analysis was undertaken using the Jandel "Peakfit" software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7, and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

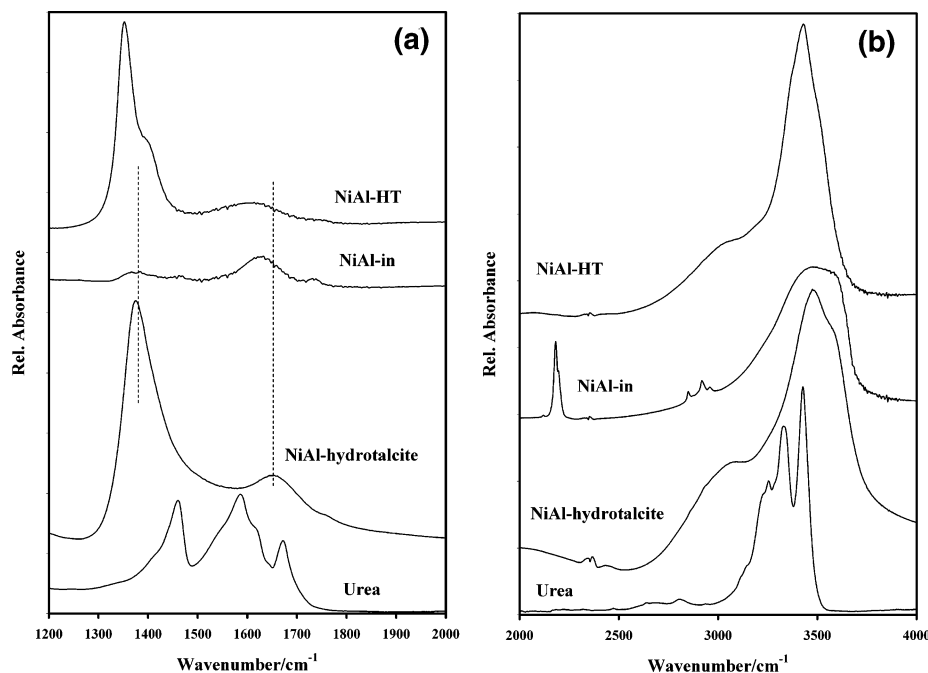


Figure 4. Infrared spectra (a) in the region between 1200 and 2000 cm^{-1} and (b) in the region between 2000 and 4000 cm^{-1} of the Ni/Al layered double hydroxide before (NiAl-in) and after (NiAl-HT) hydrothermal treatment in comparison to pure Ni/Al hydrotalcite and urea.

Results and Discussion

Powder X-ray diffraction patterns of the solids obtained indicate after drying and after hydrothermal treatment a hydrotalcite-like structure has been formed (Figure 1). For sample NiAl-in, the basal reflections are recorded at 7.98 (003), 3.98 (006), and 2.59 Å (009), respectively, which corresponds to a lattice parameter “*c*” of 23.93 Å, while the (110) reflection is recorded at 1.528 Å, thus indicating a lattice parameter “*a*” of 3.056 Å. For the hydrothermally treated sample NiAl-HT the basal reflections are recorded at 8.11, 3.94, and 2.59 Å (*c* = 24.33 Å), while the diffraction due to planes (110) is recorded at 1.530 Å (*a* = 3.06 Å). The element chemical analysis indicates that the Ni/Al molar ratio is close to 2.0, as in the original solution (Table 1). The hydrothermal treatment results in a relative increase in carbon content and a strong decrease in the N/C ratio from 0.81 to 0.008, which indicates a change in the hydrotalcite interlayer composition.

The thermal behavior of the two hydrotalcite samples has been studied by thermogravimetric and differential thermal analysis (Figure 2). Sample NiAl-in shows a rapid weight loss of approximately 15% during heating to 150 °C, which is accompanied by a broad endothermic effect in the DTA curve at the same temperature. A second weight loss of approximately 20% is observed above 200 °C. This step corresponds with a much sharper endothermic effect in the DTA at 300 °C. In contrast, the hydrothermally treated sample NiAl-HT shows increased thermal stability, with the first weight loss now observed between 150 and 200 °C, while the second weight loss step is now not only at a higher temperature but also in a narrower temperature range between 200 and 350 °C. The corresponding DTA pattern shows two sharp endothermic maxima at 280 and 380 °C.

It is well-known that upon heating, dissolved urea $\text{CO}(\text{NH}_2)_2$ decomposes under the liberation of hydroxyl ions, which can be used to promote the hydrolysis of metal ions and the formation of metal (oxo-)hydroxides or, as in this study, layered double hydroxides. The N/C ratio of 2 for urea has decreased to a value close to 1 in the hydrotalcite (actually 0.81, but some

carbonate will be present adsorbed on the surface, thereby decreasing the measured N/C ratio) and to almost 0 in the hydrothermally treated hydrotalcite. This may be an indication of the intercalation of a “ $\text{CO}(\text{NH}_2)$ ” anion in the hydrotalcite, while one NH_2 group is lost during the hydrolysis reaction. The hydrothermal treatment then can convert the complex anion into a carbonate anion.

To get a better understanding of the processes involved in the formation of the hydrotalcite upon the decomposition of urea and the following hydrothermal treatment, infrared and Raman spectra have been obtained (Figures 3–5). For comparative reasons also the corresponding infrared and Raman spectra of pure urea and Ni/Al hydrotalcite have been included in this study (Figure 4).

The vibrational spectra of urea in gas, liquid, and solid form are well-known.^{15–17} In the solid-state urea is a planar molecule with C_{2v} symmetry. The infrared and Raman spectra of solid urea are characterized by a C=O stretching mode (A_1), symmetric and antisymmetric NCN stretching modes (A_1 and B_2), a NCN bending mode (A_1), and a NCO bending mode (B_2). In addition, a CN_2 out-of-plane wagging mode (B_1) and twelve modes involving hydrogen atoms, including two symmetric (A_1 and B_2) modes and two antisymmetric stretching modes (A_1 and B_2), two HNH bending modes (A_1 and B_2), and in-plane and out-of-plane NH_2 wagging and twisting modes ($2A_2$ and $2B_1$). In an earlier work,¹⁸ the Raman spectrum of urea showed the NH_2 stretching modes at 3242, 3323, 3357, and 3435 cm^{-1} , which is very close to the infrared bands shown in Figure 3 at 3255, a broad band at 3330, and at 3427 cm^{-1} . The corresponding C=O bands were observed in the Raman spectra around 1649 and 1581 cm^{-1} (hydrogen-bonded), the NCO band at 1047 cm^{-1} , and the NCN band at 1012 cm^{-1} . In this study the infrared spectrum shows similar bands at 1672 cm^{-1} and an overlapping complex of three bands around 1587, 1461, 1411, 1146, 1050, and 1005 cm^{-1} .

NiAl-in shows in the infrared spectrum in the OH-stretching region a broad band around 3480 cm^{-1} accompanied by minor bands around 2957, 2922, and 2850 cm^{-1} plus a strong set of

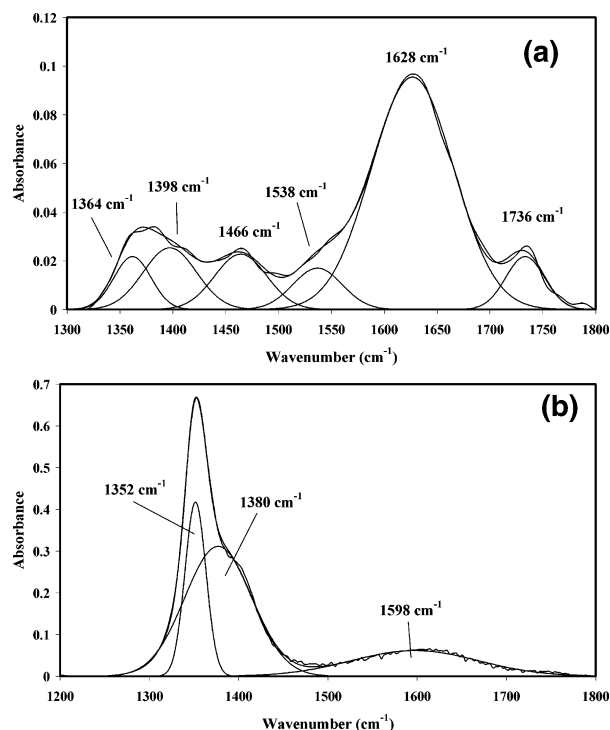
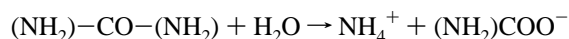


Figure 5. Band component analysis of (a) the region between 1300 and 1800 cm^{-1} of the Ni,Al layered double hydroxide before (NiAl-in) and (b) the region between 1200 and 1800 cm^{-1} after (NiAl-HT) hydrothermal treatment.

bands at 2182 and 2196 cm^{-1} . The corresponding Raman spectrum is more informative with strong bands at 3629, 3471, and 3228 cm^{-1} superimposed on a very broad band centered around 3480 cm^{-1} . The weak bands observed in the infrared spectrum have much stronger equivalents in the Raman spectrum at 2960, 2932, 2883, and 2850 cm^{-1} . The infrared bands around 2185 cm^{-1} are absent in the Raman spectrum. A small band is observed at 1718 cm^{-1} just next to the water bending vibration at 1615 cm^{-1} . None of these strong bands observed in the infrared and Raman spectra can be associated with urea.

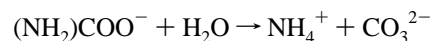
The chemical analysis indicated the presence of a nitrogen-containing compound in the interlayer of the hydrotalcite. Infrared and Raman bands in the region around 2900 cm^{-1} are in general characteristic for C–H and N–H bands, while the region around 2000–2200 cm^{-1} is characteristic for NH twisting vibrations in NH_2 or NH_3 groups. The region around 1680–1740 cm^{-1} can be ascribed to C=O vibrations due to the fact that NH_2 is one of the strongest resonance-electron donor groups causing the shift toward lower frequency.¹⁹ On the basis of the observation of bands associated with both NH vibrations and C=O vibrations, the following reaction is thought to occur during the synthesis:



During this reaction the anion $(\text{NH}_2)\text{COO}^-$ has been incorporated into the hydrotalcite structure in the interlayer instead of carbonate.

Hydrothermal treatment of the intercalated hydrotalcite results in the decomposition of the interlayer $(\text{NH}_2)\text{COO}^-$ through reaction with interlayer water, resulting in the formation of

CO_3^{2-} and NH_4^+ , after which the ammonia escapes to the solution:



This change can be observed in the infrared and Raman spectra where the bands associated with NH vibrations have disappeared (Figures 3 and 4) and instead the normal spectra of CO_3^{2-} hydrotalcite is exhibited. The distinct carbonate bands in the infrared spectrum at 1348 and 1386 cm^{-1} are easily recognized together with a sharp band at 1060 cm^{-1} in the Raman spectrum.²⁰ The strong basic medium also gives rise to liberation of ammonia, which coordinates unprecipitated Ni^{2+} cations, forming $[\text{Ni}(\text{NH}_3)_6]^{2+}$ species, identified by its typical light blue color in the supernatant solution.

Conclusions

Homogeneous precipitation of Ni,Al layered double hydroxide by urea hydrolysis does not lead in a first step to formation of the carbonate-intercalated material, but this material is only formed after hydrothermal treatment, through decomposition of the intermediate interlayer species $(\text{NH}_2)\text{COO}^-$, which presence has been undoubtedly identified by vibrational spectroscopy.

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