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Acrylate Intercalation and in Situ Polymerization in Iron-, Cobalt-, or Manganese-Substituted Nickel Hydroxides

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A chimie douce route based on successive redox and exchange reactions has allowed us to prepare new hybrid organic–inorganic materials, composed of polyacrylate macromolecules intercalated into layered double hydroxides (LDHs), deriving from Ni(OH)$_2$. Monomer intercalation and in situ polymerization mechanisms have appeared to be strongly dependent upon the nature of the substituting cation in the slabs. In the case of iron-based LDHs, a phase containing acrylate monomeric intercalates has been isolated and identified by X-ray diffraction and infrared spectroscopy. Second, interslab free-radical polymerization of acrylate anions has been successfully initiated using potassium persulfate. In cobalt- or manganese-based LDHs, one-step polymerization has been observed, leading directly to a material containing polyacrylate intercalate.

Introduction

Hybrid organic–inorganic materials (HOIM) have received growing attention over the past 10 years, in particular because they are attractive candidates for optical devices, catalysts, sensor coatings, etc.[1] One of the most exciting and promising synthesis strategies is probably the insertion of organic molecules into the galleries of inorganic lattices, including 3-D frameworks, 2-D layered hosts, 1-D tunnel hosts, etc.[2,3] The insertion of organic macromolecules is also of great interest from the point of view of intercalation chemistry and polymer science and potentially of use in the areas of catalysis, sorption, high-strength materials, ...[4] From this standpoint, layered inorganic hosts have attracted great attention, such as phyllosilicates,[5–9] metal dichalcogenides MS$_2$ (with M = Mo, Ti),[10–12] iron oxide chloride FeOCl,[13]

vanadium pentoxide gels V$_2$O$_5 \cdot n$H$_2$O,[14–16] and molybdenum oxide MoO$_3$.[17,18] Among the most reported intercalation routes, there is direct intercalation of preformed macromolecules,[5,6,9,14,15,17] precipitation of mineral slabs[19,20] or restacking after exfoliation in a macromolecular solution,[10,11] interslab polymerization of intercalated monomers,[7,12,18,21,22] and redox intercalative polymerization (RIP).[8,13,16,23] For the latter, the intercalation process is accompanied by the spontaneous reduction of mineral components and oxidative polymerization of the monomers.

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Layered double hydroxides (LDHs), known as anionic clays, have also gained much attention in the field of HOIM.[24] Organic-free LDHs are used as catalyst supports, electrode materials, anion exchangers, etc.[25,26] They can be described by the general formula $[M_{1-y}^{II}L_y^{III}(OH)_2]$-$[X^{n-}]_{y/n}[H_2O]_z$ and will be denoted in this paper as LDH($M_{1-y}L_y$-X). Their structure is composed of stacked $[M_{1-y}^{II}L_y^{III}(OH)_2]$ slabs, where L^{III} is partially substituted for M^{II} metallic cations. To balance the positive charge excess, the interslab space contains X^{n-} anions, whose amounts are theoretically directly related to their own negative charges (n) and to the concentration of L trivalent cations within the slabs (y). Water molecules are also co-intercalated and contribute to the structure's stabilization, via a strong hydrogen-bonding network with slab hydroxyls and intercalated anions.

Whereas many organic anions, such as carboxylates, have been intercalated in LDHs,[24,27,28] few reported studies deal with the intercalation of macromolecules.[29−41] Their most common preparation methods are based upon the LDH anionic exchange properties or their ability to be precipitated from metal nitrate-salt precursors in the presence of dissolved anionic species.[24] The anionic exchange route has been explored by Kato and co-workers, who have obtained the acrylate derivative from the LDH(MgAl-nitrate) phase and subsequent interslab polymerization by thermal treatment in the presence of potassium persulfate.[29] Schwarz and co-workers have used the same approach with 4-styrenesulfonate anions in reconstructed LDH(MgAl).[31] Choy and co-workers have reported the direct intercalation of DNA fragments in similar phases [41] and their potential use as nonviral vectors.[42] The coprecipitation method has been investigated by Messersmith and Stupp for LDH(CaAl-poly(vinyl alcohol))[32−35] and by Lerner and co-workers for accommodating poly-(acrylic acid), poly(vinyl sulfonate), or poly(styrenesulfonate) bilayers in LDH(MAl), with M = Mg, Ca, or Co, and LDH(ZnL), with L = Al or Cr.[37,38] Challier and Slade have reported the coprecipitation synthesis of LDH(CuCr-terephthalate) and LDH(CuAl-hexacyanoferrate) and the oxidative polymerization of aniline in these pillared hosts, induced by their Cu^{II} oxidant character.[36] Slade and co-workers have intercalated poly(α,β-aspartate) into LDH(MgAl) via direct coprecipitation in the presence of the preformed macromolecules or in situ thermal polycondensation of aspartate intercalate[39] Finally, Kato and co-workers have reported the swelling of LDH(MgAl-dodecyl sulfate) by acrylonitrile and its subsequent polymerization initiated by benzoyl peroxide.[30]

A new route for LDH($Ni_{1-y}L_y$) preparation (with L = Co or Fe) was developed in our laboratory a few years ago and applied to the intercalation of several mineral and polyoxometalate anions.[43−46] This three-step method consists of dissociating the building of the $Ni_{1-y}L_yO_2$ slabs (synthesis of sodium nickelate using high-temperature solid-state chemistry) from the anionic intercalation. The latter is preceded by an oxidizing hydrolysis step, leading to a γ-oxide hydroxide phase, which is subsequently reduced in the presence of the anions, which have to be intercalated. Recently, this *chimie douce* method has been extended to the intercalation of organic species, such as acrylate, methacrylate, or 4-pentanoate anions in LDH($Ni_{0.70}Fe_{0.30}$).[40] It has also been shown that thermal treatment of the acrylate intercalate in the presence of potassium persulfate allows monomer interslab polymerization.

The main goals of this paper consist in reporting new experimental results concerning the intercalation and polymerization of acrylate anions in LDH($Ni_{0.70}L_{0.30}$). The influence of the nature of the L cation within the LDH slabs (L = Fe, Co and Mn), the synthesis route, and the particle morphology were investigated respectively on the basis of infrared (IR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) experiments.

Experimental Section

Preparation of LDH($Ni_{0.70}L_{0.30}$-acrylate) by Solid-State Chemistry and Subsequent Chimie Douce Reactions (L = Fe or Co). The preparation procedure consists of three successive steps as previously described:[40,44] (i) building of the $Ni_{0.70}L_{0.30}O_2$ slabs via the preparation of $NaNi_{0.70}L_{0.30}O_2$-substituted sodium nickelate by solid-state reaction at 750 °C; (ii) oxidizing hydrolysis of the previous phase in a 5 M KOH/0.8 M NaClO solution (100 mL for 1 g of sodium nickelate), leading to a γ-oxide hydroxide phase; (iii) reduction of the γ-oxide hydroxide phase using an excess of 5 M H_2O_2 (1 mL for 1 g of γ-oxide hydroxide) in an aqueous solution of acrylic acid and sodium acrylate, in such proportions that pH is adjusted to 4.3. The dispersion is stirred at room temperature for 1 h, after adding H_2O_2. The suspension is then recovered by filtration, washed with deionized water, and dried at 50 °C.

Preparation of LDH($Ni_{0.70}L_{0.30}$-acrylate)[#] by Coprecipitation and Subsequent Chimie Douce Reactions (L = Mn or Co).

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Since the preparation of the starting $NaNi_{0.70}L_{0.30}O_2$ nickelate by solid-state reaction is not possible with L equal to Mn,[47] a LDH($Ni_{0.70}Mn_{0.30}$-carbonate) phase was prepared using the co-precipitation method:[48,49] 8.02 g of $NiSO_4$ and 2.32 g of $MnSO_4$ (7:3 molar ratio) were dissolved in 100 mL of water. A 20 mL volume of 5 M H_2O_2 was added to the solution, to achieve the oxidation of the manganese in the following step. The resulting solution was added dropwise into 100 mL of 2 M NaOH, containing 4 g of dissolved Na_2CO_3. It should be noticed that effective manganese oxidation takes place when the salt solution and the NaOH solution are mixed, that is, in basic conditions. The suspension was vigorously stirred for 4 h, recovered by filtration, washed with deionized water, and dried at 50 °C. The LDH($Ni_{0.70}Mn_{0.30}$-carbonate) phase, thus obtained, was oxidized into a γ−oxide hydroxide, which in turn can be reduced by H_2O_2 in the presence of acrylate anions, in the same experimental conditions as for iron- or cobalt-based phases, leading to a material with intercalated acrylate anions. This material is denoted as LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#], where the superscript # symbol means "prepared from an exprecipitated phase".

To establish some comparisons with the manganese-based phase, similar synthesis was performed from $NiSO_4$ and $CoSO_4$ precursors and led to LDH($Ni_{0.70}Co_{0.30}$-acrylate)[#]. This route cannot, however, be applied to iron-substituted nickel hydroxides, because, as far as we know, no common agent is sufficiently efficient for oxidizing iron-based LDHs to corresponding γ-oxide hydroxides.

A "reference" manganese-based phase was also obtained after reducing the manganese-based γ-oxide hydroxide, by means of H_2O_2, without any acrylate anions in the reaction medium. This phase is denoted as LDH($Ni_{0.70}Mn_{0.30}$)$_{ref}$[#]. Previous studies have shown that reducing a γ-oxide hydroxide phase by H_2O_2 in decarbonated water and in an air-free atmosphere leads to LDHs intercalated with OH^- anions.[50] Nevertheless, the more the phase was aged in the solution, the more an exchange of OH^- anions for carbonate ones was favored. The obtained phase contains therefore co-intercalated OH^- and CO_3^{2-} anions.

Attempted in Situ Polymerization. Interslab free-radical polymerization of acrylate monomers was performed by heating 500 mg of LDH($Ni_{0.70}L_{0.30}$-acrylate) (L = Fe, Co, Mn) at 60 °C for 24 h in 100 mL of a 7.4×10^{-5} M initiator solution ($K_2S_2O_8$).

Characterization Techniques. XRD patterns were recorded with a scan step of 0.04° (2θ) for 15 s on a Siemens D5000 diffractometer, equipped with a copper anticathode (Cu Kα) and a diffracted beam monochromator. FTIR spectra were obtained by using a Perkin-Elmer "Spectrum One" spectrophotometer equipped with a diffuse reflectance sphere. The preparation of the samples consisted in dispersing and gently grinding the powder in KBr.

Chemical analyses were performed by inductive coupled plasma (ICP) emission spectroscopy for Ni, Fe, Co, and Mn and by elementary organic microanalysis for C and H, at the CNRS facility in Vernaison.

To perform scanning electronic microscopy (SEM), a 2-nm layer of platinum was deposited cathodically on powder samples. Micrographs were recorded with a Hitachi S4500 field emission microscope with an accelerating voltage of 3 kV.

Results and Discussion

XRD Characterization of Acrylate-Intercalated LDHs. As reported elsewhere in details,[43,45] from a general point

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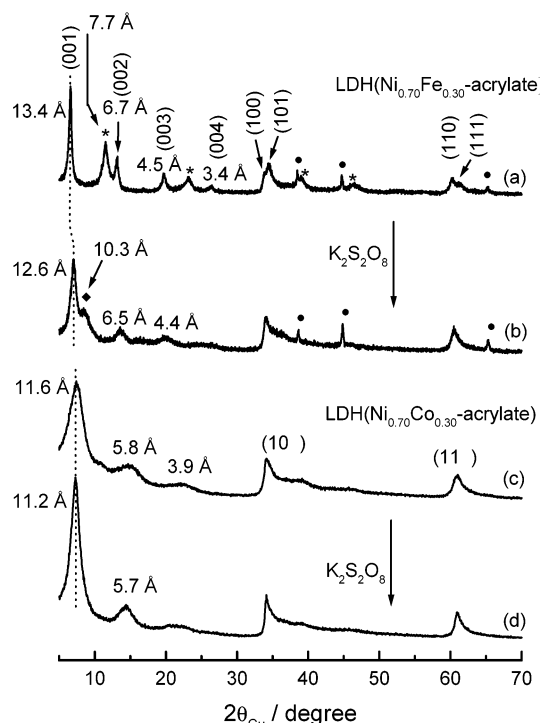(50) Borthomieu, Y. Thesis, University Bordeaux I, 1990.

Figure 1. XRD patterns of LDH($Ni_{0.70}L_{0.30}$-acrylate) (L = Fe, Co) before and after treatment by $K_2S_2O_8$. The distance attributed to the first diffraction line at lowest angles corresponds to the interslab distance. Key: *, lines due to the parasitic LDH($Ni_{0.70}Fe_{0.30}$-CO_3) phase; ◆, lines due to the parasitic LDH($Ni_{0.70}Fe_{0.30}$-S_2O_8 or SO_4) phase; ●, lines due to the sample holder.

of view, the carbonate-inserted LDH phases, prepared by solid-state chemistry and subsequent chimie douce reactions, exhibit rather good crystallinity properties. They crystallize in the trigonal system (S.G.: $R3m$), with a $P3$ structural type, which corresponds to an (AB BC CA) oxygen packing (only the oxygen atoms of the slabs are considered for the packing description).[51] Indexation of the XRD pattern can be performed with a hexagonal cell, with three slabs/cell.

(1) LDH($Ni_{0.70}Fe_{0.30}$-acrylate). (a) Material before Treatment by $K_2S_2O_8$. The XRD pattern of the LDH($Ni_{0.70}Fe_{0.30}$-acrylate) phase, obtained through the solid-state/chimie douce method, is displayed in Figure 1a. It shows the coexistence of two phases. As indicated in Figure 1a, the indexation of the XRD lines of the first phase (reported in the figure) is performed with a hexagonal cell, with a necessary one slab/cell, the cell parameters being $a = 3.07$ Å and $c = 13.4$ Å. The interreticular distance of the (001) first diffraction peak corresponds to the interslab distance of 13.4 Å. This value, consistent with already reported values for acrylate guest molecules (13.8 Å for LDH(MgAl)[29] and 13.6 Å for LDH(NiFe)[40]), suggests that the intercalation of acrylate anions within the interslab space is effective in our material. The other (002), (003), and (004) peaks can also be observed, which shows that the lamellar character of the material is very pronounced. Although air was carefully excluded from the reactor and water decarbonated, a second LDH phase is detected, with a shorter interlayer distance of 7.7 Å and corresponding to LDH($Ni_{0.70}Fe_{0.30}$-carbonate), as confirmed by IR spectroscopy, presented in a forthcoming section.

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Indexation of this phase can be performed with a hexagonal cell, with three slabs/cell (hexagonal parameters: $a = 3.07$ Å and $c = 23.03$ Å). The total exclusion of carbonate anions from the interslab space of LDHs is known to be difficult, because of the small size of a carbonate anion versus its charge.[29,37,52]

(b) Material after Treatment by K₂S₂O₈. Interslab polymerization was attempted by thermally treating the LDH phases in the presence of potassium persulfate. The use of this water-soluble initiator for such a purpose has already been reported.[29,31,40] After treatment by $K_2S_2O_8$, the color of the material is unchanged (orange), which suggests that the obtained phase is still a reduced one. Indeed, if the pristine material had been oxidized by $K_2S_2O_8$ into γ-oxide hydroxide, its color would have turned black. Moreover, the quantity of $K_2S_2O_8$ is insufficient to oxidize the whole material into γ-oxide hydroxide.

The XRD patterns of LDH($Ni_{0.70}Fe_{0.30}$-acrylate) before and after treatment by $K_2S_2O_8$ can be compared in Figure 1a,b. The treatment by $K_2S_2O_8$ induces a strong broadening of the XRD lines. Two phases, respectively with 12.6 and 10.3 Å interlamellar distances, are observed. The interslab distance of the major LDH phase decreases from 13.4 Å to 12.6 Å, the latter value being close to that obtained for direct intercalation of polyacrylate anions into LDH phases (12 Å for LDH(MgAl) and 12.4 Å for LDH(CaAl) and LDH(ZnAl)).[37] Besides, the (10l) and (11l) lines, observed in the 33−45 and 60−65° ($2\theta_{Cu}$) ranges for the pristine LDH($Ni_{0.70}Fe_{0.30}$-acrylate) phase, are replaced by two large and asymmetric bands. The position of the (11l) band, corresponding to the metal−metal semidistance within the slab, is unchanged, showing that the resulting phase is still a reduced one, in accordance with the unchanged color of the material, and confirming, thus, the nonoxidation of the slab metallic ions within the pristine LDH($Ni_{0.70}Fe_{0.30}$-acrylate) by $K_2S_2O_8$. Large and asymmetric bands were already observed for LDHs containing large metavanadate chains, and it was established that they result from microdistortions within the slabs, due to the electrostatic interactions being difficult to accommodate between the long chains and the slabs.[44] In the present case, the broadening of the lines in bands could suggest successful polymerization of the acrylate entities; the carboxylate functions of the macromolecules would have to face, locally, the slab trivalent cations that are responsible for the positive charge excess. Such a hypothesis will be confirmed by IR spectroscopy. Near the principal peak corresponding to a 12.6 Å distance, another line is observed, corresponding to a 10.3 Å distance. This line was not present in the XRD pattern of the pristine material, which instead exhibits diffraction peaks that correspond to LDH($Ni_{0.70}Fe_{0.30}$-CO_3). This evolution may correspond to the exchange of the carbonate anions, present in the interslab space of the pristine material, for persulfate or sulfate anions. Indeed, the intercalation of $S_2O_8^{2-}$ anions into a LDH($Ni_{0.70}Fe_{0.30}$) phase, carried out in the laboratory,[53] as well as of a sulfate bilayer,[54]

leads to interslab distances around $10-11$ Å. This possible evolution is supported by a previous study, performed in our laboratory, which had shown that, in such experimental polymerization conditions, the carbonate anions present in the pristine phase were exchanged for sulfate anions. Nevertheless, in the latter case, the interslab distance of the final phase was close to 9 Å, probably as a result of a monolayer arrangement of the sulfate anions.[40]

(2) LDH($Ni_{0.70}Co_{0.30}$-acrylate). Following the same experimental procedure, a cobalt-substituted nickel hydroxide was synthesized. Strong differences were observed in comparison with iron-substituted material, right from the monomer intercalation. The overall shapes of the XRD patterns before and after treatment by $K_2S_2O_8$, reported in Figure 1c,d, respectively, are very similar to each other and to the diagram obtained for the iron-based material after polymerization. The diffraction peaks are broader and less well-defined than in the case of the starting LDH($Ni_{0.70}Fe_{0.30}$-acrylate) phase. Only one phase is observed, compared to two phases in the case of iron-based LDH, with an interslab spacing of 11.6 Å rather than 13.4 Å for the iron-substituted phase. The presence of the second and third order (00l) diffraction peaks should also be noted. The shape of the lines, in the 33−45 and 60−65° ($2\theta_{Cu}$) ranges (broad and asymmetric), can be attributed, as for the iron-based phase, to microdistortions within the slabs.

After treatment by $K_2S_2O_8$, a pure phase is obtained (Figure 1d), contrary to the case of the iron-based phase. No parasitic LDH($Ni_{0.70}Co_{0.30}$-SO_4) or LDH($Ni_{0.70}Co_{0.30}$-S_2O_8), characterized by a diffraction line at around $9-10$ Å, is detected. Moreover, the contraction of the interslab distance (11.6 to 11.2 Å) is weaker than for the iron-based phases (13.4 to 12.6 Å).

As a result of these observations, it would appear that a spontaneous polymerization reaction occurs simultaneously to the acrylate intercalation process.

(3) LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#] and LDH($Ni_{0.70}Co_{0.30}$-acrylate)[#]. As previously mentioned, the preparation of the starting $NaNi_{0.70}Mn_{0.30}O_2$ nickelate by a solid state reaction is not possible, so that the manganese-substituted LDH was first prepared using the coprecipitation method.[48,49] XRD patterns, presented in Figure 2, show the relation among the obtained LDH($Ni_{0.70}Mn_{0.30}$-CO_3)[#] phase, manganese-based γ-oxide hydroxide, and LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#] before treatment by $K_2S_2O_8$ and LDH($Ni_{0.70}Mn_{0.30}$)ref[#]. XRD patterns of the reduced phases, obtained in the presence of acrylate anions (Figure 2d) or their absence (Figure 2c), are almost similar. The indexation of the XRD patterns must be performed with a hexagonal cell, with three slabs/cell, as indicated in Figure 2. The hexagonal parameters are $a = 3.06$ Å and $c = 22.8$ Å for LDH($Ni_{0.70}Mn_{0.30}$-CO_3)[#], $a = 3.05$ Å and $c = 22.9$ Å for LDH($Ni_{0.70}Mn_{0.30}$)ref[#], and $a = 3.07$ Å and $c = 23.5$ Å for LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#]. The general shape of the LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#] XRD patterns (Figure 2d) looks like that obtained for a phase

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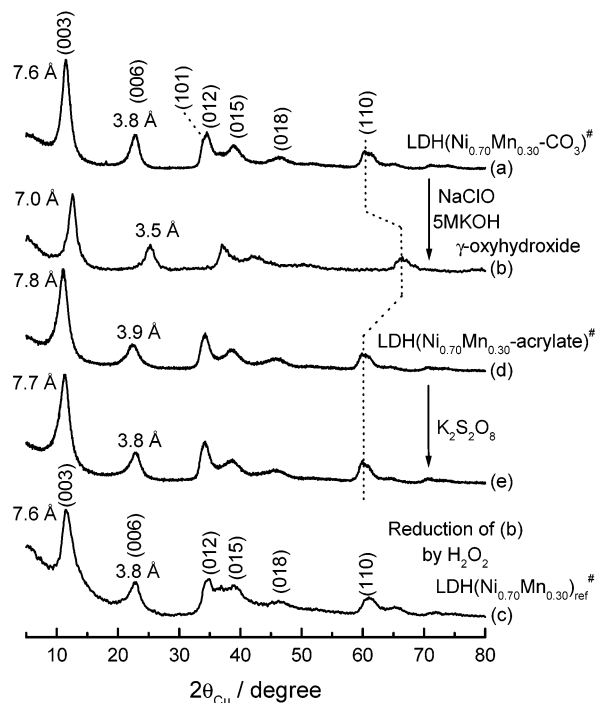
Figure 2. XRD patterns of (a) LDH(Ni$_{0.70}$Mn$_{0.30}$-CO$_3$)$^\#$, (b) γ-oxide hydroxide, (c) LDH(Ni$_{0.70}$Mn$_{0.30}$)$_{ref}$$^\#$, and LDH(Ni$_{0.70}Mn_{0.30}$-acrylate)$^\#$ (d) before and (e) after treatment by K$_2$S$_2$O$_8$.

Figure 3. XRD patterns of LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate)$^\#$ before and after treatment by K$_2$S$_2$O$_8$.

containing intercalated carbonate anions, the interslab distance being indeed 7.8 Å before being treated by K$_2$S$_2$O$_8$. It may be wondered whether carbonate ions could not be inserted into the material instead of the target acrylate entities. The answer will be given in a forthcoming section.

To better understand the fact that the interslab distance is 7.8 Å for LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$ (compared to 11.6−13.4 Å for the phases prepared by the solid-state/chimie douce route), a homologous LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate)$^\#$ was prepared by means of the same coprecipitation route. The XRD pattern of this phase before being treated by K$_2$S$_2$O$_8$ is reported in Figure 3. As in the case of LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$, the indexation of the XRD pattern can be performed with a hexagonal cell, with three slabs/cell. The hexagonal parameters are $a = 3.04$ Å and $c = 23.3$ Å.

In the case of LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$ and LDH-(Ni$_{0.70}$Co$_{0.30}$-acrylate)$^\#$, the XRD patterns are very similar before and after treatment by K$_2$S$_2$O$_8$, which suggests that no change was induced by the attempted polymerization treatment (Figures 2e and 3b).

Chemical Analysis. In the case of the iron-substituted material, the presence of the parasitic LDH(Ni$_{0.70}$Fe$_{0.30}$-CO$_3$) and LDH(Ni$_{0.70}$Fe$_{0.30}$-S$_2$O$_8$ or SO$_4$) phases prevents any quantitative determination of the chemical formula on the basis of chemical analysis. Meanwhile, elemental analysis, performed for LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate) after treatment by K$_2$S$_2$O$_8$, allowed us to determine its chemical composition (Table 1). It should be noticed that, in this material family, the nickel ions are divalent, while the cobalt ions are trivalent.[55] As the cobalt-based phase is pure (no parasitic
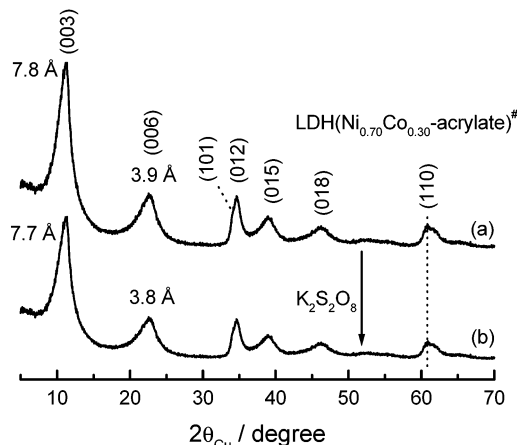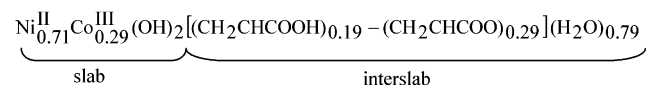
LDH(Ni$_{0.70}$Co$_{0.30}$-CO$_3$) phase), the carbon can be considered only as belonging to the organic acrylate species. The Co/(Ni + Co) ratio is very close to the nominal one, used for the material preparation. The value of the C/(Ni + Co) ratio (1.43) leads to 0.48 acrylate monomer unit/formula element. The achievement of the electroneutrality within the material requires that a 0.29 negative charge must be brought by polyacrylate anions, the other part (0.19) having to be protonated or, eventually, grafted to the slabs. But, as mentioned in the next section, an anion exchange of macromolecules for carbonate anions was successful, making the grafting unnecessary. The following formula can be proposed, on the basis of the data gathered in Table 1:

$$\underbrace{Ni^{II}_{0.71}Co^{III}_{0.29}(OH)_2}_{\text{slab}}\underbrace{[(CH_2CHCOOH)_{0.19}-(CH_2CHCOO)_{0.29}](H_2O)_{0.79}}_{\text{interslab}}$$

Elemental analysis of the LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$ phase is presented in Table 1, compared to the chemical analysis of the pristine carbonate phase. The C/(Ni + Mn) atomic ratio is three times higher in the LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$ phase than in the pristine LDH(Ni$_{0.70}$Mn$_{0.30}$-CO$_3$)$^\#$ phase (0.99 versus 0.31 respectively) (Table 1), confirming thus that acrylate anions are intercalated in the interslab space. This leads to 0.33 acrylate monomer units/metallic cation. The fact that the interslab distance is 7.8 Å for LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$ versus 13.4 Å for LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate) suggests that the acrylate anions are differently arranged in the interslab space of both materials. In LDH(Ni$_{0.70}$Mn$_{0.30}$-acrylate)$^\#$, the thickness of the acrylate anion seems to correspond to the diameter of an oxygen anion, as in the case of the carbonate anion, which suggests that the acrylate entities may be parallel to the slabs. Nevertheless, the maximum acrylate entities which can be intercalated, parallel to the slabs, is 0.35 anion/metallic cation of the slabs; this value is calculated by assuming approximately 5.7 × 5.3 Å^2 dimensions, calculated with the Cerius^2 4.0 program.[56] But, as mentioned in a previous study
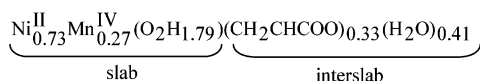
(55) Delmas, C.; Borthomieu, Y.; Faure, C.; Delahaye, A.; Figlarz, M. *Solid State Ionics* **1989**, *32/33*, 104.

(56) *Cerius^2 4.0 Quantum Mechanic Chemistry*; Molecular Simulations Inc.: San Diego, CA, 1998.

Table 1. Chemical Analysis and Values of the A/(Ni + L) (L = Co, Mn) Molar Ratios for Various Elements in the LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate), LDH(Ni$_{0.70}$L$_{0.300}$-acrylate)$^{\#}$ (L = Mn, Co), and LDH(Ni$_{0.70}$Mn$_{0.30}$-CO$_3$)$^{\#}$ Phases

| | | A | | | | acrylate motifs | |
		Ni	L	C	H	per Ni + L	attempted formula
LDH(Ni$_{0.70}$Co$_{0.30}$-polyacrylate)	wt %	28.8	12.0	11.9	3.6	0.48	Ni$_{0.71}$^{II}Co$_{0.29}$^{III}(OH)$_2$[(CH$_2$CHCOOH)$_{0.19}$-
	at. A/(Ni + L)	0.71	0.29	1.43	5.22		(CH$_2$CHCOO)$_{0.29}$](H$_2$O)$_{0.79}$
	theoret wt %	29.5	12.1	12.2	3.7		
LDH(Ni$_{0.70}$Mn$_{0.30}$-polyacrylate)$^{\#}$	wt %	33.3	11.3	9.2	2.8	0.33	Ni$_{0.73}$^{II}Mn$_{9.27}$^{IV}(O$_2$H$_{1.79}$)(CH$_2$CHCOO)$_{0.33}$(H$_2$O)$_{0.41}$
	at. A/(Ni + L)	0.73	0.27	0.99	3.60		
	theoret wt %	34.8	12.1	9.7	3.0		
LDH(Ni$_{0.70}$Mn$_{0.30}$- CO$_3$)$^{\#}$	wt %	29.2	12.1	2.6	2.5		Ni$_{0.69}$^{II}Mn$_{0.31}$^{IV}(OH)$_2$(CO$_3$)$_{0.31}$(H$_2$O)$_{0.74}$
	at. A/(Ni + L)	0.69	0.31	0.31	3.47		
	theoret wt %	30.7	13.2	2.9	2.7		
LDH(Ni$_{0.70}$Co$_{0.30}$-polyacrylate)$^{\#}$	wt %	28.8	12.7	7.4	3.0	0.29	Ni$_{0.69}$^{II}Co$_{0.31}$^{III}(OH)$_2$(CH$_2$CHCOO)$_{0.29}$(H$_2$O)$_{0.70}$
	at. A/(Ni + L)	0.69	0.31	0.98	4.23		
	theoret wt %	29.9	13.6	7.9	3.4		

on manganese-based LDHs intercalated with carbonate anions[48,49] and confirmed here by titration, the oxidation state of manganese ions in these compounds is +4. This means that, for steric reasons, the charge compensation cannot be performed only by anionic insertion. This consideration leads us to assume the existence of proton deficiency in the slabs and to propose the following formula:

$$\underbrace{Ni^{II}_{0.73}Mn^{IV}_{0.27}(O_2H_{1.79})}_{slab}\underbrace{(CH_2CHCOO)_{0.33}(H_2O)_{0.41}}_{interslab}$$

In the case of LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate)$^{\#}$, the chemical analysis confirms the presence of intercalated acrylate species, the C/(Ni + Co) ratio being 0.87, which corresponds to 0.29 acrylate monomer unit/metallic cation of the slab (Table 1). The proposed formula is thus

$$\underbrace{Ni^{II}_{0.69}Co^{III}_{0.31}(OH)_2}_{slab}\underbrace{(CH_2CHCOO)_{0.29}(H_2O)_{0.70}}_{interslab}$$
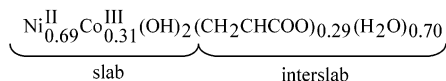
The amount of hydroxyl (1.98), determined from the experimental data, has been rounded to 2.

IR Spectroscopy Study. (1) Materials Prepared by the Solid-State/Chimie Douce Route. (a) Iron-Based Materials. The IR spectrum of the LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate) material is reported in Figure 4a. It confirms the presence of intercalated acrylate anions; in particular, the band, corresponding to the C=C valence vibration (ν(C=C)), is observed at 1638 cm^{-1}. The complete assignation is gathered in Table 2 and is consistent with that of sodium acrylate, as previously described elsewhere.[57] The strong vibration band, observed around 1360 cm^{-1} and assigned to the "CH bending" mode of acrylate anions, also corresponds to the ν_3(CO$_3$) vibration band. The strong intensity of the observed band is consistent with the presence of carbonate anions in the material and the XRD observation of a parasitic LDH(Ni$_{0.70}$Fe$_{0.30}$-CO$_3$) phase. In the LDH, the absence of some vibration frequencies generally associated with sodium acrylate probably results from the constrained environment surrounding acrylate anions, which are involved in a hydrogen-bond network with the hydroxide slabs and the water molecules.
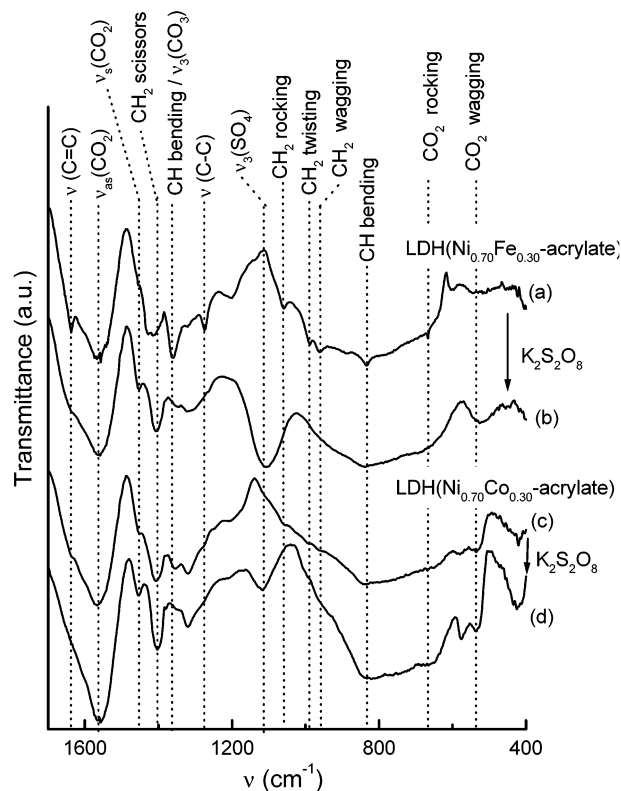
(57) Feairheller, W. R.; Katon, J. E. *Spectrochim. Acta* **1967**, *23A*, 2225–2232.

Figure 4. IR spectra of LDH(Ni$_{0.70}$L$_{0.30}$-acrylate) (L = Fe, Co) before and after treatment by K$_2$S$_2$O$_8$.

IR spectroscopy investigation of the LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate) material after treatment by K$_2$S$_2$O$_8$ shows the disappearance of the bands associated with the C=C double bonds at 1638 cm^{-1}, all the other bands still being present (Figure 4b) with a lower intensity. This confirms the chain polymerization of intercalated acrylate monomers within the interslab space of the LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate) phase. Moreover, the appearance of a large band around 1100 cm^{-1}, having a strong intensity and assigned to the ν_3(SO$_4$) vibration, confirms the presence of sulfate or persulfate anions. The presence of a unique band, corresponding to ν_3(SO$_4$) vibration, does not allow any definite conclusion to be drawn regarding the nature of the parasitic phase, LDH(Ni$_{0.70}$Fe$_{0.30}$-SO$_4$) or LDH(Ni$_{0.70}$Fe$_{0.30}$-S$_2$O$_8$). Simultaneously, the band at 1361 cm^{-1}, resulting from the superimposition of the ν_3(CO$_3$) vibration band and the "CH bending" vibration band, strongly decreases. This result

Table 2. Assignment of the Different Vibration Bands of the LDHs before and after Treatment by $K_2S_2O_8$

assgnt	sodium acrylate (cm^{-1})	Fe-based LDH		Co-based LDH		Mn-based LDH[#]		Co-based LDH[#]	
		before $K_2S_2O_8$	after $K_2S_2O_8$	before $K_2S_2O_8$	after $K_2S_2O_8$	before $K_2S_2O_8$	after $K_2S_2O_8$	before $K_2S_2O_8$	after $K_2S_2O_8$
$\nu(C=C)$	1640	1638							
$\nu_{as}(CO_2)$	1540–1570	1549	1559	1565	1559	1559	1568	1558	1556
$\nu_s(CO_2)$	1450	1453	1455	1454	1455	1451	1456	1454	1453
CH_2 scissors	1430	1420	1405	1407	1406	1414	1406	1399	1405
CH bending	1368	1361	1354	1356	1356	1357	1355	1358	1357
$\nu(C-C)$	1285	1275		1274			1275		
CH_2 rocking	1055	1062		1061		1060	1040	1039	1039
CH_2 twisting	991	990		991		991		990	
CH_2 wagging	962	960		956		941	941		
CO_2 deformatn	902								
CH bending	837	832	840	834	839	833	834	834	839
CO_2 rocking	663	660	660	660	660	656	653	656	654
CO_2 wagging	526	529	531	530	530			531	534

confirms the transformation of the parasitic LDH($Ni_{0.70}Fe_{0.30}$-CO_3) phase, initially observed, into the parasitic LDH-($Ni_{0.70}Fe_{0.30}$-SO_4) or LDH($Ni_{0.70}Fe_{0.30}$-S_2O_8) phase.

(b) Cobalt-Based Materials. The IR spectra of the LDH($Ni_{0.70}Co_{0.30}$-acrylate) phase before and after being treated by $K_2S_2O_8$ are reported in Figure 4c,d, respectively. The overall shape of the spectrum of LDH($Ni_{0.70}Co_{0.30}$-acrylate) before treatment by $K_2S_2O_8$ is very similar to that observed for LDH($Ni_{0.70}Fe_{0.30}$-acrylate) after treatment by $K_2S_2O_8$; most of the acrylate-related infrared bands are present (Table 2). The band associated with the C=C double bond is barely detected before treatment by $K_2S_2O_8$ and has completely disappeared after treatment. This observation allows to conclude on the spontaneous polymerization of the acrylate monomers, simultaneously to their intercalation in the interslab space of the LDH. This result is confirmed by the fact that the intensities of the acrylate-related infrared bands are weaker than for the iron-based phase before treatment by $K_2S_2O_8$. Besides, the $\nu_3(CO_3)$ vibration band, superimposed on the "CH bending" one, is not very intense, confirming the absence of a parasitic LDH($Ni_{0.70}Co_{0.30}$-CO_3) phase. After treatment by $K_2S_2O_8$, the intensity of the $\nu_3(SO_4)$ vibration band is much weaker than in the case of the iron-based material. This result shows that a small number of sulfate or persulfate entities is co-intercalated in the interslab space, in agreement with the absence of any diffraction peak around 10 Å in the XRD pattern of the LDH($Ni_{0.70}Co_{0.30}$-acrylate) after treatment by $K_2S_2O_8$.

(2) Materials Prepared by the Coprecipitation/Chimie Douce Route. (a) Manganese-Based Materials. The IR spectra of the reduced phases, obtained from the manganese-based oxide hydroxide, are gathered in Figure 5. The IR spectrum of LDH($Ni_{0.70}Mn_{0.30}$)$_{ref}$[#] reveals a $\nu_3(CO_3)$ vibration band around 1360 cm^{-1}, having a relatively significant intensity (Figure 5e). This behavior results from the exchange of some OH^- anions for carbonate anions while LDH($Ni_{0.70}Mn_{0.30}$)$_{ref}$[#] was in the reducing solution.[50] On the contrary, the $\nu_3(CO_3)$ vibration band is not observed in the spectrum of the phase containing intercalated acrylate anions (LDH($Ni_{0.70}Mn_{0.30}$-acrylate)[#]) (Figure 5a). Moreover, the IR spectrum of this phase before treatment by $K_2S_2O_8$ contains the vibration bands of acrylate with weak intensity (Table
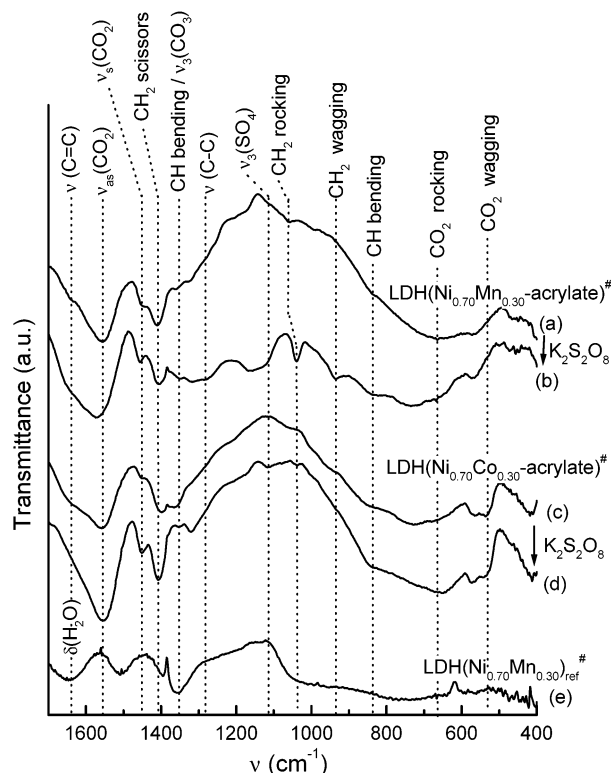
Figure 5. IR spectra of LDH($Ni_{0.70}L_{0.30}$-acrylate)[#] (L = Mn, Co) before and after treatment by $K_2S_2O_8$ and of LDH($Ni_{0.70}Mn_{0.30}$)$_{ref}$[#].

2), the $\nu(C=C)$ vibration band being barely detected (Figure 5a). The overall results seem to show that spontaneous polymerization occurs simultaneously to the intercalation step, as in the case of LDH($Ni_{0.70}Co_{0.30}$-acrylate) before treatment by $K_2S_2O_8$. Besides, the $\nu_3(SO_4)$ vibration band is detected after treatment by $K_2S_2O_8$ but with a weak intensity (Figure 5b). This result shows that the concentration of sulfate or persulfate anions within the interslab space is lower than in the LDH($Ni_{0.70}Fe_{0.30}$-acrylate) phase.

(b) Cobalt-Based Materials. The IR spectrum of LDH-($Ni_{0.70}Co_{0.30}$-acrylate)[#] before treatment by $K_2S_2O_8$ confirms the absence of carbonate anions in the interslab space, the intensity of the $\nu_3(CO_3)$ band around 1360 cm^{-1} being very weak (Figure 5c). Besides, the $\nu(C=C)$ band is barely visible. After treatment by $K_2S_2O_8$, the $\nu(C=C)$ band has disappeared

and the $\nu_3(SO_4)$ vibration band was barely detected, compared to the one observed for LDH(Ni$_{0.70}$Co$_{0.30}$-polyacrylate) prepared by the solid-state/chimie douce route. This result is probably due to a higher congestion of the interslab space in LDH(Ni$_{0.70}$Co$_{0.30}$-acrylate)$^\#$ than in the case of LDH-(Ni$_{0.70}$Co$_{0.30}$-acrylate), resulting from the anion arrangement, parallel to the slabs, which could limit the intercalation of sulfate or persulfate anions.

As a result of this study, it appears that spontaneous polymerization reaction occurs simultaneously to the acrylate intercalation process for cobalt- and manganese-based materials, contrary to the iron-based material, for which the phase containing intercalated acrylate monomers was isolated. Hydrogen peroxide, as a reducing agent during this intercalation step, is not involved in this spontaneous polymerization because it does not allow one to initiate the acrylate polymerization, under these conditions of concentration, temperature, and duration.[40] Nevertheless, we are not able to explain the difference in polymerization behavior between the iron-based material and the cobalt- and manganese-based materials.

Scanning Electron Microscopy Experiments. The differences of the interslab distance and of the carbon ratio between LDHs prepared by the solid-state/chimie douce and by the coprecipitation/chimie douce route indicate that the first step (solid-state reaction or coprecipitation) has a strong influence on the macromolecule interslab amount and arrangement. Indeed, only the first step is different in the preparation route of LDHs. SEM images reveal that texture and particle size are different for the two preparation routes (Figure 6). The particles of acrylate-intercalated LDHs (whatever the slab-substituting cation), obtained by solid-state reaction in the first step, are about 5 μm in diameter and well-defined in shape, with angular outlines and a slightly exfoliated texture, which results from its intercalation/deintercalation history (Figure 6a,b). LDHs obtained from coprecipitation as the first step consist of strongly aggregated particles (Figure 6c,d). These morphological differences could influence the intercalation kinetics of acrylate entities in the interslab space of the LDHs.

In the case of phases prepared by the coprecipitation/chimie douce route, the fact that the particles are smaller brings up the question of a possible adsorption of a nonnegligible quantity of acrylate species at the grain surface. Actually, the powders are washed with bidistilled water before their drying and characterization, which allows one to put back the adsorbed species (if there are any) into the solution. Besides, if the majority of acrylate anions were adsorbed, the charge compensation into the material would be problematic and the intercalation of another anion, probably a carbonate anion, would be necessary. However, no carbonate anion is detected by IR spectroscopy, which proves that acrylate entities are truly intercalated.

Anion Interslab Arrangement. (1) LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate). From a general point of view, the interslab space thickness can be calculated by subtracting the hydroxide slab thickness from the observed interslab distance, deduced from the c parameter. Assuming a 4.6 Å slab thickness, like for
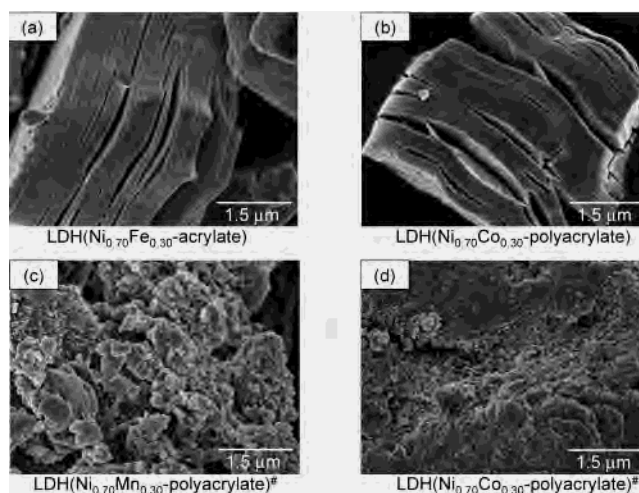
Figure 6. SEM photographs of various LDHs, before K$_2$S$_2$O$_8$ treatment: (a) LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate); (b) LDH(Ni$_{0.70}$Co$_{0.30}$-polyacrylate); (c) LDH(Ni$_{0.70}$Mn$_{0.30}$-polyacrylate)$^\#$; (d) LDH(Ni$_{0.70}$Co$_{0.30}$-polyacrylate) $^\#$.

β(II)-Ni(OH)$_2$, the 13.4 Å observed interslab distance for LDH(Ni$_{0.70}$Fe$_{0.30}$-acrylate) before treatment by K$_2$S$_2$O$_8$ leads to a 8.8 Å interslab thickness. This value is higher than the length of acrylate molecules in complete extension (about 6 Å, calculated on the basis of simulations with the Cerius^2 4.0 program[56]). The interslab distance can therefore be supposed as resulting from a bilayer arrangement, schematized in Figure 7a. The acrylate anions would be disposed to have their double bonds around the center of the interslab space, and the carboxylate groups would face the inorganic slabs. The basal spacing would result from the balance of the electrostatic attractions between the slabs and the electrostatic repulsion between C=C double bonds.[40]

(2) LDH(Ni$_{0.70}$L$_{0.30}$-polyacrylate)$^\#$ (L = Co, Mn). In the case of materials containing intercalated polyacrylate species, the interslab distance depends on the preparation route (around 12 Å for solid-state/chimie douce reactions or 7.8 Å for coprecipitation/chimie douce reactions). This implies a difference in the macromolecules arrangement in the interslab space. Lerner and co-workers claimed that the interslab distances, obtained for LDH intercalated with polyacrylate anions (around 12 Å), are consistent with those expected for the incorporation of bilayers of anionic polymers.[37] In this case, the carboxylate groups are placed on the same side of the chain, facing one of the inorganic slabs, and the carbon chains are arranged as a planar zigzag in the middle of the interslab space, to minimize the electrostatic repulsion between the hydrophobic and the hydrophilic parts (Figure 7b). However, the 12 Å value for the interslab distance could also correspond to a monolayer of macromolecules, with the carboxylate groups facing the slabs and alternating along the chain, as drawn in Figure 7c. This macromolecule conformation would indeed lead to a theoretical interslab distance of around 12 Å, which is also compatible with the observed interslab distances for LDH(Ni$_{0.70}$L$_{0.30}$-polyacrylate) (L = Fe, Co). However, the bilayer conformation drawn in Figure 7b implies the presence of around two times more acrylate monomer units than the
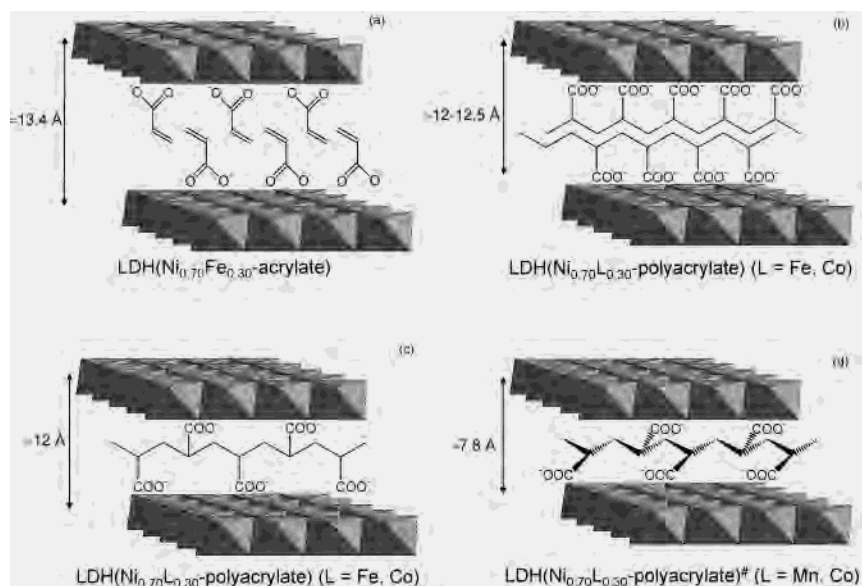
Figure 7. Schematic representation of the hypothetical arrangement of intercalated species in the LDHs: (a) acrylate anions in the LDH($Ni_{0.70}Fe_{0.30}$-acrylate); (b) polyacrylate anions as a bilayer in the LDHs prepared by solid-state/chimie douce reactions; (c) polyacrylate anions as monolayers in the LDHs prepared by solid-state/chimie douce reactions; (d) polyacrylate anions as monolayers in the LDHs prepared by coprecipitation/chimie douce reactions.

monolayer conformation (Figure 7c). The results, which are deduced from the chemical analysis of LDH($Ni_{0.70}Co_{0.30}$-polyacrylate) (Table 1) (0.48 acrylate monomer unit/metallic cation), seem to be more in agreement with the bilayer hypothesis, for which there is 0.50 acrylate monomer unit/metallic cation, than with the monolayer hypothesis (0.25 acrylate monomer unit/metallic cation). These values of 0.25 or 0.50 acrylate monomer unit were established from theoretical formulas, by considering the ratio of the monomer area to that of the slab area. Nevertheless, these hypothetical conformations of polyacrylate anions are idealistic and do not take into account, correctly, the arrangement of chains with regard to one another, parallel to the slab plane. The density of acrylate species can therefore be modulated in the second direction of this plane.

On the contrary, for LDH($Ni_{0.70}L_{0.30}$-polyacrylate)[#] (L = Mn, Co), which are obtained by the coprecipitation/chimie douce route, the observed distances are lower, indicating a different arrangement of the macromolecules in the interslab space. The 7.8 Å observed distance is indeed characteristic of the presence of only one oxygen layer in the interlamellar space. Compared to the configuration drawn in Figure 7c, it could be supposed that there may be a change in the conformation of the macromolecules, to reach a thickness of the carbon chain close to the thickness of an oxygen ion (Figure 7d). This conformation would explain the 7.8 Å interslab distances, observed in these phases. Besides, this hypothesis agrees with the chemical analysis results, which have shown a lower C/(Ni + L) (L = Mn, Co) molar ratio for LDH($Ni_{0.70}L_{0.30}$-polyacrylate)[#], suggesting that these phases contain less acrylate monomer unit than the phases prepared by the solid-state/chimie douce route (around 0.3 versus 0.5).

Conclusion

This study has shown that acrylate anions may be readily intercalated in LDHs deriving from $Ni(OH)_2$ using an original method involving several chimie douce reaction steps. In the case of iron-based LDH, the phase containing intercalated acrylate anions has been isolated and characterized by XRD and IR spectroscopy. Second, interslab free-radical polymerization of acrylate anions has been successfully initiated by sodium persulfate at 60 °C. On the contrary, in the case of cobalt- and manganese-based LDHs, a one-step intercalation/polymerization seems to occur, leading directly to LDHs containing polyacrylate intercalate.

Besides, the first preparation step for the LDHs (solid-state reaction or coprecipitation) seems to have an influence on the arrangement of the macromolecules within the interslab space, leading to different interslab distances: around 12−12.5 Å for the materials prepared by the solid-state reaction/chimie douce route and around 7.8 Å for the materials prepared by the coprecipitation/chimie douce route

Further experiments are currently in progress, in particular for extracting and characterizing the macromolecules, to better understand the polymerization mechanisms. The results will be presented in a forthcoming paper.[58]

(58) Vaysse, C.; Guerlou-Demourgues, L.; Delmas, C.; Duguet, E. *Macromolecules* **2003**, submitted for publication.