

Thermal Evolution of Carbonate Pillared Layered Hydroxides with (Ni, L) (L = Fe, Co) Based Slabs: Grafting or Nongrafting of Carbonate Anions?

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The thermal evolution, from room temperature up to 300 °C, of layered double hydroxides (LDHs) with (Ni, Co) or (Ni, Fe) based slabs and containing intercalated carbonate anions, was studied. A new lamellar phase, exhibiting a 6.5–6.6 Å interslab distance, was observed in the 200–260 °C temperature range. The infrared study and the chemical analysis results allowed us to give prominence to a monografting of carbonate anions to the slabs. The thermogravimetric studies seem to indicate that intercalated water is first lost, followed by a monografting of carbonate anions. A stay in water of the 200 °C thermally treated phase leads to a reintercalation of water molecules. The interslab distance indeed reincreases up to the value of the pristine material, reinforcing the hypothesis of the monografting.

Introduction

Layered double hydroxides (LDHs) constitute a large class of minerals and synthetic materials whose general formula is $[M^{II}_{1-y}L^{III}_y(OH)_2]^{y+}X_{y/p}^{p-}[H_2O]_z$. Their structure is based on stacked brucite-type $M^{II}_{1-y}L^{III}_y(OH)_2$ slabs, where L^{III} cations are partially substituted for M^{II} ones. Such substitution induces an excess of positive charge, which is balanced by X^{p-} anions, intercalated in the interslab space. Water molecules are also cointercalated in the interslab space and participate in stabilizing the structure through their involvement in a hydrogen bond network.^{1,2}

Direct synthesis of LDHs can be carried out by various methods, as coprecipitation or hydrothermal synthesis.³ The $L^{III}/(M^{II} + L^{III})$ ratio is strongly dependent on the final compound stability. An original preparation method, involving the slab formation at high temperature, followed by several chimie douce reaction steps, was developed in our lab a few years ago.^{4–6} This method consists of decoupling

the formation of the $M_{1-y}L_yO_2$ slabs from the anion intercalation itself. The inserted anion amount is thus directly related to the anion negative charge and to the L trivalent cation concentration within the slabs, which is fixed during the slab building. Nevertheless, this method implies the presence of 3d cations with various oxidation states and the existence of the high-temperature stable starting layered oxide.

LDHs containing intercalated $M_2O_7^{2-}$ (M = Mo, W) oxomolybdate or oxotungstate anions, made of two corner-sharing MO_4 tetrahedra, were very recently obtained in our laboratory by the previously described method.⁷ The thermal study of these materials has given prominence to a grafting of the oxoanions to the slabs, via the substitution of one oxygen atom of each tetrahedron for hydroxyls belonging to two consecutive slabs.⁸ Such behavior was also observed by Besse and colleagues for LDHs containing intercalated CrO_4^{2-} and $Cr_2O_7^{2-}$ entities.^{9–12} Moreover, the thermal

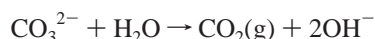
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decomposition of these materials is significantly delayed with regard to that of homologous carbonate-inserted phases, which may be due to the presence of the large bigrafted oxometalate pillars in the former materials. In order to further understand the thermal behavior of carbonate-inserted LDHs, an accurate study of the thermal decomposition mechanism of LDHs with (Ni, Fe) and (Ni, Co) based slabs and containing intercalated carbonate anions was undertaken in the present work.

In spite of numerous recent studies, controversies exist concerning the grafting or nongrafting phenomenon of the carbonate anions to the slabs. This behavior seems to be very difficult to elucidate, and the authors propose very different hypotheses. According to Kanezaki, from room temperature to 200 °C, the layered structure, with a 7.8 Å basal spacing, is stable.^{13–15} Between 200 and 400 °C, a metastable phase, with a 6.6 Å basal spacing, is observed. This phase would also be a layered material, containing interlayer hydroxyl groups, coming from the reaction between the carbonate anions and the water molecules of the interslab space, following the equation



According to Rives, this hypothesis is not acceptable on the basis of anion size considerations:¹⁶ the sterical hindrances of one hydroxyl group and of one carbonate anion, parallel to the slabs, are identical within the interslab space, and should therefore lead to similar interslab distances for both LDHs intercalated either with OH⁻ ions or with CO₃²⁻ ions. That is the reason why Rives suggests another mechanism: the carbonate anions would react with some hydroxyl groups of the slabs, which are converted into oxide ions, according to the following reaction.



Some hydroxyl groups from the layers would thus be converted to oxide ions, and the carbon dioxide, formed within the interslab space, would be eliminated. The existence of this O²⁻ anion in the presence of the hydroxyl groups of the slabs is then questionable. Some other authors suggest that the decrease of the basal spacing from 7.8 to 6.6 Å could be explained by a bigrafting of the carbonate anions to the slabs.^{17–20} The grafting of the carbonate anions would be achieved via the substitution of two oxygen atoms of the

CO₃²⁻ ion, for two slab hydroxyl groups, which can belong to the same slab or to two adjacent ones, depending on the authors. Stanimirova and co-workers claim indeed that the carbonate anion is bilinked to the same slab via two first neighbor oxygen atoms. Such a configuration is not reasonable because the shortest O–O distance within the slab, higher than 3 Å in any case, is not compatible with the sterical characteristics of the CO₂ group: to our knowledge, the O–O distance in the free carbonate entity is equal to 2.20 Å (calculated on the basis of a C–O distance of 1.27 Å and an O–C–O angle of 120°).²¹ The distances which can be expected for the grafted entity would range from 2.08 Å (calculated on the basis of a C–O distance of 1.27 Å and an angle of 110°, as in COCl₂) to 2.30 Å (calculated on the basis of a C–O distance of 1.27 Å and an angle of 130°, as in R–COO– carboxylic acids).²¹ These values of 110° and 130° correspond to the minimum and maximum values of the angle formed with the carbon, in different compounds.

The present work aimed therefore at clarifying the structural evolution of interlamellar carbonate ions during a thermal treatment of carbonate-inserted LDHs, from in situ and ex situ X-ray diffraction results, infrared spectroscopy, chemical analysis, and thermogravimetric analysis coupled with mass spectrometry.

Experimental Section

Preparation of LDH_{Ni,Fe}(CO₃) and LDH_{Ni,Co}(CO₃). The preparation of these materials was performed by chimie douce reactions, as previously described in detail.⁴ First, the NaNi_{0.70}L_{0.30}O₂ (L = Fe, Co) sodium nickelate was prepared via a high-temperature solid state reaction and was then hydrolyzed in an oxidizing medium (5 M KOH + 0.8 M NaClO), in order to obtain the γ-oxyhydroxide phase. One gram of this material was then dispersed in suspension into a solution containing 4 g of Na₂CO₃ in 500 mL of distilled water. The reduction was carried out by adding 50 mL of 5 M H₂O₂ to this solution. After 24 h of stirring, the obtained LDHs were filtered, washed, and dried at 40 °C.

In order to investigate a potential grafting of the carbonate ions to the slabs after a thermal treatment, the LDH_{Ni,Co}(CO₃) phase was treated at 200 °C under an oxygen flow, for 16 h, and a rehydration reaction of the obtained material in distilled water during 24 h was attempted.

Characterization Techniques. X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer (Cu Kα), with a scan step of 0.04° (2θ) for 15 s.

In situ XRD measurements were carried out in the 30–300 °C temperature range for both LDH_{Ni,Fe}(CO₃) and LDH_{Ni,Co}(CO₃), by using an INEL X-ray diffractometer equipped with a cobalt anticathode, a forward monochromator, a CPS 120 curved sensitive detector, and a high-temperature FURCAP furnace, with the following conditions of sequential temperature increase (2 °C/min) and of temperature holding time (10 min) before each 1 h measurement.

The FTIR spectra were obtained by using a Perkin-Elmer Spectrum One spectrophotometer equipped with a diffuse reflectance sphere. The materials were dispersed and gently ground in KBr powder, placed in the diffuse reflectance sphere, and analyzed.

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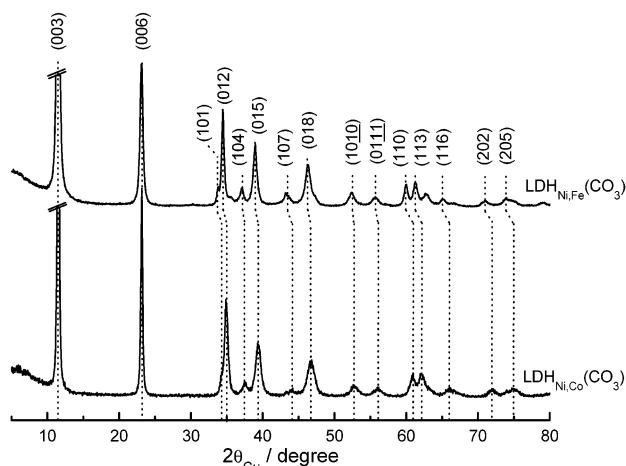


Figure 1. XRD patterns of the $\text{LDH}_{\text{Ni,L}}(\text{CO}_3)$ materials (L = Fe, Co).

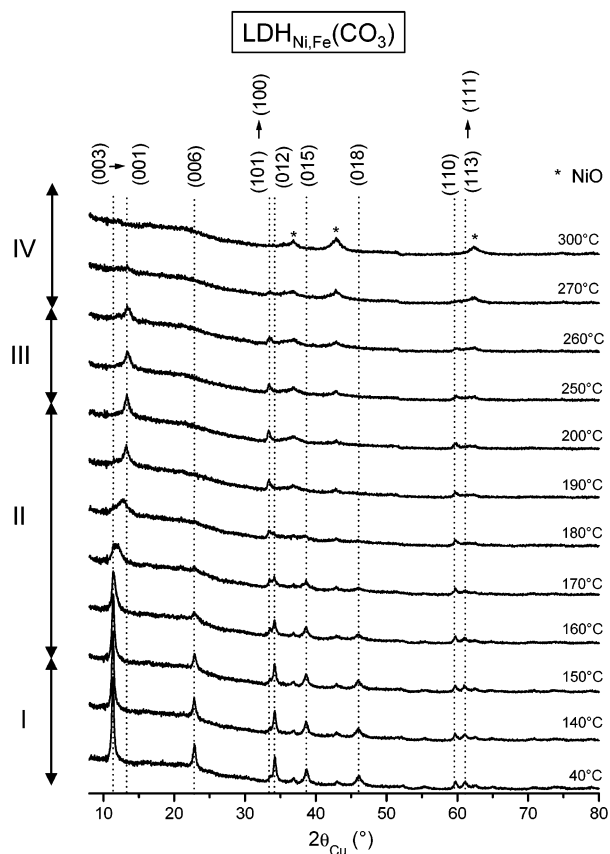


Figure 2. In situ XRD patterns showing the decomposition of $\text{LDH}_{\text{Ni,Fe}}(\text{CO}_3)$ in the 30–300 °C temperature range.

The thermogravimetric analysis (TGA), coupled with mass spectrometry, was performed at a rate of +3 °C/min, from room temperature to 800 °C under an oxygen flow.

Chemical analyses were performed by inductively coupled plasma (ICP) emission spectroscopy for Ni, and Co, and by elementary organic microanalysis for C and H, at the CNRS facility in Vernaison. The oxygen amount was not experimentally determined. For establishing the chemical formula, it was calculated by difference from 100%.

Results and Discussion

Structural Study of Starting Materials. The XRD patterns of the $\text{LDH}_{\text{Ni,Fe}}(\text{CO}_3)$ and $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$ phases are

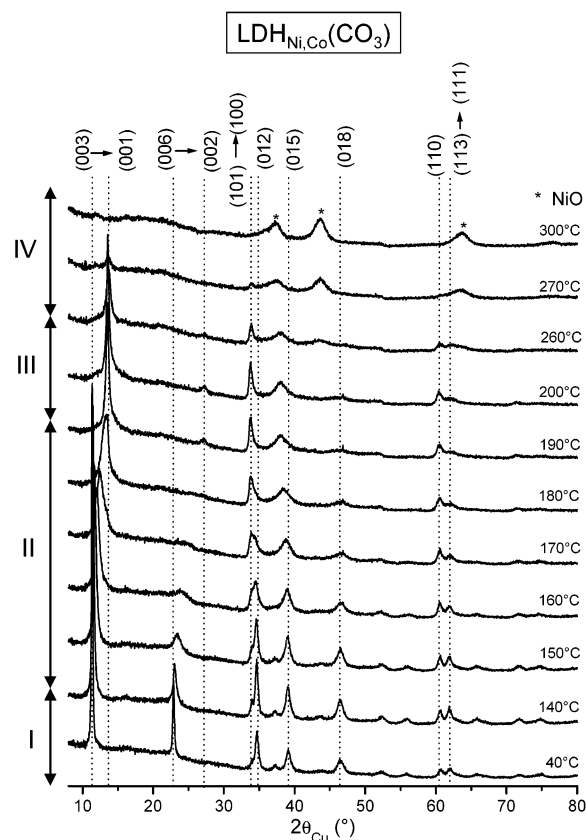


Figure 3. In situ XRD patterns showing the decomposition of $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$ in the 30–300 °C temperature range.

presented in Figure 1. These phases crystallize in the trigonal system (S.G.: $R3m$), with a P3 slab oxygen packing (AB BC CA). Indexation of their XRD patterns can be performed with a hexagonal cell, with three slabs per cell. The hexagonal parameters ($a = 3.08 \text{ \AA}$ and $c = 23.08 \text{ \AA}$ for $\text{LDH}_{\text{Ni,Fe}}(\text{CO}_3)$, $a = 3.04 \text{ \AA}$ and $c = 23.04 \text{ \AA}$ for $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$) are in agreement with those already reported in the literature.^{22,23}

In Situ Dynamical XRD Study of the Thermal Evolution. A general view of the in situ XRD patterns of $\text{LDH}_{\text{Ni,Fe}}(\text{CO}_3)$ and $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$ in the whole temperature range is shown in Figure 2 and Figure 3, respectively. For both materials, experiments were performed for a large number of temperatures. Only few of them, corresponding to the strong changes in the XRD patterns, are reported in Figures 2 and 3. In each case, four temperature domains can be distinguished, as indicated in the figures.

The thermal evolution of the interreticular distance of the first (00 l) line, which reflects the interslab distance, is represented in Figure 4, where the above-defined temperature domains have also been reported.

In the first domain, the successive XRD patterns do not exhibit any strong change, especially concerning the line positions. Nevertheless, a progressive decrease of the intensity ratio of the (006) line to the (003) one can be observed.

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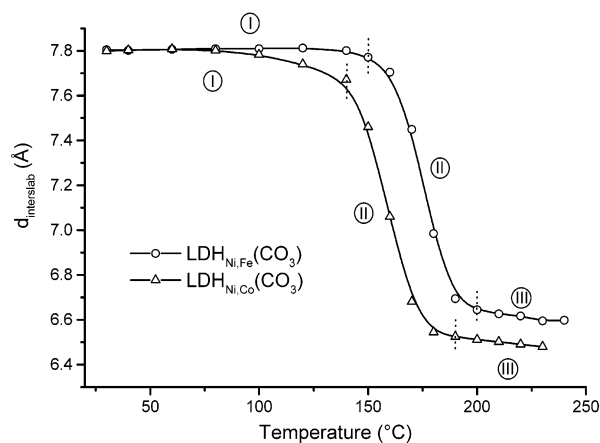


Figure 4. Evolution of the interlamellar distance of the decomposition product of the LDH_{Ni,L}(CO₃) materials (L = Fe, Co) as a function of the calcination temperature.

This behavior can be correlated with the beginning of the interlamellar water extraction. Indeed, a simple simulation of the XRD patterns of a phase, based on NiO₂ slabs and containing oxygen atoms located in the center of the interslab space, was performed; when the amount of interslab oxygen atoms is continuously lowered, from 1 down to 0 oxygen per slab metal ion, a progressive significant decrease of the intensity ratio of the (006) line to the (003) one is observed. The value of 1 oxygen atom per metal corresponds approximately to the starting LDH while the value of 0.3 is reached after removing the overall interlamellar water.

As emphasized by the evolution of the XRD patterns (Figures 2 and 3) and of the interslab distance in Figure 4, the second domain is characterized by a strong modification of the shape and positions of the (00*l*) lines. The (00*l*) lines are shifted to higher angle values, and the interlamellar distance of the material obtained at the end of domain II is close to 6.5 Å in the case of LDH_{Ni,Co}(CO₃) and to 6.6 Å in the case of LDH_{Ni,Fe}(CO₃). Similar behavior was already reported by several authors for LDHs with (Mg, Al) slabs.^{13–15,19} The intensity ratio of the (002*l*) line to the (00*l*) one strongly decreases, which can be attributed to the departure of the remaining overall interlamellar water molecules and a possible grafting of the carbonate anions to the slabs, as suggested in the literature.^{17–20}

In the third domain, the material formed at the end of the previous domain seems to be quite stable, as indicated by the absence of any drastic line modification.

In the fourth domain, the diffraction lines vanish, and only three broad peaks, corresponding to a NiO-type oxide, are finally observed. No iron or cobalt oxide is detected, so that the formula of this oxide may be (Ni_{1-x}L_x)_{2/(2+x)}O (L = Fe³⁺, Co³⁺). The oxides, which are formed in the 300–500 °C temperature range, are poorly crystallized, in agreement with the results reported in the literature.²⁴ The layered structure is completely destroyed at 270 °C for LDH_{Ni,Fe}(CO₃) and at 280 °C for LDH_{Ni,Co}(CO₃).

The structure of the material formed at the end of domain II, around 200 °C, and which is stable all along domain III,

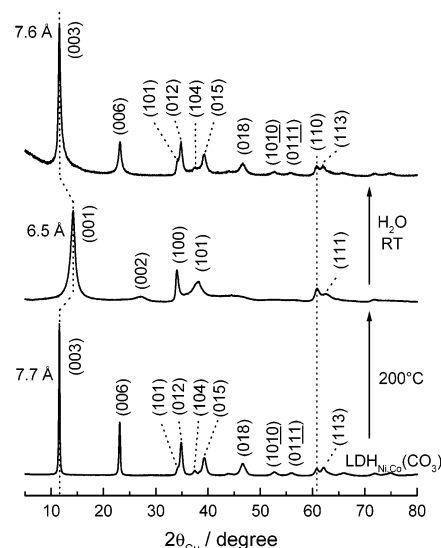


Figure 5. XRD patterns of LDH_{Ni,Co}(CO₃), after a thermal treatment at 200 °C and after rehydration of the lattice.

will now be investigated in detail in the case of LDH_{Ni,Co}(CO₃). The in situ dynamical XRD study, previously presented, as well as the TGA results, which will be detailed later, suggest indeed a similar behavior for LDH_{Ni,Fe}(CO₃).

Study of the Material Obtained after a Thermal Treatment at 200 °C of LDH_{Ni,Co}(CO₃). (a) XRD Study. The evolution of the XRD patterns after a thermal treatment at 200 °C and attempted rehydration in water is represented in Figure 5.

After a thermal treatment at 200 °C in air, the new phase is a layered structure. Only four strong diffraction peaks, broader than in the starting material, are observed. The line that is located around 35° (2θ_{Cu}) for the heated material can no longer be indexed as (101) or (012). This line must be indexed as (100) for the heated material. Therefore, the rhombohedral symmetry (three slabs per unit cell) disappears, leading to a hexagonal symmetry (one slab per unit cell). This change in symmetry shows that the (AB BC CA) oxygen packing of the starting material changes upon heating to the (AB AB) one. Therefore, a slab gliding has occurred. In spite of a slight modification in the shape of the doublet close to 60° (2θ_{Cu}), the position of the (110) line is unchanged, which shows that the metal–metal distance within the metal oxide slab is maintained after thermal treatment. In addition the displacement of the first two diffraction peaks at low angle value indicates a significant decrease of the interslab distance, from 7.7 Å in the starting material down to 6.5 Å after treatment at 200 °C. Moreover, the intensity ratio of the (002) line to the (001) line is strongly lowered with regard to the ratio of the (006) line to the (003) one in the starting material, in agreement with the in situ XRD results. A decrease of the basal spacing down to around 6.8–7.3 Å was already observed in LDHs containing intercalated oxoanions, like CrO₄²⁻ and Cr₂O₇²⁻,^{9–12} V₂O₇⁴⁻,⁵ and Mo₂O₇²⁻ and W₂O₇²⁻.⁸ It was attributed to the grafting of the inserted anions to the slabs, via the substitution of a hydroxyl group of the slabs by one oxygen atom of the anion. In the case of LDH_{Ni,Co}(CO₃), the contraction of the interslab

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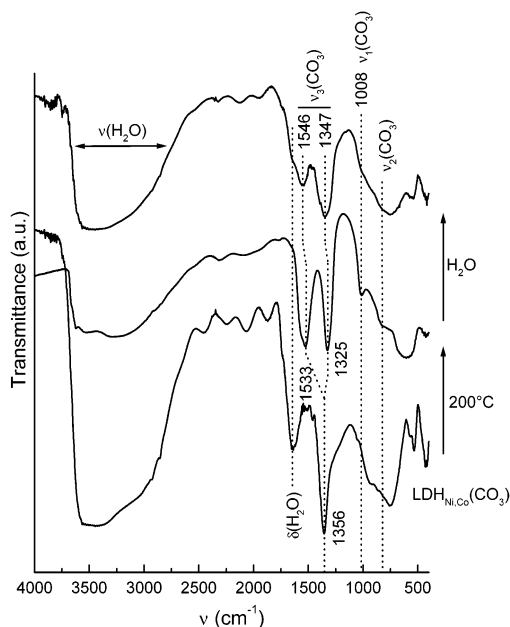


Figure 6. IR spectra of $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$, after a thermal treatment at 200 °C and after rehydration of the lattice.

space cannot be so easily explained because the final distance (6.5 Å) is lower than that expected from the geometric configuration of carbonate entities, monografted to the slabs by one oxygen, which can be evaluated to around 6.8–7.2 Å.

As far as the attempted rehydration is concerned, Figure 5 shows close similarity between the XRD patterns of the starting LDH material and the final phase. The fact that the initial oxygen packing and interslab distance are recovered suggest an effective water reintercalation into the interslab space. The XRD pattern can be indexed again with three slabs per cell ($a = 3.04$ Å and $c = 22.95$ Å), with a P3 oxygen packing, since the intensity of the (104) line is lower than that of the (015) line. The intensity ratio of the (006) line to the (003) line in the final material has reincreased with regard to the ratio of the (002) line to the (001) line in the thermally treated material, which shows an increase of the electronic density within the interslab space and confirms the presence of reintercalated water. Nevertheless, the diffraction peaks in the rehydrated material are slightly broader than in pristine $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$. Such behavior could be attributed to a grain fragmentation, induced by the strains resulting from the deintercalation–reintercalation process of the water molecules, as well as from a change in the slab packing when the pristine material is thermally treated and then rehydrated.

In order to better understand the geometric configuration adopted by the carbonate anions in the interslab space during the thermal treatment and after rehydration, an IR study was performed.

(b) IR Spectroscopy Study. The evolution of the IR spectra of pristine $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$, after a thermal treatment at 200 °C and after rehydration, is presented in Figure 6. The IR spectrum of the initial material has been intensively

discussed elsewhere.^{4,25} The broad band between 3000 and 3500 cm^{-1} and the band at 1630 cm^{-1} are attributed to the stretching and bending modes respectively of adsorbed and structural intercalated water molecules. The $\nu_3(\text{CO}_3)$ vibration band around 1360 cm^{-1} is characteristic of carbonate anions in D_{3h} planar symmetry. The $\nu_2(\text{CO}_3)$ vibration band is also present around 820 cm^{-1} .

When the $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$ phase is heated up to 200 °C, the $\delta(\text{H}_2\text{O})$ vibration band disappears and the $\nu(\text{H}_2\text{O})$ band intensity seems to strongly decrease, which indicates the water departure from the material. The remaining wide band in the 3000–3500 cm^{-1} range no longer corresponds to the valence vibration of water molecules but must be attributed to the $\nu(\text{OH})$ valence vibration band, which is considerably broadened because the hydroxyl groups are subjected to strong interactions with the carbonate ions. In fact, in pristine $\text{LDH}_{\text{Ni,Co}}(\text{CO}_3)$, as well as in all the LDH phases, the wide band in the 3000–3500 cm^{-1} results always from the overlap of the $\nu(\text{H}_2\text{O})$ and broad $\nu(\text{OH})$ valence vibration bands. Moreover, the ν_3 band of carbonate anions splits into two new bands, at 1325 and 1533 cm^{-1} , while a band appears simultaneously at 1008 cm^{-1} , which can be attributed to the $\nu_1(\text{CO}_3)$ vibration band. This behavior corresponds to a lowering of the symmetry of the carbonate anions, from D_{3h} to C_{2v} . According to Nakamoto,²⁶ the carbonate anion is bidentate if the $\Delta\nu$ discrepancy between the splitted vibrational ν_3 bands is higher than 300 cm^{-1} , and unidentate for lower $\Delta\nu$ values. In our case, $\Delta\nu$ is close to 200 cm^{-1} , which indicates a monografting of the carbonate anions to the slabs. Such behavior was already reported by Tessier et al. for zinc-substituted nickel hydroxides.²⁷

In the rehydrated material, two splitted bands are maintained for the $\nu_3(\text{CO}_3)$ vibration, which shows that the carbonate anions are still monografted to the slabs. In addition, after rehydration reaction, the intensity of the $\nu(\text{H}_2\text{O})$ vibration band reincreases while the $\delta(\text{H}_2\text{O})$ vibration band reappears as a shoulder around 1650 cm^{-1} , suggesting a reintercalation of water molecules. In the final rehydrated material, the reincrease of the interslab distance up to 7.6 Å is therefore essentially due to the reintercalation of water molecules, the carbonate anions remaining grafted to the slabs. This reintercalation of water molecules reinforces the hypothesis of the monografting, since this process was not observed for LDHs containing oxometalate intercalated anions, for which the anions are bidentate to two consecutive slabs.^{8,9}

In order to confirm these results, chemical analyses of initial LDH, after thermal treatment and after rehydration, were performed.

(c) Elemental Analysis. The A/(Ni + Co) atomic ratios, which were calculated on the basis of the weight percentage

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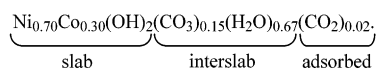
Table 1. Values of the A/(Ni + Co) Molar Ratios for Various Elements in the LDH_{Ni,Co}(CO₃) Phase without Any Treatment, after a Thermal Treatment at 200 °C, and after Rehydration^a

Treatment		A			
		Ni	Co	C	H
No treatment	Weight %	34.52	14.95	1.73	2.82
	A/(Ni+Co)	0.70	0.30	0.17	3.35
	Calculated Weight %, deduced from Ni _{0.70} Co _{0.30} (OH) ₂ (CO ₃) _{0.15} (H ₂ O) _{0.67} (CO ₂) _{0.02} (1)	35.80	15.41	1.78	2.93
200 °C	Weight %	39.74	16.70	1.84	1.83
	A/(Ni+Co)	0.70	0.30	0.16	1.91
	Calculated Weight %, deduced from Ni _{0.70} Co _{0.30} (OH) ₂ (CO ₃) _{0.15} (2)	40.35	17.37	1.77	1.98
	Calculated Weight %, deduced from Ni _{0.70} Co _{0.30} (OH) _{1.85} O _{0.15} (CO ₃) _{0.15} (H ₂ O) _{0.03} (CO ₂) _{0.01} (1)	40.13	17.23	1.88	1.89
H ₂ O, room temperature	Weight %	38.08	16.00	1.82	2.53
	A/(Ni+Co)	0.70	0.30	0.17	2.75
	Calculated Weight %, deduced from Ni _{0.70} Co _{0.30} (OH) _{1.85} O _{0.15} (CO ₃) _{0.15} (H ₂ O) _{0.45} (CO ₂) _{0.02} (1)	37.57	16.17	1.86	2.52

^a (1) These formulas are deduced from the experimental results. (2) This formula is based on the loss of intercalated water molecules and adsorbed “CO₂ species”, from the formula of the starting LDH phase.

values, are reported in Table 1 for pristine LDH_{Ni,Co}(CO₃), after a thermal treatment at 200 °C and after rehydration of the lattice.

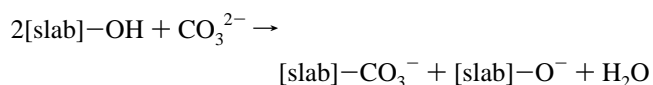
It should be remembered that, in this material family, the nickel ions are divalent, while the cobalt ions are trivalent.²⁸ In order to ensure the overall charge balance within the starting phase, 0.30 negative charge has to be brought by 0.15 CO₃²⁻ anion. The 0.02 remaining C atom is attributed to adsorbed “CO₂ species”, so that the formula may be written as follows:



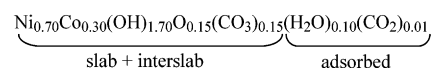
The above formula is in agreement with those usually obtained for carbonate LDH phases and for hydroxalcalite-type materials.¹

For the material treated at 200 °C, it should be noticed that the Ni, Co, and C weight percents increase, compared to those found in the starting LDH, while the H weight percent decreases. This result is in agreement with the loss of the interslab water molecules. Two different formula hypotheses can be envisaged for the heated material. One can first assume a total water removal, the carbonate remaining free within the interslab space, or envisage in a second hypothesis a dehydration coupled with a monografting of the carbonate entities to the slabs. The first hypothesis

would lead to the following theoretical formula: Ni_{0.70}Co_{0.30}(OH)₂(CO₃)_{0.15}. The elemental weight percents, calculated on the basis of this formula, are reported in Table 1. It appears clearly that the carbon (1.77%) and hydrogen (1.98%) amounts are not in good agreement with the experimental values (1.84% and 1.83%, respectively). In fact, the experimental value of the H amount suggests that the slabs may be partially deprotonated as a result of the carbonate grafting. If the monografting behavior is assumed, 0.15 slab OH⁻ ion is replaced by 0.15 CO₃²⁻ anion, and the 0.15 OH⁻ anion captures 0.15 H⁺, coming from hydroxyl groups of the slabs, according to the scheme



This hypothesis leads to the following theoretical “chemical” formula:



The amounts of CO₂ and H₂O adsorbed species were calculated on the basis of the experimental values of the C/(Ni + Co) and H/(Ni + Co) ratios. The results of the chemical analysis are in better agreement with this hypothesis than with the previous one. In conclusion, the chemical analysis results appear to be in accordance with the IR study concerning the carbonate grafting.

(28) Delmas, C.; Borthomieu, Y.; Faure, C.; Delahaye, A.; Figlarz, M. *Solid State Ionics* **1989**, *32/33*, 104.

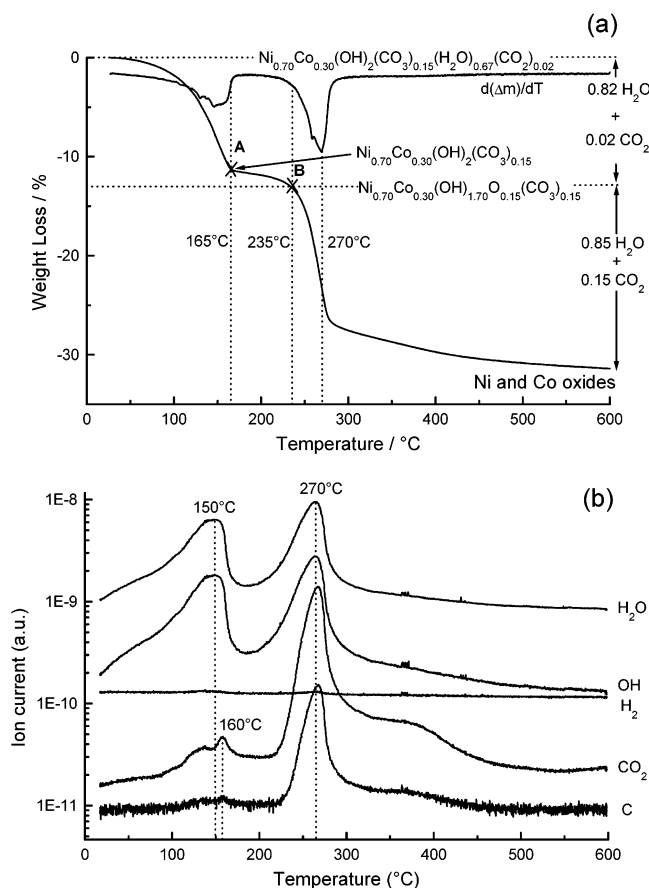
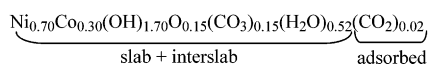


Figure 7. TGA curve (a) and coupled mass spectrometry curve (b) of LDH_{Ni,Co}(CO₃). Point A corresponds to the theoretical weight loss percent after the complete dehydration of the material, the carbonate ions being still free; point B corresponds to the theoretical weight loss percent after the complete dehydration of the material and the complete carbonate monografting.

The 200 °C thermally treated LDH_{Ni,Co}(CO₃) phase was stirred in water during 24 h at room temperature and then chemically analyzed. The results show that the Ni, Co, and C weight percents decrease, while the H weight percent increases. This result is in agreement with reintercalation of water molecules in the interslab space, leading to the formula



Let us note that the number of water molecules in the rehydrated LDH_{Ni,Co}(CO₃) phase is lower than in the starting LDH_{Ni,Co}(CO₃) phase (0.52 versus 0.67, respectively). This tendency is in accordance with the fact that the intensity ratio of the (006) line to the (003) line is lower in the rehydrated phase than in the pristine LDH (see Figure 5) and also with the existence, in the infrared spectra, of weaker $\nu(\text{H}_2\text{O})$ and $\delta(\text{H}_2\text{O})$ vibration bands for the rehydrated phase than for the pristine LDH_{Ni,Co}(CO₃) phase.

The overall results reinforce the hypothesis of a monografting of the CO₃²⁻ anions to the slabs.

(d) Thermogravimetric Analysis (TGA) Coupled with Mass Spectrometry. The thermal behavior of LDH_{Ni,Co}(CO₃) and LDH_{Ni,Fe}(CO₃) was investigated by TGA, coupled with

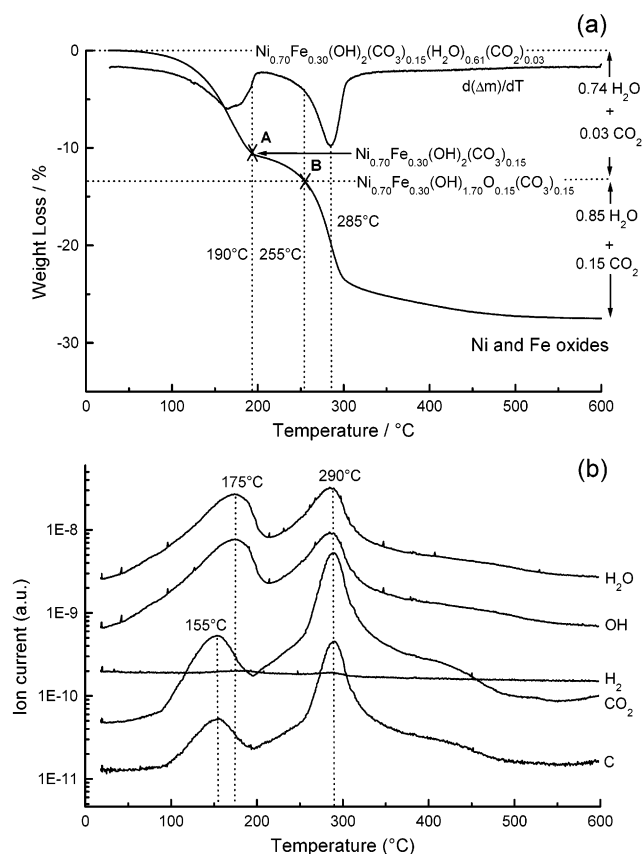


Figure 8. TGA curve (a) and coupled mass spectrometry curve (b) of LDH_{Ni,Fe}(CO₃). Point A and point B have the same meaning as in Figure 7.

mass spectrometry. The TGA curves, as well as the analysis of the evolved decomposition products by mass spectrometry, are presented in Figure 7 and Figure 8 for both materials.

It is well-known that the LDHs lose weight generally in two stages: (i) dehydration of interlamellar water molecules and (ii) dehydroxylation of the double hydroxide layers and destruction of the material.^{13,15} Even if the derivative curves obtained from the TGA curve present two peaks, they do not correspond exactly to the two phenomena, mentioned above. The first weight loss stage, which ranges from room temperature up to 235 °C for LDH_{Ni,Co}(CO₃) and 255 °C for LDH_{Ni,Fe}(CO₃), may be interpreted in terms of adsorbed and intercalated water removal, coupled with the grafting of the CO₃²⁻ species to the slabs. The coupled mass spectrometry confirms, in each case, these results. The two ionic current peaks correspond to H₂O⁺ and OH⁺. These peaks, corresponding to H₂O⁺ and OH⁺, are assigned to the removal of interlayer water molecules, and to the dehydroxylation of the sheets due to the grafting of the carbonate anions to the slabs. The small CO₂⁺ and C⁺ ionic currents, which are also observed, are related to carbon dioxide physically adsorbed at the surface of the particles.^{16,29,30} As indicated in Figure 7a in the case of LDH_{Ni,Co}(CO₃), point A was placed by calculating the theoretical weight loss percent after complete

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(30) Perez-Ramirez, J.; Mul, G.; Kapteijn, F.; Moulijn, J. *J. Mater. Chem.* **2001**, *11*, 821–830.

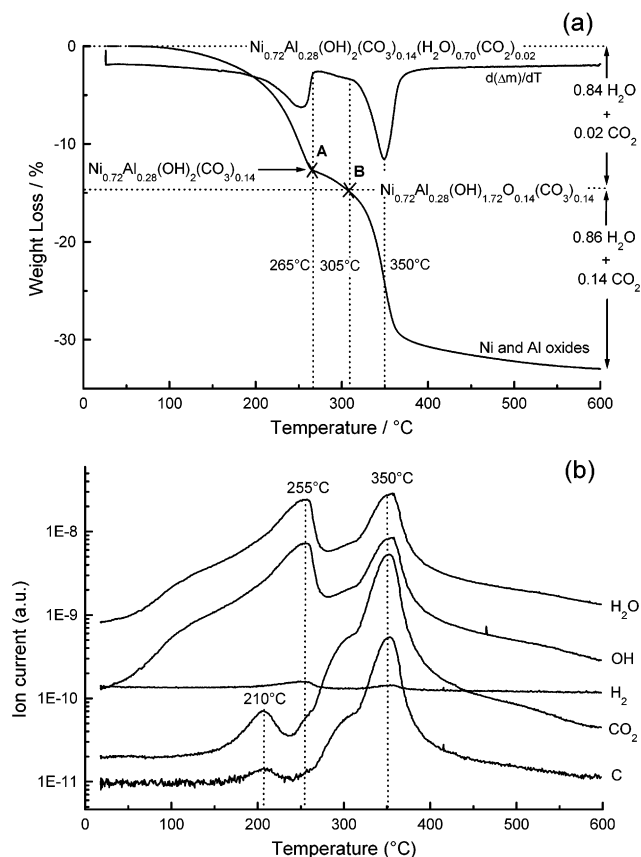


Figure 9. TGA curve (a) and coupled mass spectrometry curve (b) of LDH_{Ni,Al}(CO₃). Point A and point B have the same meaning as in Figure 7.

dehydration of the material, the carbonate ions being still free (formula: Ni_{0.70}Co_{0.30}(OH)₂(CO₃)_{0.15}), and point B was placed by calculating the theoretical weight loss percent, by considering the material as totally dehydrated, with a complete carbonate monografting (formula: Ni_{0.70}Co_{0.30}(OH)_{1.70}O_{0.15}(CO₃)_{0.15}, in accordance with chemical analysis results). This means that carbonate grafting seems to take place on the pseudoplateau between 160 and 235 °C. Similar behavior can be observed for LDH_{Ni,Fe}(CO₃) (Figure 8). As in the case of LDH_{Ni,Co}(CO₃), point A would correspond to complete dehydration of LDH_{Ni,Fe}(CO₃), without any grafting of the carbonate anions (formula: Ni_{0.70}Fe_{0.30}(OH)₂(CO₃)_{0.15}), and point B to the dehydrated material, all the carbonate anions being monografted (formula: Ni_{0.70}Fe_{0.30}(OH)_{1.70}O_{0.15}(CO₃)_{0.15}).

The second weight loss stage corresponds to the dehydroxylation end, to the loss of the carbonate species and to the destruction of the materials. This is confirmed by the mass spectrometry results, which reveal strong CO₂⁺ and C⁺ ionic currents, simultaneously with the H₂O⁺ and OH⁺ ones.

A comparative TGA study was carried out for a homologous LDH phase based on mixed (Ni,Al) slabs (phase denoted as LDH_{Ni,Al}(CO₃)). The corresponding curves are presented in Figure 9. It appears that the LDH_{Ni,Al}(CO₃) phase exhibits a thermal behavior that is similar to those of the cobalt or iron phases, except that the decomposition steps

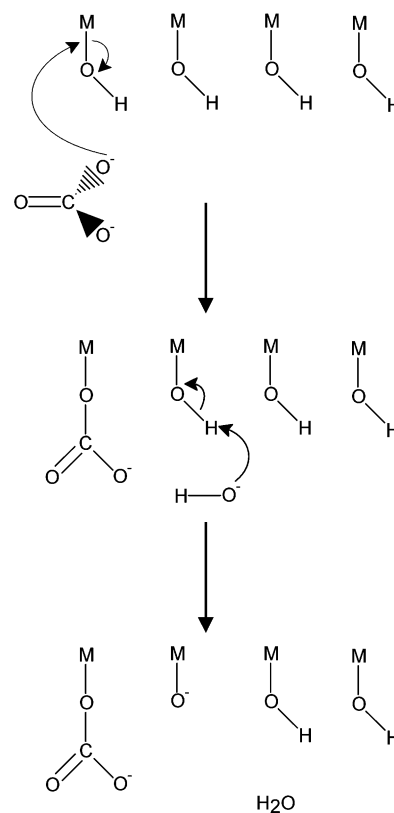


Figure 10. Schematic representation of the grafting mechanism of carbonate anions to the slab.

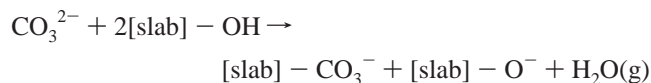
are strongly delayed. The dehydrated grafted phase appears at 305 °C in the case of Al, against around 235 or 255 °C for Co and Fe, respectively, while the second derivative curve peak is at 350 °C for LDH_{Ni,Al}(CO₃), versus 285 °C for LDH_{Ni,Fe}(CO₃) and 270 °C for LDH_{Ni,Co}(CO₃). In other terms, the TGA measurements show a higher thermal stability of LDH_{Ni,Al}(CO₃), compared to LDH_{Ni,Fe}(CO₃) and LDH_{Ni,Co}(CO₃). This behavior could be due to a higher affinity of the water molecules for aluminum than for iron or cobalt, which would entail a delayed departure of water molecules from the interslab space in the case of LDH_{Ni,Al}(CO₃).

It should be noticed that, even if the weight differences between the grafted and the nongrafted materials are small, the curve shapes are similar for the three studied materials, which suggests that there is no random behavior due to a preciseness problem.

Discussion

All the characterization techniques have shown that a moderate thermal treatment of the LDHs induces the formation of a new phase, which is still lamellar, and which is characterized by a lower interslab distance (approximately 6.5–6.7 Å versus 7.7 Å for the starting materials). It has been shown that carbon dioxide is almost not lost during this thermal treatment, meaning that the carbonate anions remain in the interslab space during this step. This behavior is explained by a monografting of the carbonate anions to the slabs; a mechanism is proposed in Figure 10. During the thermal treatment, an ionocovalent bond is established between one cation of the slab and one oxygen of the

carbonate anion, through the replacement of one hydroxyl group of the slab. This hydroxyl group deprotonates another one, in order to form a water molecule. The mechanism is schematically resumed in the following equation:



Our conclusions, that is, monografting of the carbonate ions, are not in agreement with Kanazaki's and Rives's hypotheses.^{15,16} To Kanazaki's mind, the interslab space was occupied by free hydroxyl groups, whereas to Rives's mind, O^{2-} ions were present within the interslab space.

The distance between the oxygen plane of the slab and the center of the oxygen atom located within the interslab space is 2.42 Å (this distance is calculated by considering an oxygen anion radius of 1.40 Å). This result leads to theoretical interslab distances varying from 6.8 to 7.2 Å, which is slightly higher than the observed ones (6.5–6.6 Å).

The interslab spacing value, close to 6.5–6.7 Å, has to be compared to the interslab distances obtained for nickel and zinc hydroxynitrates, $\text{Ni}_{1+x}(\text{OH})_{2x}(\text{NO}_3)_2$ and $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$, which are 6.88 and 7.038 Å, respectively.³¹ In this case, the NO_3^- anion is linked to the slab by one N–O bond, this distance being close to 1.40 Å. The C–O distance, close to 1.27 Å,²¹ is shorter, which can explain the lower interslab

distances in the thermally treated $\text{LDH}_{\text{Ni},\text{Co}}(\text{CO}_3)$ and $\text{LDH}_{\text{Ni},\text{Fe}}(\text{CO}_3)$ phases.

Conclusion

The thermal evolution of carbonate intercalated LDHs, studied in the present work, allowed us to answer the question of grafting or nongrafting of the carbonate anions, which was controverted in the literature. The infrared spectroscopy and the chemical analysis results lead us unambiguously to conclude to a monografting of carbonate anions to the hydroxyl slabs. This grafting results from the creation of a strong ionocovalent bond between the carbonate anion and the metallic cation of the slabs, via the substitution of some hydroxyl groups of the slabs by one oxygen atom of carbonate anions. TGA measurements have shown that the loss of interslab water and the monografting of the carbonate anions can be quite well separated. The hypothesis of this monografting is reinforced by the fact that water molecules can be reintercalated in the interslab space of the thermally treated material, stirred in water during 24 h. This reintercalation was not possible for oxometalate intercalated LDHs; in this case, the oxometalate anions were bigrafted to two consecutive slabs, preventing thus the reintercalation of water molecules within the interslab space.

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