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Tentative Mechanisms for Acrylate Intercalation and in Situ Polymerization in Nickel-Based Layered Double Hydroxides

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ABSTRACT: New hybrid organic−inorganic materials, based on polyacrylate macromolecules intercalated into Layered Double Hydroxides (LDHs) deriving from $Ni(OH)_2$, were prepared through an original route made of successive redox exchange reactions (*chimie douce* synthesis). The nature of the substituting metallic cation in the slabs appears to strongly influence monomer intercalation and in situ polymerization mechanisms. So, the phase containing intercalated acrylate monomer anions has been isolated in the case of iron-based LDH and then interslab free-radical polymerization of acrylate anions has been successfully initiated by potassium persulfate. On the other hand, a one-step process occurs in cobalt- and manganese-based LDHs, leading straight to LDHs containing polyacrylate anions. In these last few cases, a free-radical polymerization mechanism is also suggested, but involving a redox initiation step where a few amount of acrylate anions would be oxidized during the intercalation reaction and would lead to the formation of radical carbonium ions. For the first time, in situ polymerized macromolecules have been extracted from interslab spaces by anionic exchange, derivatized into poly(methyl acrylate) and analyzed by size exclusion chromatography. As expected from the above mechanisms, only oligomers have been detected, with weight-average molar masses ranging from 300 to 2900 g/mol vs polystyrene standards.

Introduction

Research efforts in the field of hybrid organic−inorganic materials (HOIM) have been continuously increasing for 15 years, in particular because these materials are attractive candidates for optical devices, separation media, catalysts, sensor coatings, structural materials, etc.[1] The promising family of layered HOIM results basically from the intercalation of organic species into the interslab space of inorganic lamellar lattices. Strategies for intercalating organic macromolecules between the slabs of host materials are mainly as follows: (i) direct intercalation of preformed macromolecules,[2−8] (ii) precipitation of mineral slabs (or restacking after exfoliation) in a macromolecular solution,[9,10] (iii) interslab polymerization of intercalated monomers,[11−15] and (iv) redox intercalative polymerization (RIP).[16−19] In this last case, the intercalation process is accompanied by a spontaneous reduction of the mineral component (Cu^{2+}−fluorohectrorite,[16] FeOCl,[17] V_2O_5,[18] $VOPO_4$, etc.[19]) and a concomitant oxidative polymerization of the monomers, which are pyrrole,[16,17] aniline, etc.[18,19]

Layered double hydroxides (LDHs), known as anionic clays, have also received attention as precursors of HOIM materials.[20] The structure of these materials consists of stacked brucite-type $[M_{1-y}^{II}\ L_y^{III}(OH)_2]$ slabs. The excess positive charge, due to the partial substitution of trivalent cations (L) for divalent cations (M), is compensated by X^{n-} anions, co-intercalated with water molecules within the interslab space. The X^{n-} interlamellar anions amount is thus theoretically directly related to their own negative charge (*n*) and to the concentration of L trivalent cations within the slabs (y). This leads to the following general formula [21,22] $[M_{1-y}^{II}\ L_y^{III}(OH)_2]^{y+}X_{y/n}{}^{n-}[H_2O]_z$, designed in this paper by the shortened formula LDH($M_{1-y}L_y$−X). The structure is stabilized by the electrostatic interactions between the slabs and the X^{n-} anions, as well as by a strong hydrogen bond network between the water molecules, the anions and the slab hydroxyls.

Whereas the intercalation of many organic anions in LDHs, such as carboxylate for example, have been reported in the literature,[20,23] and references given in those references, only some studies deal with the intercalation of macromolecules.[24−36] Their most common preparation routes are the coprecipitation method or the anionic exchange route.[20,37] The coprecipitation method was successfully used for synthesizing intercalate based on LDH(CaAl) and poly(vinyl alcohol),[27−30] poly(acrylic acid), poly(vinylsulfonate) or poly(styrenesulfonate).[32,33] The swelling by acrylonitrile of LDH(MgAl−dodecyl sulfate) and its subsequent polymerization, initiated by benzoyl peroxide was also reported.[25] The anionic exchange route was investigated by Kato and co-workers for intercalating acrylate anions in LDH(MgAl−nitrate),[24] and by Schwarz and co-workers for intercalating 4-styrenesulfonate anions in reconstructed LDH(MgAl).[26] Recently, the synthesis of poly(2-hydroxyethyl methacrylate)/LDH(MgAl−dodecyl sulfate) nanocomposite materials was reported.[38] In such a case, LDH(MgAl−dodecyl sulfate) was delaminated under high mechanical shear in 2-hydroxyethyl methacrylate, and after the free-radical polymerization of the monomer the inorganic component was still in the delaminated form.

A new preparation route of LDH($Ni_{1-y}L_y$) (with L = Co or Fe), decoupling the building of the $Ni_{1-y}L_yO_2$ slabs from the anionic intercalation, was developed in our laboratory a few years ago and applied to the intercala-

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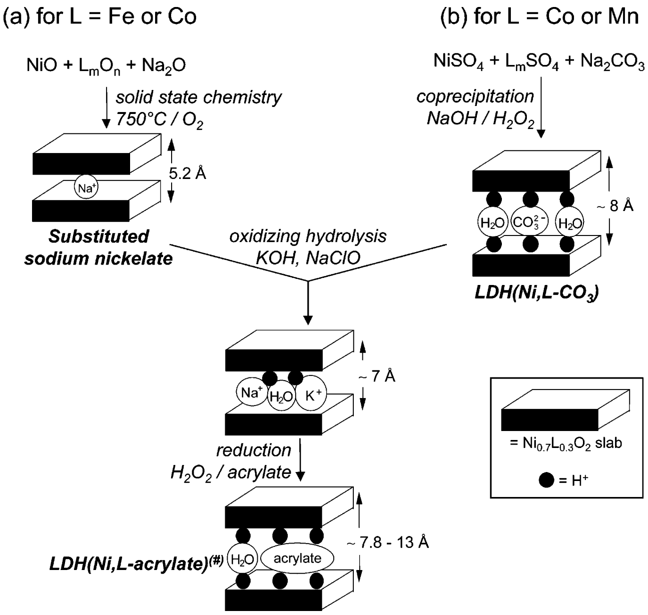

Figure 1. Scheme of the successive reaction steps involved in the preparation of LDHs: (a) route based on solid-state reactions at high temperature and subsequent *chimie douce* reactions; (b) route based on coprecipitation and subsequent *chimie douce* reactions.

tion of inorganic[39−42] and organic anionic species.[35,43] In particular, we have already reported the possibility to intercalate acrylate anions in LDH($Ni_{0.7}Fe_{0.3}$) to perform, in a second stage, their free-radical polymerization through treatment by potassium persulfate $K_2S_2O_8$ at 60 °C. We have also demonstrated the feasibility of the direct intercalation of preformed polyacrylate macromolecules by a similar *chimie douce* route.[35] More recently, the influence of the trivalent cation nature was performed in our lab, with the synthesis and the crystallographic characterization of new phases based on cobalt- and manganese-substituted nickel hydroxide.[43]

The main goals of the present paper consist in reporting new experimental results allowing to propose original mechanisms for acrylate intercalation and in situ polymerization reactions in LDH($Ni_{0.7}L_{0.3}$), depending on the nature of the L metallic cation within the LDH slabs (L = Fe, Co and Mn). Our efforts concerning the deintercalation and the size exclusion chromatography analysis (SEC) of the interslab-polymerized macromolecules are also presented and correlated to the suggested intercalation/polymerization mechanisms.

Experimental Section

The starting materials were analytical reagent grade and used without further purification. Water, decarbonated by bidistillation, was used in all experiments, which were performed under CO_2-free atmosphere.

Preparation of LDH($Ni_{0.7}L_{0.3}$—Acrylate) (L = Fe or Co) by Solid-State Chemistry and Subsequent *Chimie Douce* Reactions. The preparation procedure consists of three successive steps as previously described [35,40,43] (Figure 1a). The $NaNi_{0.7}L_{0.3}O_2$-substituted sodium nickelate was prepared at 750 °C and used as the starting material for the *chimie douce* reactions. The γ-oxyhydroxide was then obtained through hydrolysis of 1 g of sodium nickelate with 100 mL of an oxidizing aqueous solution (5 M KOH/0.8 M NaClO). Its reduction was performed by dropping an excess of 5 M H_2O_2 (1 mL for 1 g of γ-oxyhydroxide) in 100 mL of an aqueous solution of acrylic acid and sodium acrylate (in such proportions that pH was adjusted to 4.3). The dispersion was stirred at room temperature for 1 h, after H_2O_2 addition. The solid phase was then recovered by filtration, washed with decarbonated water and dried at 50 °C under argon flow for 15 h.

Preparation of LDH($Ni_{0.7}L_{0.3}$−Acrylate)[#] (L = Co or Mn) by Coprecipitation and Subsequent *Chimie Douce* Reactions. As the preparation of the starting $NaNi_{0.7}Mn_{0.3}O_2$ nickelate by solid-state reaction is not possible,[44] a precursor LDH($Ni_{0.7}Mn_{0.3}$−CO_3) phase was prepared by the coprecipitation method [45,46] (Figure 1b): 8.02 g of $NiSO_4$ and 2.32 g of $MnSO_4$ precursors (7:3 molar ratio) were dissolved into 100 mL of water and 20 mL of 5 M H_2O_2 was added, to achieve the manganese oxidation in the next step. The precipitation was performed by adding dropwise this solution to 100 mL of a 2 M NaOH aqueous solution containing 4 g of Na_2CO_3. The suspension was vigorously stirred for 4 h, and the solid phase was recovered by filtration, washed with decarbonated water, and dried at 50 °C. The manganese-based γ-oxyhydroxide is obtained by an oxidizing hydrolysis of LDH($Ni_{0.7}Mn_{0.3}$−CO_3) with the same experimental conditions than for iron- or cobalt-based phases. The previously described protocol was then applied to the reduction to LDH($Ni_{0.7}Mn_{0.3}$−acrylate)[#], where the [#] distinguishing symbol means “prepared from an ex-precipitated phase”. A LDH($Ni_{0.7}Co_{0.3}$−acrylate)[#] phase was also prepared according to similar experimental conditions in order to compare both routes.

Tentative in Situ Polymerization. Interslab free-radical polymerization of acrylate monomers was performed by heating 500 mg of LDH($Ni_{0.7}L_{0.3}$−acrylate)[(#)] (L = Fe, Co, Mn) at 60 °C for 24 h in 100 mL of a 7.4×10^{-5} M $K_2S_2O_8$ aqueous solution. The powder was recovered by filtration, washed with decarbonated water, and dried at 50 °C under argon atmosphere for 15 h.

Macromolecule Extraction and Derivatization. The macromolecules were extracted from the interslab spaces through an anionic exchange of polyacrylate anions for carbonate anions. For this purpose, 500 mg of LDH($Ni_{0.7}L_{0.3}$−polyacrylate) (L = Fe, Co, Mn) were dispersed in 50 mL of water containing 4 g of Na_2CO_3. The suspension was vigorously stirred for 4 days at room temperature. The solid phase was recovered by filtration, washed and dried under air atmosphere at 50 °C for 15 h. The X-ray diffraction (XRD) analysis showed that the inorganic is pure and XRD lines are consistent with those of LDH($Ni_{0.7}L_{0.3}$−carbonate) with an interslab space of 7.8 Å. The filtrate was recovered, acidified with H_2SO_4 and water was removed. Poly(acrylic acid) was then extracted in methanol from the salt mixture. The macromolecules, in solution in methanol, were then refluxed in the presence of H_2SO_4 for 48 h, to be derivatized into poly(methyl acrylate), which is soluble in THF for SEC experiments. The efficacy of the treatment was checked with a commercial poly(acrylic acid) ($\overline{M}_w = 5000$ g·mol^{-1}). After derivatization, its molar mass, as determined by SEC, was $\overline{M}_w = 5450$ g·mol^{-1} vs polystyrene standards, demonstrating that the esterification experimental conditions do not affect the molar mass distribution.

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). FTIR spectra were obtained by using a Perkin-Elmer “Spectrum One” spectrophotometer, equipped with a diffuse reflectance sphere; the preparation of the materials consisted in dispersing and gently grinding the powder in KBr.

Macromolecule molar masses were estimated by size exclusion chromatography (SEC) analysis in THF, using polystyrene standard calibration (three-column pack: 25, 150, and 1000 nm). The results are polystyrene equivalent molar masses.

Results and Discussion

Figure 1 displays both synthetic routes used in this study. The route based on a preliminary solid-state reaction (Figure 1a) does not work for manganese derivatives[44] and the second one (Figure 1b) cannot be used for the synthesis of iron-based LDHs because, as far as we know, no common reagent is oxidizing enough to oxidize LDH(NiFe$-$CO$_3$) into the γ-oxyhydroxide phase. Nevertheless, both routes converge quickly with similar last steps consisting of electron-transfer processes (*chimie douce* method). It may be noticed that, in reduced phases (LDH phases), the metal oxidation state are +II for nickel, +III for iron, +III for cobalt, and +IV for manganese, respectively. However, in sodium nickelate, the nickel oxidation state is +III and in the most oxidized phase (γ-oxyhydroxide) the average oxidation state of metal atoms is close to 3.5. These strong variations in the oxidation state of the transition metals do not change the slab formula but do modify the interslab chemical composition for ensuring charge compensations. So, alkaline cations (Na$^+$, K$^+$), protons and anions are successively inserted and exchanged within the interslab space.[39] If the reduction reaction is performed in air without special care, it is well-known that the inserted anions are the small and highly charged CO$_3^{2-}$ anions, originating from the atmospheric CO$_2$.[24,32,47] As a last preliminary comment, it may be noticed that in every nickel-based γ-oxyhydroxide phases used in this study the trivalent cation concentration was adjusted to $y \sim 0.30$. Further experiments, which are not described there, have shown that the amount of intercalated monomer is proportional to y (from 0.20 to 0.50 for iron and from 0.20 to 0.40 for cobalt; outside of theses ranges, corresponding LDHs are not stable). Nevertheless the monomer concentration is negligible upon the intercalation and polymerization stages, and that is why the y parameter will not be varied in this paper.

Iron-Based Material. XRD patterns of the LDH(Ni$_{0.7}$Fe$_{0.3}$$-$acrylate) phase before and after treatment by K$_2$S$_2$O$_8$ are displayed in Figure 2, parts a and b, respectively. As reported elsewhere in details,[43] in the case of the pristine acrylate-intercalated material, the XRD pattern shows the coexistence of two phases, the X-ray diagram of which can be described in the hexagonal system. From a general point of view, for one given LDH phase, the first line at lower 2θ values corresponds to the interslab distance, which is directly affected by the presence and the arrangement of any guest intercalated species. As indicated in Figure 2a, the minority phase exhibits an interslab distance of 7.7 Å, which is attributed to a parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) phase, although air was carefully excluded and water decarbonated in any experiments. The interslab distance of the majority phase is close to 13.4 Å. This value is consistent with already reported values for identical guest molecules (13.8 Å for LDH(MgAl)[24] and 13.6 Å for LDH(NiFe)[35]).

Interslab polymerization of acrylate monomers was attempted by thermal treatment of the LDH phase in the presence of potassium persulfate. The obtained phase is still a reduced one, as suggested by the unchanged color of the phase (orange) and checked by chemical titration. Indeed, K$_2$S$_2$O$_8$, which is an oxidant, could have oxidized the pristine material into γ-oxyhydroxide, although this phase was in excess. The appearance of a black phase, such as γ-oxyhydroxide, was not observed. The XRD pattern exhibits the presence of two new phases, with an interslab distance of 12.6 Å for the majority phase and 10.3 Å for the minority one (Figure 2b). This 12.6 Å distance is consistent with those obtained for direct intercalation of polyacrylate anions into LDH phases (12 Å for LDH(MgAl), 12.4 Å for LDH(CaAl) and LDH(ZnAl),[32] and 12.6 Å for LDH(NiFe)[35]). So, the interslab distance of the majority pristine LDH phase decreases from 13.4 to 12.6 Å. Besides, as shown by the absence of any peak at 7.7 Å, the parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) detected with the pristine phase has disappeared. Indeed, a preliminary study showed that, in these experimental conditions, persulfate or sulfate anions, originating from the potassium persulfate initiator may be anionically exchanged with carbonate anions in LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) and lead to the formation of LDH(Ni$_{0.7}$Fe$_{0.3}$$-SO_4$ or S$_2$O$_8$), whose the interslab distance is in the 9$-$10.3 Å range.[35] So, the parasitic phase detected after K$_2$S$_2$O$_8$ treatment is probably the result of anionic exchange reactions in the pristine parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) phase.

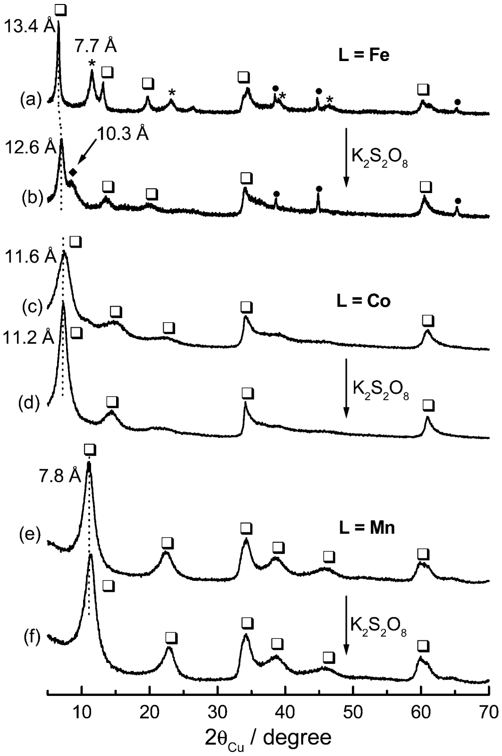

Figure 2. XRD patterns of LDH(Ni$_{0.7}$Fe$_{0.3}$$-$acrylate) (a) before and (b) after treatment with K$_2$S$_2$O$_8$ at 60 °C; LDH(Ni$_{0.7}$Co$_{0.3}$$-$acrylate) (c) before and (d) after treatment with K$_2$S$_2$O$_8$ at 60 °C; LDH(Ni$_{0.7}$Mn$_{0.3}$$-$acrylate)$^{\#}$ (e) before and (f) after treatment by K$_2$S$_2$O$_8$ at 60 °C. The distance attributed to the first diffraction line at lowest angles corresponds to the interslab distance. Key: (□) lines due to the majority LDH(Ni$_{0.7}$L$_{0.3}$$-$acrylate) phase; (∗) lines due to the parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) phase; (◆) lines due to the parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-S_2O_8$) or LDH(Ni$_{0.7}Fe_{0.3}$$-SO_4$) phases; (●) lines due to the aluminum sample holder.

All these interpretations from the XRD patterns are in agreement with the IR spectra presented in Figure 3, parts a and b. Indeed, the vibration bands, characteristic of the acrylate anion, have been observed in the pristine material, such as the band assigned to ν(C=C) at 1638 cm^{-1} (Figure 3a). The band, in the range of 1360 cm^{-1} may be attributed to the CH bending mode of acrylate anions, but its strong intensity is more readily explained by the ν_3(CO$_3$) band resulting from the presence of the parasitic LDH(Ni$_{0.7}$Fe$_{0.3}$$-CO_3$) phase. After treatment by K$_2$S$_2$O$_8$, the ν(C=C) band has disappeared, while all the other bands are still present (Figure 3b), consistently with a complete acrylate polymerization within the interslab spaces. The anionic exchange reaction between carbonate ions and sulfate

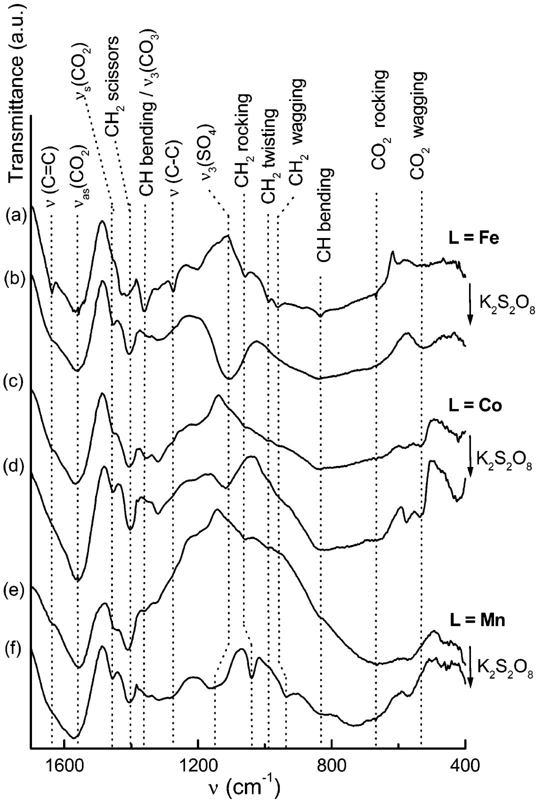

Figure 3. IR spectra of LDH($Ni_{0.7}Fe_{0.3}$−acrylate) (a) before and (b) after treatment with $K_2S_2O_8$ at 60 °C; LDH($Ni_{0.7}Co_{0.3}$−acrylate) (c) before and (d) after treatment with $K_2S_2O_8$ at 60 °C; LDH($Ni_{0.7}Mn_{0.3}$−acrylate)$^{\#}$ (e) before and (f) after treatment by $K_2S_2O_8$ at 60 °C.

or persulfate anions is confirmed by the strong decrease of the $\nu_3(CO_3)$ band at 1360 cm^{-1} and the appearance of the very strong $\nu_3(SO_4)$ band in the range of 1100 cm^{-1}.

Cobalt-Based Material. As shown by XRD patterns (Figure 2, parts c and d) and IR spectra (Figure 3, parts c and d), strong differences may be observed in the behavior of cobalt-based LDHs in comparison with the iron-substituted material. First, the absence of any carbonate parasitic phase, which would coexist with the pristine or $K_2S_2O_8$-treated phases must be noticed. Second, the band corresponding to the ν(C═C) vibration is much slighter for the cobalt-based pristine material (Figure 3c) than for the iron-based pristine material (Figure 3a). Last, the thermal treatment in the presence of $K_2S_2O_8$ does not seem to have noticeable effect on the structure and the chemical composition of the cobalt-based LDH: the contraction of the interslab distance from 11.6 to 11.2 Å is weaker than that for the iron-based material, no sulfate or persulfate parasitic phase is detected on XRD pattern and only a slight band assigned to $\nu_3(SO_4)$ is observable on the IR spectrum (Figure 3d). These observations suggest that the most part of acrylate molecules would be spontaneously polymerized during the intercalation step. The thermal treatment in the presence of $K_2S_2O_8$ would just allow to complete the polymerization, as shown by the complete disappearance of the ν(C═C) band (Figure 3d).

Manganese-Based Material. XRD patterns of LDH($Ni_{0.7}Mn_{0.3}$−acrylate)$^{\#}$ before and after thermal treatment in the presence of $K_2S_2O_8$ are gathered on Figure 2, parts e and f. When compared to the cobalt-based material, the main difference concerns the interslab distance, which is equal to 7.8 Å for manganese-based material against 11.6 Å for LDH($Ni_{0.7}Co_{0.3}$−acrylate). At first sight, this shorter distance could be due to the intercalation of carbonate anions, instead of the target acrylate entities. Nevertheless, the IR spectrum confirms the presence of intercalated acrylate monomer units (Figure 3e), through the presence of the slight ν(C═C) band. In LDH(ML−polyacrylate), it is generally accepted that an interslab distance of about 12 Å is consistent with a bilayer arrangement of the macromolecules between the inorganic slabs.[32] A distance of 7.8 Å, as reported here, is unusual and could correspond to a monolayer arrangement as demonstrated elsewhere.[43] The occurrence of such a phenomenon is supposed to be related to the first step of the synthesis route (solid-state reaction or coprecipitation reaction, schematized in Figure 1). Indeed, a cobalt-based LDHs prepared from a precipitated precursor (Figure 1b) has a similar interslab distance of 7.8 Å. Chemical analysis of the cobalt-based samples has led to propose the following formulas: $Ni_{0.71}Co_{0.29}(OH)_2[-(CH_2CHCOOH)_{0.19}-(CH_2CHCOO)_{0.29}-](H_2O)_{0.79}$ for LDH($Ni_{0.7}Co_{0.3}$−acrylate) (chimie douce) and $Ni_{0.69}Co_{0.31}(OH)_2[-(CH_2CHCOO)_{0.29}-](H_2O)_{0.70}$ for LDH($Ni_{0.7}Co_{0.3}$−acrylate)$^{\#}$ (precipitation).

The formulas suggest that the amount of intercalated acrylate monomer unit is roughly two times lower in the ex-precipitate material than in the material prepared by solid-state chemistry.

After treatment by $K_2S_2O_8$, the slight changes in structure and chemical composition are similar to those observed in cobalt-based materials. These results are consistent with a spontaneous polymerization reaction taking place simultaneously to the acrylate intercalation process. In both systems, only a small amount of acrylate monomers remains unpolymerized, as shown by the very small intensity of the ν(C═C) band.

SEC Characterization of Macromolecules. The macromolecules were extracted from the interslab space of the LDH materials by anionic exchange reactions of polyacrylate anions for carbonate anions, as described in the Experimental Section. The XRD and the IR analyses of the resulting LDH phase (not presented here) have revealed an interslab distance of 7.7 Å and the appearance of the $\nu_3(CO_3)$ band around 1360 cm^{-1}, which are consistent with a LDH($Ni_{0.7}L_{0.3}$−carbonate) phase (L = Fe, Co, Mn) and therefore with the success of the macromolecule extraction. The recovered poly(acrylate) macromolecules were derivatized into poly(methyl acrylate) in order to be analyzed by SEC in THF.

A typical SEC chromatogram of such macromolecules is presented in Figure 4 and similar molar mass distributions were observed whatever the $K_2S_2O_8$-treated LDH($Ni_{0.7}L_{0.3}$−acrylate)$^{(\#)}$ phase from which the macromolecules were extracted. They are mainly made of a mixture of oligomers, whose the weight-average molar mass varies from 300 to 900 g·mol^{-1} vs polystyrene standards, with a small proportion of longer macromolecules (between 900 and 2900 g·mol^{-1} vs polystyrene standards).

Tentative Mechanisms for Acrylate Intercalation and in Situ Polymerization. In the case of iron-based materials, all experiments show the occurrence of an intercalation/polymerization mechanism based on two well-separated steps: (i) the intercalation of acrylate anions, the driving force of which is the compensation

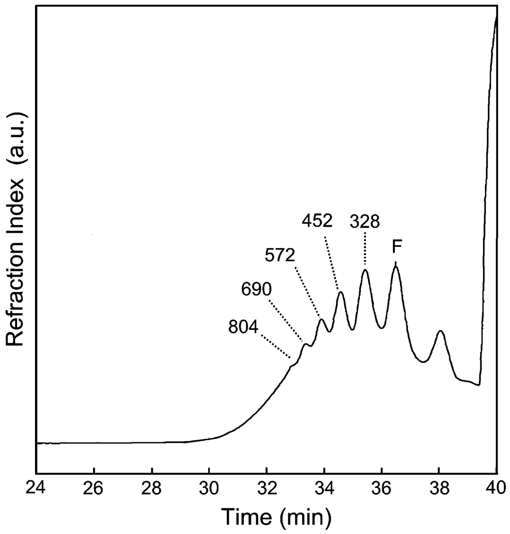

Figure 4. SEC chromatogram of poly(methyl acrylate) macromolecules obtained by extraction of poly(acrylate) anions from the interslab space of LDH($Ni_{0.7}Mn_{0.3}$−polyacrylate)# and methanol derivatization. The values, indicated on the diagram are the weight-average molar masses corresponding to each peak, expressed in g·mol^{-1} vs polystyrene standards; F means flow marker.

of the excess positive charge brought by Fe^{III} in the slabs during the reduction step, and (ii) the in situ free-radical polymerization of intercalated monomers. Further experiments have been performed for checking the effective role played by $K_2S_2O_8$ in this last step. A thermal treatment at 60 °C for 24 h (in the experimental polymerization conditions), but without $K_2S_2O_8$, has not led to noticeable changes in the XRD pattern of the LDH($Ni_{0.7}Fe_{0.3}$−acrylate) phase. On the contrary, the XRD pattern (not shown here) of this same phase treated by $K_2S_2O_8$, but at 25 °C, exhibits a contraction of its interslab distance (from 13.4 Å to 12 Å) and the IR spectrum shows the disappearance of the ν(C=C) band (Figure 5). These results are consistent with the requirement of $K_2S_2O_8$ for initiating the in situ polymerization of the acrylate anions. Besides, the intensity of the $\nu_3(SO_4)$ band around 1100 cm^{-1} is weaker for the material obtained at 25 °C than that observed at 60°C. This phenomenon may be explained by a slower decomposition rate at 25 °C than at 60°C of $S_2O_8^{2-}$ into $SO_4^{\bullet-}$ radical anions. To date, it is not possible to demonstrate where the initiation stage occurs, but the fact that the polymerization is nearly complete and that the molar masses of the macromolecules are low is more likely consistent with an initiation step within the interslab space (from some co-intercalated $S_2O_8^{2-}$ or $SO_4^{\bullet-}$ species) rather than at the layer border.

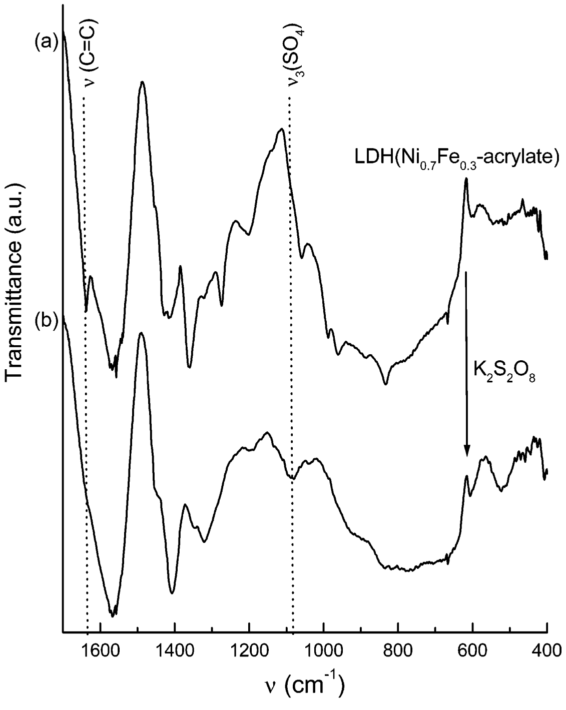

Figure 5. IR spectra of LDH($Ni_{0.7}Fe_{0.3}$−acrylate) (a) before and (b) after treatment by $K_2S_2O_8$ at 25 °C.

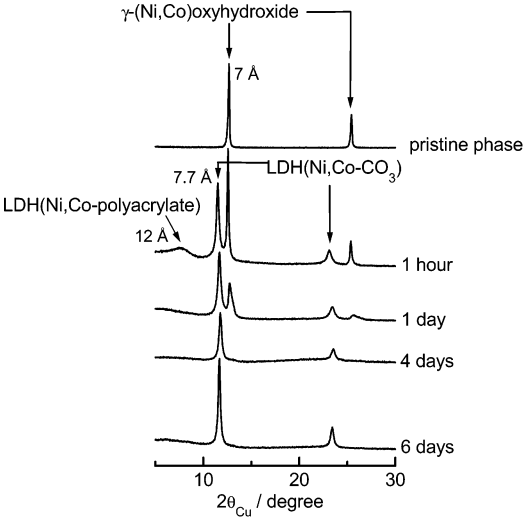

Figure 6. Evolution of the XRD patterns of a cobalt-based γ-oxyhydroxide phase as a function of the staying time in an aqueous solution containing acrylate anions.

Concerning cobalt- and manganese-based materials, it would appear that a spontaneous polymerization reaction occurs simultaneously to the acrylate intercalation step. Hydrogen peroxide cannot be involved in this spontaneous polymerization, because this phenomenon would be also observed in the case of iron-based materials and because it has been previously checked that H_2O_2 do not initiate the acrylate polymerization, in these conditions of concentration, temperature and duration.[35] Further experiments have been performed in order to better understand this spontaneous polymerization phenomenon. To account for the exact role played by acrylate anions with regards to the polymerization in the LDH($Ni_{0.7}Co_{0.3}$−acrylate) phase, the behavior of the corresponding γ−oxyhydroxide phase in the absence of reducing agent (H_2O_2) was studied. First, it has been checked that this γ-oxyhydroxide phase is stable for several days in suspension in water (the XRD pattern remains unchanged). Then, as presented in Figure 6, when this phase has been put in suspension in an aqueous solution containing acrylate anions (pH = 4.3, i.e. under the polymerization conditions), it has been slowly reduced. Indeed, two LDH phases have appeared: a minority one containing (poly)acrylate anions (with an interslab distance of about 12 Å) and a majority one containing carbonate anions (with an interslab distance of 7.7 Å). As the reaction time has increased, the reduction of the γ-oxyhydroxide phase has been completed and a progressive exchange of polyacrylate anions for carbonate ones has occurred. Six days later, a single LDH($Ni_{0.7}Co_{0.3}-CO_3$) phase has been obtained.

From a mechanism point of view, the reduction of the γ-oxyhydroxide phase is necessarily accompanied by the intercalation of anionic species for compensating the excess positive charge created in the slabs and by the concomitant oxidation of the acrylate anions (the only species which are apparently able to reduce the γ-oxyhydroxide phase). As the carboxyl group cannot be more oxidized without being destroyed, it appears that the oxidized part may be the C=C bond, leading to the formation of a radical cation $CH_2^{\bullet}-CH^{+}COO^{-}$. Therefore, the radical cation would react with nucleophilic species, such as water molecules, leading to $CH_2^{\bullet}$-$CHOHCOO^{-}$ active centers, capable to initiate a free-radical polymerization. So, when the reduction of the γ-oxyhydroxide phase is performed by adding H_2O_2, it is most likely that H_2O_2 is the main reducing agent, explaining the rapid reduction into LDH phase and the concomitant intercalation of large amounts of acrylate anions. Nevertheless, acrylate anions may also act as competitive reducing agents and a small part of them could be oxidized into the above-mentioned $CH_2^{\bullet}$-$CHOHCOO^{-}$ active centers, initiating the free-radical polymerization of non-oxidized acrylate anions co-intercalated within the interslab space.

This last mechanism cannot be absolutely classed as a RIP-type mechanism as observed in some layered hybrid systems,[16-19] where the inorganic slabs may be readily reduced in the presence of monomer capable to polymerize through an oxidative process (pyrrole,[16,17] aniline[18,19]). In this case, all monomer molecules are oxidized for polymerizing, and therefore, there is theoretically a direct correlation between the number of the reduced metallic centers in the slabs and the number of polymerized monomer units.

The mechanism proposed in this study for cobalt- and manganese-based LDHs is most likely comparable to that described by Solomon and Loft, when they reported the spontaneous interlamellar polymerization of hydroxymethacrylate monomers in aluminosilicate montmorillonite containing oxidizable metallic center, such as iron.[48] They proposed a mechanism based on an electron transfer from the mineral (changing Fe^{II} into Fe^{III}) to the C=C bond of the monomer leading to the formation of a radical anion, rapidly transformed in the presence of proton donors into free-radicals. So, they explained also the conversion into poly(hydroxymethacrylate) by a propagation step based on a free-radical mechanism. Therefore, as far as we know, the acrylate/LDH system reported in the present paper would be the second example of such an electron-transfer initiation step for acrylic monomer polymerization in layered inorganic materials, with the major difference that, here, the monomer would be oxidized during this step, whereas it would be reduced in the already reported system.

Finally, Solomon and Loft observed that the spontaneous polymerization was possible in intercalates where the monomers are arranged in one layer of inclined molecules, but not in systems with one or two monomer layers laying flat.[48] In our acrylate/LDH system, the similar behaviors of cobalt- and manganese-based materials seem to indicate that the monomer arrangement between the slabs is less determining.

Today, we are not able to explain the difference in polymerization behavior between the iron-based materials on one hand and the cobalt- and manganese-based materials on the other hand.

Conclusion

The intercalation of acrylate anions in LDHs deriving from $Ni(OH)_2$ by an original method involving several *chimie douce* reaction steps has been successful. According to the nature of the substituting cation (L = Fe, Co, or Mn) for nickel, the intercalation/polymerization process may be performed in one or two steps. Mechanisms have been proposed for explaining each behavior, even if the determining role of the substituting cation has yet to be defined. For the first time, the in situ polymerized macromolecules have been extracted by anionic exchange reactions from the interslab space, and their analysis by SEC has shown the presence of oligomers. These obtained oligomers are consistent with the proposed mechanisms.

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