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Hydrolysis in Polyol: New Route for Hybrid-Layered Double Hydroxides Preparation

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A new route has been investigated for layered double hydroxides (LDH) preparation using hydrolysis of metal salt precursors in polyol medium (ethylene glycol and diethylene glycol) under reflux. It constitutes a simple way to prepare hybrid LDH in soft chemistry conditions. The process of LDH formation rests on progressive extraction of aluminum from an insoluble complex, which is conditioned by water addition and presence of divalent metallic cations. We focused on the preparation of LDH with cation compositions NiAl and CoAl. Many advantages are demonstrated over the standard coprecipitation method, in terms of phase purity and morphology. Indeed, this method avoids the use of any other precipitation reagents and pH or atmosphere control. The formation of LDH and presence of acetate in the interlayer region was confirmed by X-ray data, IR spectroscopy, and ionic chromatography. Moreover, controlled calcinations of as-prepared LDH allow preparing mixed oxides with enhanced specific surface area properties (up to 250 m^2/g) and narrow pore range distributions in the mesoporous region of interest for catalytic applications.

Introduction

Due to their high versatility and wide range of composition, layered double hydroxides[1] (LDH ideal formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{+x}[A_m^{-x/m}\cdot nH_2O]$) are attracting a lot of attention as potential candidates for a large number of applications such as anionic exchangers, catalyst precursors,[2] and catalyst supports and also for use in the polymer industry[3] and in environmental remediation.[4] In all of these applications, surface and porosity properties of the materials are of great importance for technological performances. The formation processes of solids are known to determine their crystallinity and morphology.[5] Several solution synthetic methods have been developed for the synthesis of LDH, to tune their structural and textural properties, such as coprecipitation by alkaline solution[6,7] at various or constant pH either in water or in water/organic solvent mixtures,[8] sol−gel route starting from metal alkoxides or acetylacetonate precursors in ethanol,[9] and coprecipitation by thermal hydrolysis of urea as a retardant precipitating agent.[10] This latter method allows the separation of nucleation and crystal growth steps during the formation of particles and favors materials with a higher crystallinity degree. Crystallite size and secondary particle morphology may then be tailored by slight modifications of the synthesis conditions, such as the precipitation rate or the nature of the reaction medium.[11]

The *polyol method* developed by Fiévet et al.[12] is one of the chemical methods to prepare nanosized metals[13] or alloy[14] powders. Suitable precursors are dispersed in liquid polyols and heated at a given temperature. The polyol used served

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as a solvent, a reducing agent, and in some cases a stabilizer too. This polyol process also turned out to be efficient for the preparation of compounds such as oxides, phosphates, sulfide,[15] and layered simple hydroxide salts.[16] Through this pathway, the polyalcohols generate the in situ formation of metal alkoxides $M(OR)n$[16−18] which may play a significant role in the mobility and stability of implied metal cations and thus in the mechanism of inorganic polymerization.

In the present study, we report the preparation of acetate (Ac)-containing layered double hydroxides $[Ni_2Al(OH)_6]Ac\cdot nH_2O$ and $[Co_2Al(OH)_6]Ac\cdot nH_2O$ (hereafter noted NiAl−Ac or CoAl−Ac) by the polyol method using acetate precursors, suspended and heated in polyols liquid. Subsequently, the addition of a controlled amount of water provides the hydrolysis reaction. We analyzed the structural characteristics and the thermal behaviors of the products thereby obtained in addition to their textural properties.

Experimental Section

Preparation of the Samples. All chemicals were of analytical grade and used without any further purification. Deionized water and 95% ethanol were used in the synthesis and washing processes.

NiAl−Ac and CoAl−Ac LDH were prepared following the polyol method.[16] In a typical preparation, 0.83 g of $Ni(CH_3COO)_2\cdot 4H_2O$ (or $Co(CH_3COO)_2\cdot 4H_2O$) and 0.27 g of $Al(CH_3COO)_2(OH)$, corresponding to a M^{2+}/Al^{3+} molar ratio equal to 2 and a total concentration of salts of 0.1 M, are dispersed in 50 mL of ethylene glycol (EG), diethylene glycol (DEG), or ethanol (Et). The suspension was heated at a convenient temperature for each solvent (90 °C for EG and DEG and reflux for Et). After 1 h under vigorous magnetic stirring and heating, although the solution was not clear because of only partial solubility of the precursors, hydrolysis is then performed by a rapid addition of 22.5 mL of water, in agreement with the hydrolysis ratio ($h = 250$). The suspension is stirred under heating for a period of time ranging from 3 to 12 h. After this period, the solution was slowly cooled at room temperature, and the precipitate was recovered by centrifugation, washed twice with ethanol, and dried in air at room temperature or in an oven at 120 °C in the case of DEG. The hydrolysis ratio $h = H_2O/(M^{II} + M^{III})$ is one of the key reaction parameters. A minimum value of h is necessary to complete the reaction. The effect of h on the synthesis achievement will be discussed in the Results section. Note that pure compounds are obtained at the highest yield for $h = 250$ at $T = 90$ °C and $h = 60$ at $T = 130$ °C, respectively, for the NiAl and CoAl samples.

To assess the specificity of the polyol method, analogous LDH phases were also prepared by the conventional coprecipitation method at fixed pH in aqueous solution.[6,19] Experimentally, 10 mL of mixed solutions of $NiCl_2$ or $CoCl_2$ (0.67 M) and $AlCl_3$ (0.33 M) were added in a reactor containing 100 mL of distilled and deionized water at room temperature under a nitrogen atmosphere to minimize the incorporation of atmospheric CO_2 and under vigorous stirring. The pH of the solution was maintained at 10.5 by simultaneous addition of a mixed solution of NaOH (1 M) and Na_2CO_3 (0.5 M). The precipitates were separated by centrifugation and washed twice with water. In the case of NiAl LDH, crystallinity of the solid was improved by hydrothermal treatment, performed in an autoclave, at 120 °C under autogenous pressure for 48 h.

Characterization. Powder X-ray diffraction (PXRD) patterns were obtained with a Siemens D501 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5415$ Å) and fitted with a graphite back-end monochromator. The samples were scanned from 2° to 70° (2θ) using steps of 0.08° and a counting time of 4 s per step.

Fourier transformed infrared (FTIR) spectra were collected on a Perkin-Elmer 16PC spectrophotometer in absorbance mode in the frequency range of 4000−400 cm^{-1} using KBr pellets. UV−visible spectra were recorded on a Shimadzu UV2101PC, equipped with diffuse reflectance accessory, in the region 200−800 nm.

Chemical analyses (Ni, Co, Al, C, H) were performed at the Vernaison Analysis Center of CNRS. Ion chromatography was performed on a Dionex DX-320. Anions were separated on an AS11 column.

Thermogravimetric analyses (TGA) were recorded on a Setaram TG-DTA92 thermogravimetric analyzer coupled with a mass spectrometry analyzer (Thermostar 300 Balzers Instruments) in the temperature range of 25−1050 °C, with a heating rate of 5 °C/min, under air or argon flow in an alumina crucible. N_2 adsorption−desorption isotherms were performed for the various samples at liquid nitrogen temperature (−196 °C) on a Fison SP 1920 instrument. Before measurement, all samples were heated at 150 °C to desorb the solvent molecules (EG and DEG) and then pretreated at 120 °C for 12 h under vacuum until the pressure was stabilized at 10^{-2} Torr. The BET surface areas were determined for the low-pressure region ($p/p^0 \leq 0.26$). The mesopore volumes and pore size distributions were calculated using the BJH models, assuming that the pore diameters are in the range of 2−50 nm.

Scanning electron microscopy (SEM) images were obtained on a JEOL 5190 microscope operating at an acceleration voltage of 15 keV. The samples for SEM were coated with C to make them conductive.

Results and Discussion

Characterizations of LDH Compounds. The chemical compositions of the different phases (Table 1) are in good agreement with the expected LDH formulas. We can quote that the experimental M^{II}/M^{III} ratio is slightly lower than the initial value ($M^{II}/M^{III} = 2.0$) especially for the synthesis performed in EG or DEG. Considering that the pH of the reaction in polyol never exceeds 6.50, the medium never fits the required pH condition for the complete precipitation of the M^{2+} and the LDH formation[20] with the desired stoichiometry. Similar trends are observed for LDH formed by extraction of Al^{3+} from alumina[21] and also with the so-called “urea method”.[10,11] The amounts of acetate measured by ionic chromatography agree with the required compensation of the charge density induced by the substitution of Al for M^{II}, when

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Table 1. Chemical Compositions of LDH−Ac Hybrid Materials, Their Crystallite Size, and Their Porosity Properties

LDH	idealized formulas	Ac/Al	fwhm (° 2θ)/ crystallite size (Å) (±5)	S_{BET} (m^2/g)	porous volume (cm^2/g)
NiAl−CO_3[a]	$[Ni_{2.0}Al(OH)_6]^+(CO_3^{2-})_{0.5}\_2.5H_2O$	−	1.1/93	72	0.38
NiAl−Ac_{Et}	$[Ni_{1.8}Al(OH)_{5.6}]^+(Ac^-)\_3.5H_2O$	1.1(2)	1.3/76	99	0.20
NiAl−Ac_{EG}	$[Ni_{1.7}Al(OH)_{5.4}]^+(Ac^-)\_0.9EG\_2.4H_2O$	1.0(6)	2.0/48	86	0.15
NiAl−Ac_{DEG}	$[Ni_{1.7}Al(OH)_{5.4}]^+(Ac^-)\_0.9DEG\_1.9H_2O$	1.1(8)	1.3/77	108	0.11
CoAl−CO_3[a]	$[Co_{2.2}Al(OH)_{6.4}]^+(CO_3^{2-})_{0.5}\_2.3H_2O$	−	0.61/214	93	0.58
CoAl−Ac_{Et}	$[Co_{1.9}Al(OH)_{5.8}]^+(Ac^-)\_3.4H_2O$	1.1(6)	1.13/93	31	0.24
CoAl−Ac_{EG}	$[Co_{1.8}Al(OH)_{5.6}]^+(Ac^-)\_0.8EG\_2.0H_2O$	1.0(7)	1.14/92	150	0.28
CoAl−Ac_{DEG}	$[Co_{1.7}Al(OH)_{5.4}]^+(Ac^-)\_0.9DEG\_1.4H_2O$	1.1(2)	1.01/107	73	0.096

[a] Coprecipitated parent LDH.

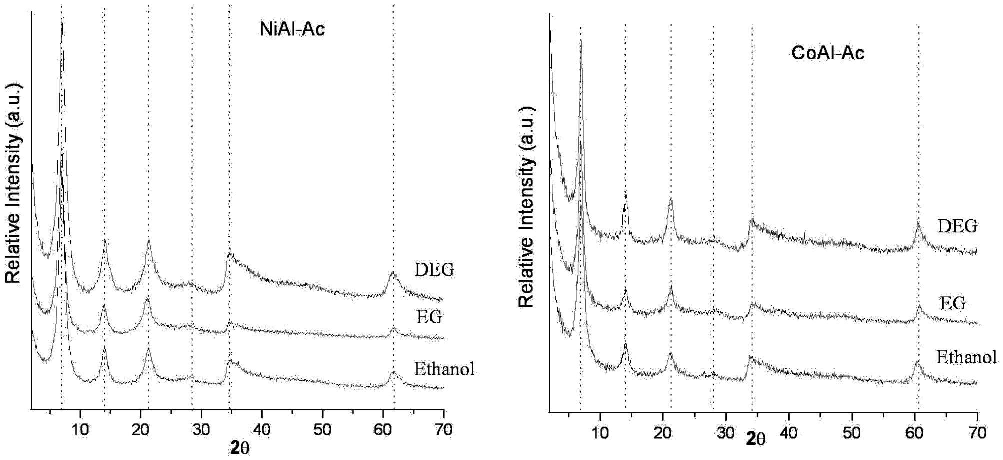

Figure 1. X-ray diffraction patterns of NiAl−Ac and CoAl−Ac LDH prepared by the polyol method in Et, EG, and DEG.

considering the accuracy in the analyses. The large excess of carbon observed for the synthesis performed in EG or DEG is attributed to residual solvent molecules, as observed for layered hydroxide simple salt.[16]

XRD patterns are typical of LDH (Figure 1) while no other crystallized phase is observed. The 00*l* reflections are similar for solids prepared in the three solvents and correspond to interlayer distances ($d \approx 1.25$ nm) close to those reported for the LDH−acetate elswhere.[22−24] This indicates that basal spacing is solely fixed by the interlayered acetate anions and not affected by the type of solvent used. Since the basal spacings reported for LDH intercalated by EG or glycerol[25,26] (0.978 and 0.960 nm, respectively) are smaller, solvent molecules may be either physisorbed or intercalated. However, TG/MS and IR analysis have demonstrated that polyol molecules are mainly physisorbed at the crystal surface, as discussed later on. The values of the **a** parameters (0.30 (±0.01) nm) are lower for the as-synthesized samples than those reported for the corresponding layered simple hydroxides.[16] Since the **a** parameter is related to the metal−metal distances, these lower values are in agreement with the introduction of Al^{3+} cations into the layered single hydroxides network, according to the Vegard's law.[27] The formation of mixed M^{2+}−Al^{3+} layers isostructural to typical NiAl and CoAl LDH phases with all the M^{2+} in an octahedral coordination has also been confirmed by UV−visible diffuse reflectance spectroscopy which shows typical d−d electron transitions characteristic of the d^7 and d^8 electron configuration for Co^{2+} and Ni^{2+} in CoAl−Ac and NiAl−Ac respectively (see Supporting Information).

Other evidences of acetate−LDH formation are provided by infrared spectroscopy. All the stretching and bending vibration modes of the organic anion are observed, besides the characteristic absorption bands of the LDH hydroxylated layers[28,29] (see Supporting Information). For products prepared in EG and DEG, the characteristic bands of polyols around 1100 cm^{-1} further confirm the presence of EG or DEG on the solids. When the amount of polyol molecules is reduced by a moderate thermal treatment (150 °C), the intensity of these bands strongly decreases, indicating that polyol molecules are mainly adsorbed at the surface of the platelets. Note that, for adsorbed glycol molecules on LDH, bands at 987 and 1020 cm^{-1} are also observed, which are not present on the spectra of free alcohol.

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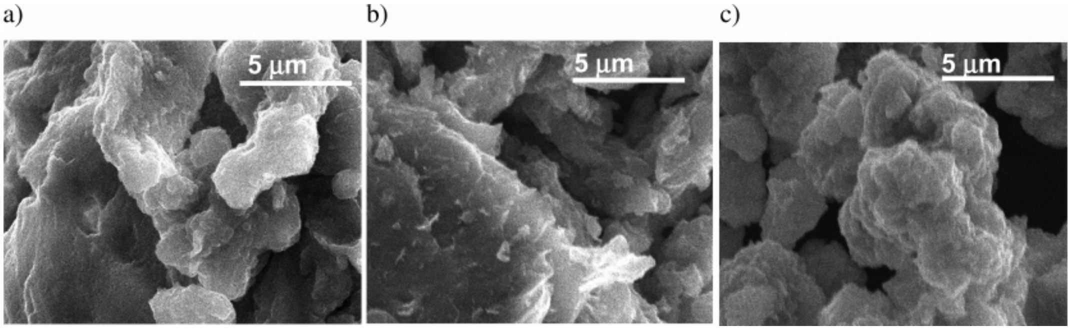

Figure 2. SEM images of NiAl−Ac obtained in (a) DEG, (b) EG, and (c) ethanol.

We must emphasize that all attempts to prepare pure NiAl−Ac or CoAl−Ac LDH by standard methods were unsuccessful. Phases were always contaminated by carbonate. Conversely, in a polyol medium, although no precaution is taken for the control of the atmosphere, the formation of LDH−CO_3 never occurs. The slight acidic pH conditions (6.5) are favorable to the prevention of carbonate intercalation. Hansen et al.[25] explained this phenomenon by the neutralization of CO_3^{2-} by acidic polyol, according to the following reaction:

$$2(CH_2OH-CHOH-CH_2OH) + CO_3^{2-} \rightleftarrows CO_2 + 2(CH_2OH-CHOH-CH_2O)^-$$

$$CH_2OH-CHOH-CH_2O^- + H_2O \rightleftarrows CH_2OH-CHOH-CH_2OH + OH^-$$

Even if some carbon dioxide is dissolved in organic solvent during the reaction process, intercalation of CO_3^{2-} in the inorganic layered structure is totally avoided. According to the literature data,[18−20] we must admit that acetate anions are incorporated at the initial step of the LDH formation, preventing any carbonate contamination.

The presence of polyol molecules during the formation steps greatly influences the LDH morphology as illustrated by the SEM pictures gathered in Figure 2. The use of organic solvent modifies the crystal growth and leads to very compact particle aggregation, as observed for LDH nanocomposites,[30] rather than to the classic “sand rose” morphology. Individual hexagonal particles cannot be distinguished anymore. It is interesting to notice that this type of morphology is not so pronounced when using ethanol. To access the crystal size of the primary particles, X-ray data were processed using the Debye Scherrer formula. The dimensions of the platelets along the *c*-direction were deduced from the full-width at half-maximum (fwhm) of the diffraction lines, according to the following relation: $L_{hkl} = K\lambda/(B_{hkl}(2\theta)\cos\theta)$, where L_{hkl} is the crystallite size, B_{hkl} the fwhm corrected from the natural line width of the diffractometer, and K a shape factor equal to 0.94 for the 00*l* reflections. The average thickness of the crystallites (Table 1) corresponds to less than 10 stacked layers, which is smaller than that for the corresponding carbonate phases.

To evidence the anion exchange properties of the as-prepared compounds and to verify their structural analogy with coprecipitated LDH, the materials were exposed to 0.1 M solution of sodium carbonate. As expected, the exchanged materials show IR spectra similar to those of coprecipitated NiAl−CO_3 and CoAl−CO_3 LDH in which the two bands characteristics of the carboxylate groups (ν_{as} and ν_s) are replaced by the carbonate band at 1375 cm^{-1}. Anion exchange is also confirmed by the decrease of the interlayer spacings from 1.26 (±0.02) nm to 0.76 nm.

Mechanism of Formation of NiAl−Ac and CoAl−Ac LDH Compounds. To understand the mechanism of LDH formation during the polyol process, the kinetics of the NiAl−Ac_{DEG} and CoAl−Ac_{DEG} synthesis (performed at 90 °C for $h = 250$) were monitored by powder X-ray diffraction (Figure 3).

The total disappearance of the diffraction lines of insoluble aluminum acetate hydroxide (PDF No.: 13−0833) is observed after 2 h of hydrolysis while typical patterns of LDH compounds simultaneously appeared. Note that the more the temperature is raised, the faster the reaction is completed.. A blank experiment was carried out in order to evaluate the ability of aluminum acetate to precipitate as hydroxy salt under the same hydrolysis conditions, without any M^{2+} addition. Neither solubilization nor hydrolysis of the Al^{3+} complex was observed. Then, it is the presence of M^{2+} in the medium which permits the progressive solubilization of aluminum complex and the coprecipitation of the mixed hydroxides. In addition, interactions between M^{2+} species in solution and the insoluble Al^{3+} complex prevent the simple hydrolysis of M^{2+} and the formation of layered simple hydroxide salt of formula $M_2(OH)_3Ac\cdot H_2O$.

These results could be related to those reported by O. Clause et al.[21] about LDH formation by extraction of Al^{3+} from Al_2O_3 during impregnation by M^{2+} amino complexes (Ni^{2+} and Co^{2+} also). Thus, the hydrotalcite-like compound formation reported here can be explained by phenomena similar to those described by the authors, i.e., adsorption, dissolution, and precipitation, but taking into account the polyol medium, implying the formation of metal alkoxyacetate intermediates.[17,18] During this reaction, concomitant mass transfers from the aluminum-based solid to the polyol solution and from the polyol solution to the LDH solid are involved.

Addition of water to acetate metal complexes forces the hydrolysis of metal complexes and prevents any reduction reactions usually observed in a polyol medium under reflux.

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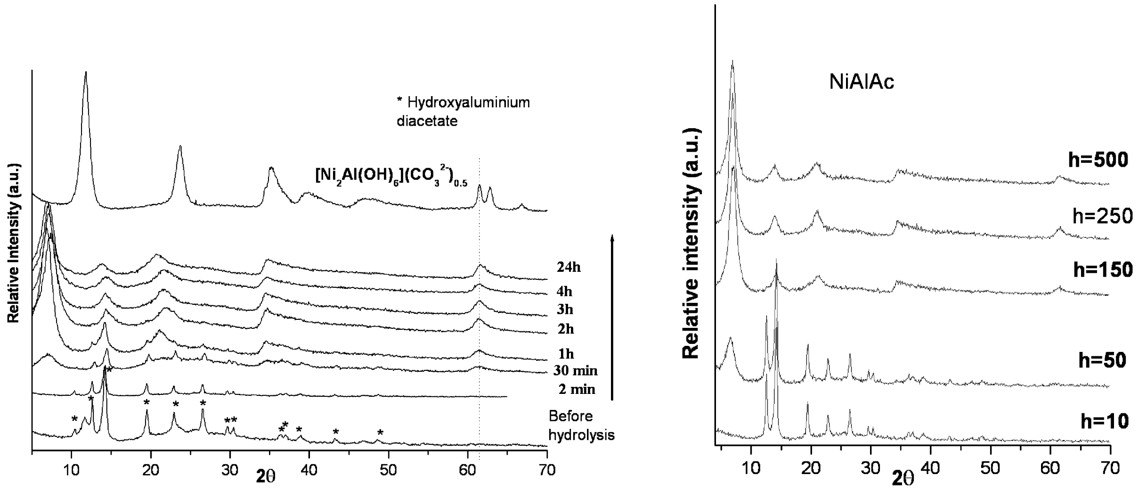

Figure 3. X-ray diffraction patterns of NiAl−Ac$_{DEG}$ versus time of hydrolysis (left) and versus *h* parameter (right).

Table 2. Thermal Decomposition Events of the As-Prepared LDH

sample	dehydration		dehydroxylation		acetate anions decomposition		total loss (wt %)
	T (°C)	LW %	T (°C)	LW %	T (°C)	LW %	
NiAl−Ac$_{DEG}$	30−150	1.5	280−550[a]		29.8		48.5
	150−280	17.0					
NiAl−Ac$_{EG}$	30−150	5.0	280−550		26.8		43.5
	150−280[a]	12.0					
NiAl−Ac$_{Et}$	30−200	11.0	200−350	12.0	350−430	7.5	37.0
					430−550	6.0	
CoAl−Ac$_{DEG}$	30−130	2.0	270−360	16.0	360−450	8.0	48.0
					450−800	9.5	
	130−200	5.0					
	200−270[a]	7.5					
CoAl−Ac$_{EG}$	30−140	5.0	240−330	8.0	330−550	13.0	38.5
	140−240[a]	8.5			550−800	4.0	
CoAl−Ac$_{Et}$	30−170	8.0	170−300	13.5	300−600	12.5	34.5

[a] With decomposition of solvent molecules.

We consider that the acetic acid liberated during hydrolysis reacts with the polyol to give ester and water. The hydrolysis ratio *h*, measured as the $H_2O/\Sigma M$ molar ratio, is the key parameter of the polyol method; a minimal value of $h = 150$ is needed at 90 °C for a complete hydrolysis for both metals as illustrated for NiAlAc$_{DEG}$ in Figure 3.

Thermal Behavior of the LDH Acetate As Prepared. NiAl and CoAl LDH matrixes being widely used as precursors for various catalytic transformations[2,31] (hydrogenation, nitrous oxide decomposition, etc.), the thermal decompositions have been investigated as well as the porosity properties of the acetate intercalated compound and the calcined samples.

The thermal decomposition of the different samples follows schemes similar to those usually described in the literature[32] for the LDH compounds, involving successive steps of dehydration, dehydroxylation, and anion decomposition. The effect of remaining alcohol molecules on the thermal decomposition appears quite clearly (see Supporting Information). In the case of samples prepared in EG and DEG, the departure of remaining solvent molecules induces higher values of total weight losses and an additional step (Table 2). Presence of EG and DEG delay the dehydroxylation and the decomposition of acetate to higher temperature, stabilizing then the inorganic lattice. In addition, these molecules appear to interact strongly with water molecules, delaying a supplementary dehydration step at higher temperature, especially for DEG. In NiAl−Ac, the acetate anions are decomposed in two well-identified steps with very different rates of decomposition, the quickest event occurring at lower temperature for EG and DEG samples.

Meanwhile, the PXRD patterns of the calcined compounds have been recorded (Figure 4). Decompositions of NiAl−Ac in amorphous mixed oxides occur at temperatures over 280 °C, temperatures lower than those observed for NiAl−CO$_3$ LDH.[32] CoAl−Ac displays even lower stability compared to NiAl−Ac. The lamellar structure of CoAl−Ac$_{DEG}$ collapses before 250 °C and already the diffraction lines of the Co_3O_4 and $CoAl_2O_4$ spinel phases appear. Kannan et al.[31] explain that the formation of spinel at such low temperature is permitted due to the easy oxidation of Co^{2+} and the thermodynamic stability of Co_3O_4.

Interestingly, at moderate thermal treatement not greater than 200 °C, NiAl−Ac$_{DEG}$ undergoes a shift of the 00*l* diffraction lines at higher angle values, indicating a decrease of the interlamellar distance from 1.24 to 0.93 nm whereas the structure of the layer is not affected (see Supporting Information). Confirmed by the TGA/MS analysis, this contraction occurs due to interlamellar water departure. The

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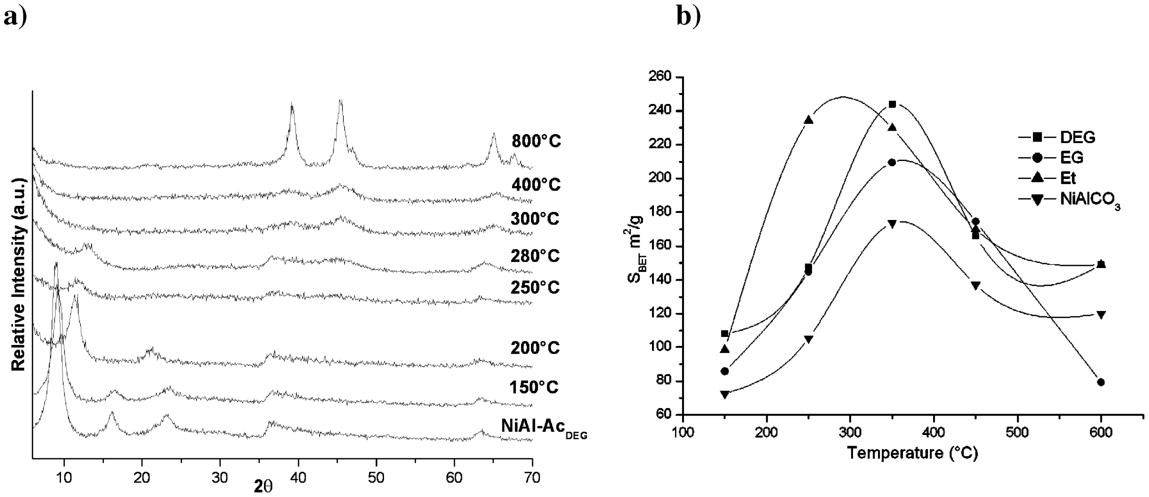

Figure 4. (a) PXRD patterns for NiAl−Ac$_{DEG}$ and (b) surface areas of NiAl compounds heated at various temperatures.

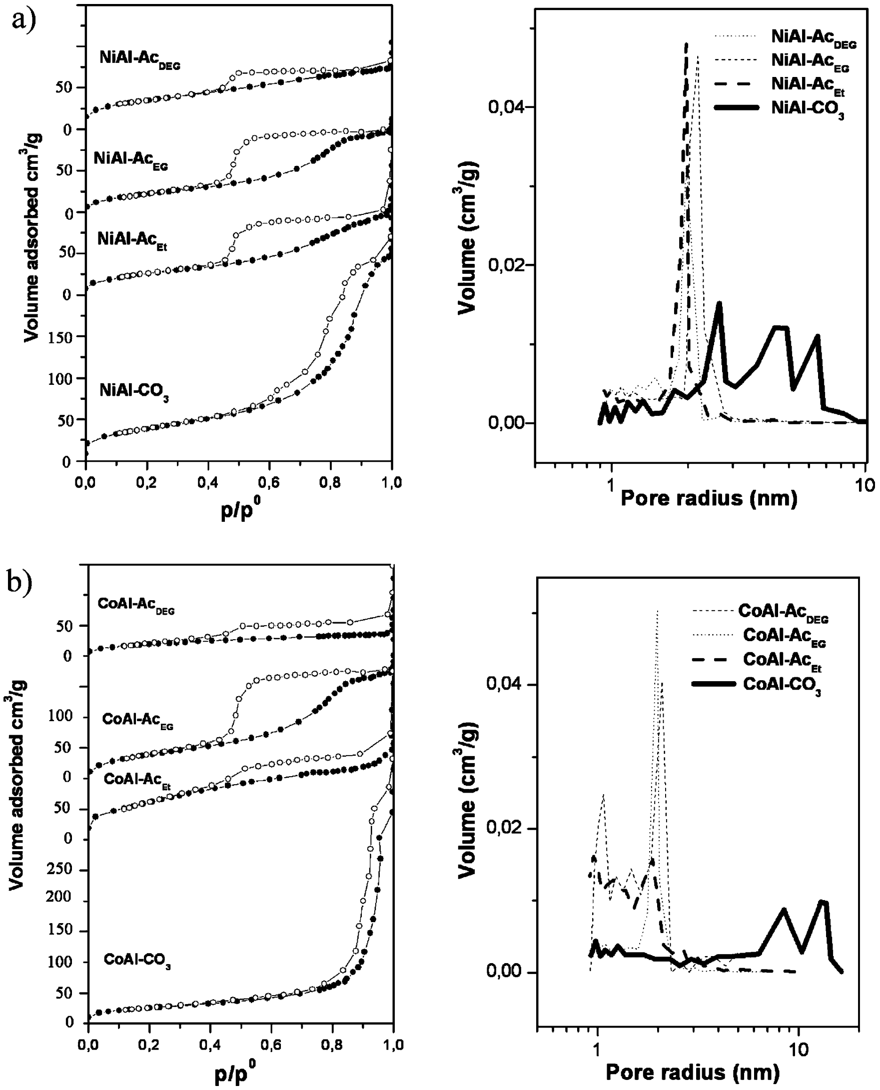

Figure 5. Nitrogen adsorption−desorption isotherms and pore size distribution of (a) NiAl and (b) CoAl samples obtained in a polyol medium and the corresponding coprecipitated LDH−CO$_3$.

observed contraction of 0.32 nm is in agreement with the van der Waals size of a water molecule monolayer.[24] With exposure to atmospheric moisture, this dehydration−hydration process appears to be partially reversible until to 150 °C. When the temperature is increased to 200 °C, the contracted phase is retained whatever the exposure time, indicating that water cannot diffuse any more in the so-treated materials. With regard to the structural data already observed for hybrid LDH[24,33] and the acetate size, this contracted phase may correspond to totally interdigitated bilayers of acetate or to a flat orientation of these anions as observed for oxalate or tartrate.[34] In fact, the available surface area per unit charge

(25 Å^2/e$^-$) of the Ni_2Al host structure may accommodate a flat orientation of the acetate anions which display a surface area of 23 Å^2. Surprisingly, such a dehydration−hydration process is not highlighted for CoAl phases, for which a moderate thermal treatment up to 200 °C only induces a broadening and a net intensity decrease of the 00*l* reflections.

The variations of Brunauer−Emmett−Teller (BET) specific surface areas versus calcination temperature of the different compounds are plotted in Figure 4. As usually observed for LDH compounds, an optimum is reached at 250 and 350 °C for CoAl−Ac and NiAl−Ac, respectively, corresponding to the transformation of the LDH structures into mixed oxide phases. The measured surface areas for the LDH−Ac prepared by the polyol route are 20% to 40% higher than values measured for coprecipitated LDH−CO_3. The comparison between nitrogen adsorption/desorption isotherms[35] of LDH−Ac (type IVb) and LDH−CO_3 (type IVa) evidences the influence of the synthetic pathways on the textural properties (Figure 5). According to Rouquerol and colleagues,[36] the type IVb isotherms are mainly dependent on network percolation. In addition, the pore size distribution of LDH−Ac is narrow and centered near 2 nm. Enhancing the surface area properties has also been reported for LDH materials prepared by the sol−gel route[9] and explained by the formation of an irregular mesoporous network, whereas the well-defined porosity reported by Malherbe et al.[8] for calcined hydrotalcite regenerated into glycerol has been attributed to the formation of new porosity at the grain boundaries of the crystallites. These different results indicate that the use of organic species (solvents[8] or precursors[9]) during the formation of the inorganic matrix induces modification of the agglomeration mechanism and allows improvement of textural properties. Similarly, it appears that the use of polyols affects strongly the way that crystallites aggregate and permits the generation of a network of small interconnected pores.

Conclusion

In the present study, pure NiAl and CoAl LDH have been prepared by an original method, consisting of hydrolysis of acetate precursors followed by inorganic polymerization in a polyol medium. This method does not require either pH or atmosphere control, which are usually required in conventional coprecipitation reactions. The LDH coprecipitation is based on the progressive dissolution of an insoluble aluminum source promoted by M^{2+} species in solution. The structural study confirms the obtention of hybrid LDH intercalated by acetate anions. The thermal treatment of these LDH materials leads to mixed oxides with very interesting and well-defined surface and porosity properties. The major advantage of this method is that the as-prepared compounds display an interesting homogeneous pore size distribution in the low level of mesoporosity (2 nm) as well as an increase of specific surface area with values 40% higher than those of coprecipitated analogous derivatives, which could improve the catalytic properties.

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Supporting Information Available: Additional figures including UV and IR spectra, XRD patterns, and thermal analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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