

Intercalation of Anionic Oxalato Complexes into Layered Double Hydroxides

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Intercalation compounds of layered double hydroxide (LDH), $M_{1-x}^{II}M_x^{III}(\text{OH})_{2A_{x/y}} \cdot n\text{H}_2\text{O}$ (with $M^{II} = \text{Zn, Cu}$ and $M^{III} = \text{Al, Cr, Ga}$), with oxalato complexes of aluminium, gallium, chromium, copper, and beryllium, were obtained via anion-exchange processes. Powder X-ray diffraction indicated that the intercalation reactions were successful. The basal spacings measured after intercalation are near 0.98 ± 0.02 nm, whatever the host matrix composition. Studies by FTIR spectroscopy confirmed the intercalation of the oxalato complex, too. In order to study the thermal decomposition of the exchanged products, TGA-coupled mass spectrometry was performed. © 2000 Academic Press

Key Words: layered double hydroxydes; oxalato complexes; intercalation chemistry; thermal decomposition; spinel oxides.

INTRODUCTION

The layered double hydroxides (LDHs) (or the so-called anionic clays) are lamellar compounds with a structure derived from that of the brucite-like structure $M^{II}(\text{OH})_2$, where trivalent metallic cations partially replace divalent ones with the consequence that a net positive charge appears on the layers, $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}$. Overall electroneutrality is obtained by intercalation between the layers of anions solvated with water molecules in variable amounts, $[A_{x/y} \cdot n\text{H}_2\text{O}]^{x-}$. The LDH generic formula is then $M_{1-x}^{II}M_x^{III}(\text{OH})_{2A_{x/y}} \cdot n\text{H}_2\text{O}$ abbreviated as $M^{II}M^{III}-A$. The main interest in such inorganic compounds arises from the basic or redox catalytic activities of their calcined derivatives for a large series of organic reactions (low alcohol synthesis, etherification, condensation reaction, polymerization) (1). According to their chemical formula, a great variety of intralayer metals ($M^{II}M^{III}$) or interlayer species A can be combined.

The intercalation of metallic complexes can be seen as a means to prepare precursors for mixed oxide catalysts and nanophase composites. It is possible under this process to tune

- the metal composition of the intermediate and final mixed metallic oxides obtained under calcination;
- the reactivity of the metal, in its both intra- and interlayer forms; and
- the crystallization of the mixed oxides, depending on the nature of the intercalated complexes.

The complexation of metallic cations by the oxalato ligand ($\text{C}_2\text{O}_4^{2-}$) forms one of the larger series of anionic monomolecular complexes, either with a charged equal to 3-, $M^{III}(\text{C}_2\text{O}_4)_3^{3-}$, or 2-, $M^{II}(\text{C}_2\text{O}_4)_2^{2-}$. Such complexes are structurally and chemically stable under a large range of pH in aqueous solutions. This allows us to envisage their intercalation in the basic LDHs host structure.

Moreover, the complexation properties of the oxalic acid and its anion $\text{C}_2\text{O}_4^{2-}$ toward metallic cations are used in the so-called oxalate process. Metal oxalates are used as precursors for the preparation of metallic oxide nanoparticles, using controlled thermal decompositions. Such complexation prevents, at medium-range temperatures, the crystallization of oxide particles. We recently extended this approach to the preparation of mixed oxides derived from oxalates containing LDHs (2) as did Traversa and co-workers (3).

A limited number of papers about intercalation of anionic complexes in LDHs have appeared in the literature (4). Only one work (5) reported on oxalato complexes containing LDHs, concerning the thermal decomposition study of the intercalation of tris-oxalato ferrate into MgAl-. In this paper, we investigate the possibility of producing fine metal oxide particles from oxalato complexes containing LDHs. We prepared and characterized a series of LDH host layers, $M^{II}M^{III}$ -, with $M^{II} = \text{Zn, Cu}$ and $M^{III} = \text{Al, Cr, Ga}$. We then intercalated oxalato complexes of the metals ($M^{III} = \text{Al, Cr, Ga, Fe}$ and $M^{II} = \text{Cu, Be}$) in these host structures. Structural and spectroscopic characterizations as well as thermal analyses of the different oxalato complexes containing LDHs are presented here.

EXPERIMENTAL

Synthesis

The LDH precursors ZnAl-Cl, ZnGa-Cl, and ZnCr-Cl with the ideal formulae $[\text{Zn}_3\text{Al}(\text{OH})_8]\text{Cl}\cdot 2\text{H}_2\text{O}$, $[\text{Zn}_3\text{Ga}(\text{OH})_8]\text{Cl}\cdot 2\text{H}_2\text{O}$, and $[\text{Zn}_2\text{Cr}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ were prepared by coprecipitation at controlled pH as described in the literature (6, 7). For the ZnGa-Cl LDHs, some modifications were made to the synthesis proposed by Fuda *et al.* (8). Mixed solutions of ZnCl_2 and $\text{Ga}(\text{NO}_3)_3$ in the expected $\text{Zn}^{2+}/\text{Ga}^{3+}$ molar ratio, having total cation concentration of 1 M, were used, and the pH was maintained during the coprecipitation at pH 8.0 by simultaneous addition of 1 M NaOH. The precursor CuCr-Cl ($[\text{Cu}_2\text{Cr}(\text{OH})_6]\text{Cl}\cdot 2\text{H}_2\text{O}$) was obtained by the hydrolysis/precipitation method based on the slow addition of 1 M CrCl_3 in an aqueous suspension of CuO (9). The slow dissolution of divalent oxide induces a controlled release of divalent metal species and the formation of the LDH phase. Chemical analyses and empirical formulae of the four precursors are given in Table 1.

Potassium tris-oxalato aluminate, ferrate, chromate, gallate $[\text{K}_3\text{Al}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, $[\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, $[\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, $[\text{K}_3\text{Ga}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, and potassium di-oxalato cuprate and beryllate were prepared following a procedure from the literature (10).

Intercalation compounds were obtained by anion exchange on the $M^{\text{II}}M^{\text{III}}\text{-Cl}$ precursors. They were performed in an aqueous solution containing the sodium salt of the anionic complexes, in three molar excess over the anion-exchange capacity. Two methods were used for the anion exchange. The standard exchange was carried out at room temperature, for 1 day, under nitrogen to prevent contamination by carbonate from atmospheric CO_2 . The second method was performed in an autoclave at 120°C , under an autogenous pressure of 2.4 bar, for 24 h. The powdered products were recovered, in all cases, after three washings, with carbonate-free deionized water and a drying at room temperature. The compounds exchanged are henceforth noted as $M^{\text{II}}M^{\text{III}}\text{-M}'\text{Ox}_{\text{exc}}$, while those obtained under hydrothermal treatment are labeled as $M^{\text{II}}M^{\text{III}}\text{-M}'\text{Ox}_{\text{au}}$.

Physical Measurements

Powder X-ray diffraction (PXRD) patterns were obtained with a Siemens D501 X-ray diffractometer using $\text{CuK}\alpha$ radiation and fitted with a graphite back-end monochromator. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 16PC spectrophotometer on pressed KBr pellets. Thermogravimetric analyses (TGA) were performed with a Setaram TG-DTA92 thermogravimetric analyzer at a typical rate of $5^\circ\text{C}/\text{min}$ under an air atmosphere. The mass spectrometer used in this study is the Thermostat 300 from Balzers Instruments. Chemical

TABLE 1
Chemical Compositions of the LDH Precursors

LDH	M^{2+}/M^{3+}	Cl^-/M^{3+}	$\text{H}_2\text{O}/M^{3+}$	Formula
ZnAl-Cl	2.93	1.13	1.9	$\text{Zn}_{2.9}\text{Al}(\text{OH})_{6.8}\text{Cl}_{1.1}\cdot 1.9\text{H}_2\text{O}$
ZnGa-Cl	2.95	1.20	2.5	$\text{Zn}_{2.9}\text{Ga}(\text{OH})_{6.8}\text{Cl}_{1.2}\cdot 2.5\text{H}_2\text{O}$
ZnCr-Cl	1.98	1.0	1.9	$\text{Zn}_{2.0}\text{Cr}(\text{OH})_{6.0}\text{Cl}_{1.0}\cdot 1.9\text{H}_2\text{O}$
CuCr-Cl	2.20	1.1	2.0	$\text{Cu}_{2.2}\text{Cr}(\text{OH})_{5.4}\text{Cl}_{1.1}\cdot 2.0\text{H}_2\text{O}$

analyses (Zn, Al, Ga, Cr, Cu, Cl, H, C) were performed in the Vernaison Analysis Center of the CNRS.

RESULTS AND DISCUSSION

Intercalation Study

Characterization of the LDH Precursors

Diffractograms of the four LDH precursors are displayed in Fig. 1. All diffraction lines were identified in the hexagonal lattice with the rhombohedral symmetry $R\bar{3}m$. The refined cell parameters are listed in Table 2. Whatever the preparation methods used, either coprecipitation for ZnAl-Cl, ZnGa-Cl, and ZnCr-Cl or hydrolysis/precipitation for CuCr-Cl, well-crystallized materials were obtained. The chemical analyses of the prepared samples are in good agreement with that expected from the conditions fixed in the synthesis.

The a cell parameter is equal to the shorter metal-metal intralayer distance and is directly related to the size of the

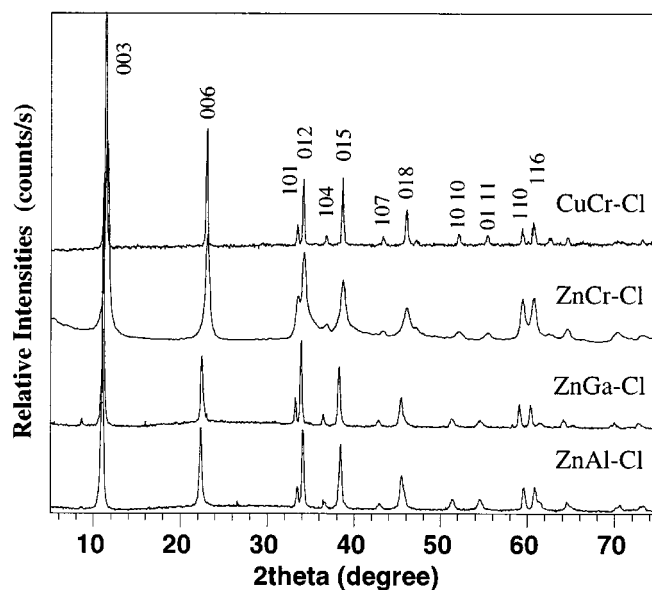


FIG. 1. X-ray diffractograms of the LDH precursors.

TABLE 2
Refined Cell Parameters of LDH Precursors

LDHs	<i>a</i> (nm)	<i>c</i> (nm)	<i>d</i> (nm)
ZnAl-Cl	0.3086	2.357	0.786
ZnGa-Cl	0.3121	2.357	0.786
ZnCr-Cl	0.3111	2.363	0.788
CuCr-Cl	0.3111	2.309	0.770

cations and the chemical composition of the sheets. With a nearly identical M^{2+}/M^{3+} ratio for ZnCr-Cl (1.98) and CuCr-Cl (2.20 (Table 1) and a similar ionic radius for Zn^{2+} (0.74 Å) and Cu^{2+} (0.72 Å), both phases displayed the same *a* value (0.311 nm). The metal-metal distance in ZnM-Cl ($M = Al^{3+}, Ga^{3+}$), for an equal M^{2+}/M^{3+} ratio (2.93 and 2.95), increases with the ionic radius of the trivalent metal (respectively 0.56 Å and 0.62 Å for Al^{3+} and Ga^{3+}). In all cases, the basal spacing is typical of LDH containing interlayered chloride anions with slight variations of the hydration state. Absence of contamination by carbonate, usually observed for the MgAl- system, is evidenced on the FTIR spectra of all precursors.

Intercalation of the Oxalato Complexes

The exchange of the anionic oxalato complexes, $AlOx_3^{3-}$, $CrOx_3^{3-}$, $GaOx_3^{3-}$, $FeOx_3^{3-}$, and $CuOx_2^{2-}$, was obtained for the four LDH matrices. The intercalation of the complexes is confirmed by the presence of the vibration bands of

the oxalato anions (11) on the FTIR spectra (Fig. 2). The X-ray patterns of the various oxalato complexes containing LDHs are displayed in Fig. 3.

In the cases of the stable tris-oxalato complexes $AlOx_3^{3-}$, $CrOx_3^{3-}$, and $FeOx_3^{3-}$, the pure LDH phases are prepared. The presence of all the vibrations bands of $FeOx_3^{3-}$ on the FTIR of the intercalated compounds confirms that $FeOx_3^{3-}$ has not undergone photodissociation, as is the case in aqueous solution. It is noteworthy that the exchange reactions of $CuOx_2^{2-}$ and $GaOx_3^{3-}$ do not lead to pure compounds. In the case of the $CuOx_2^{2-}$ intercalation the diffraction lines of either moolooite, $Cu(C_2O_4)$, or $Cu(OH)_2$ appear always beside the LDH diagram, whatever the exchange conditions used. This is explained by the lowest stability of the copper oxalato anion which tends to lose one oxalate ligand. The formation of the stable copper oxalate byproduct with CuCr- $AlOx$ and CuCr- $CrOx$ shows the high reactivity of the CuCr- matrix toward the various oxalato complexes involving decomplexation of the anion. This high reactivity of the CuCr- layers has already been reported in a paper (12) on the grafting of organic anions in LDHs and is explained by the presence of two OH labile ligands around the distorted d^9 Cu^{2+} ions. Surprisingly, the ZnAl- matrix, which is generally stable under standard exchange reactions, undergoes partial hydrolysis by the oxalato gallium complex, even in mild exchange conditions; the undesired $Zn(C_2O_4)$ phase is still formed. No explanation has been proposed so far.

The X-ray patterns of the various oxalato complexes containing LDH display strong similarities. Unfortunately, the low number of observed diffraction lines prevents the

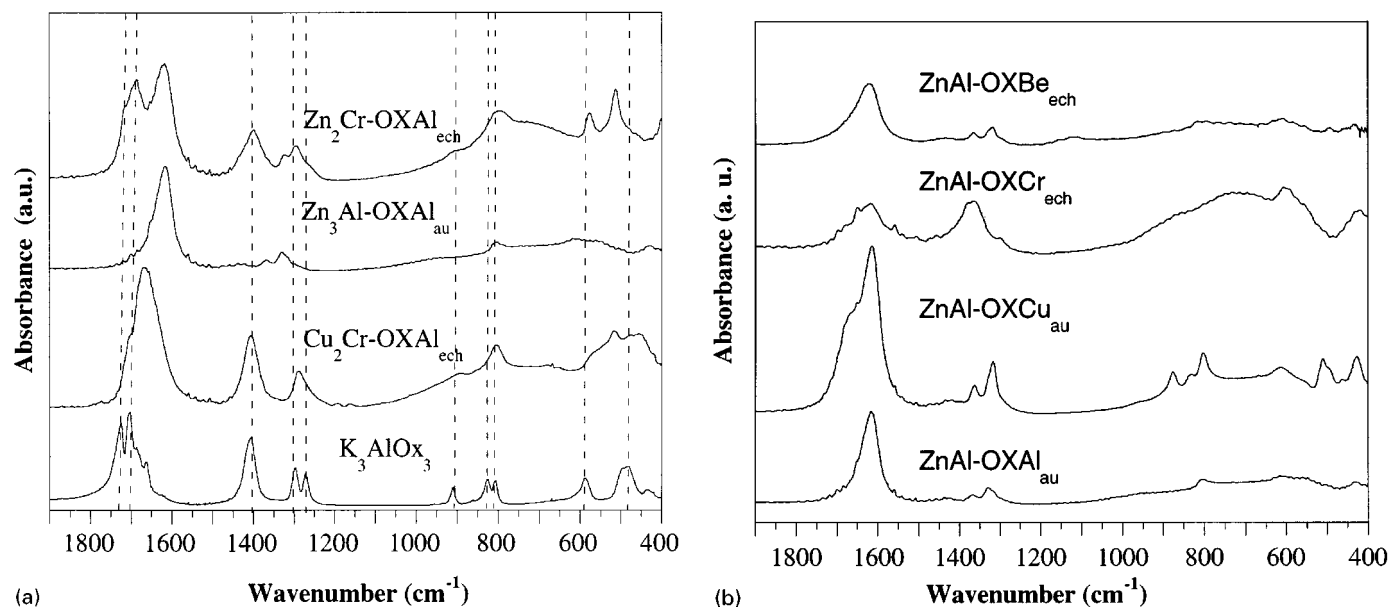


FIG. 2. FTIR spectra of (a) $AlOx$ containing LDHs and (b) ZnAl LDH intercalated by oxalato complexes.

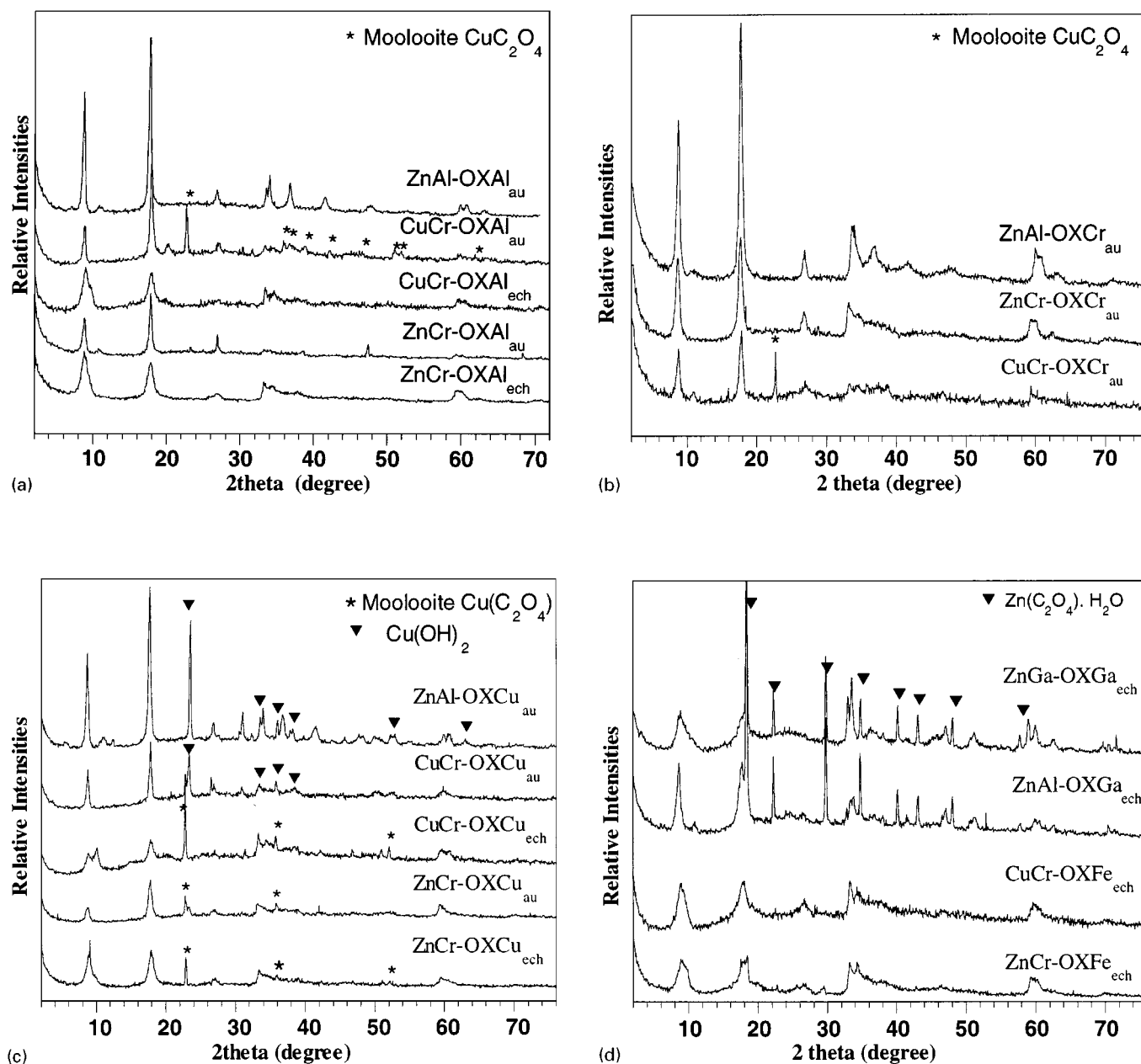


FIG. 3. X-ray diffractograms of LDHs containing (a) AlOx, (b) CrOx, (c) CuOx, and (d) GaOx and FeOx.

cell parameters refinement which was only realistic for ZnAl-AlOx ($a = 0.3081(2)$ nm and $c = 2.973(3)$ nm). The basal spacing for the other phases was determined from the mean value of the first two (001) peaks (Table 3). The interlayer distances are short and in the same order range (0.967–0.997 nm). Values are lower than the one measured by Carlino and co-workers (6) for MgAl-FeOx (1.052 nm), but the authors reported for this last compound a co-intercalation with CO_3^{2-} anion which explains, in our opinion, the higher basal spacing.

The basal spacing for the ion-exchange reaction products is directly related to the orientation of the intercalated complexes. The four oxalato complexes MOx_3^{3-} are nearly the same size and display the pseudo-octahedral symmetry ($D3d$) (Fig. 4a). The projection of the molecules in the plane perpendicular to its C_3 axis shows a building block with six oxygen atoms in the front plane and six other in the back plane. Such a geometry can easily fit in the interlayer octahedral sites formed by 3 + 3 OH of two adjacent layers (Fig. 4b). In such an orientation the complex with its C_3 axis

TABLE 3
Basal Spacing of the Oxalato Complexes Containing LDHs

LDH	AlOx_3^{3-}	CrOx_3^{3-}	GaOx_3^{3-}	FeOx_3^{3-}	CuOx_2^{2-}
ZnAl-Cl	0.991	0.989	0.983	–	0.991
ZnGa-Cl	–	–	0.969	–	–
ZnCr-Cl	0.984	0.991	–	0.976	0.997
CuCr-Cl	0.991	0.967	–	0.973	0.972

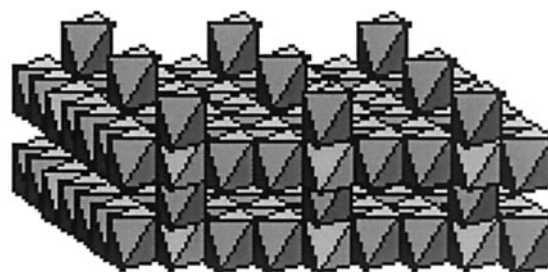


FIG. 5. Ideal distribution of MOx_3^{3-} pillars in the LDH interlayer domains.

parallel to the c direction of the layered structure can interact with the host structure with a maximum number of hydrogen bonds. A theoretical interlayer distance based on the formula $d = d_{\text{lay}} + 2d_{\text{lay/anion}} + l_{\text{anion}}$ can be calculated (13, 14), where d_{lay} is the thickness of the octahedral layers (0.21 nm), $d_{\text{lay/anion}}$ is the distance between the adjacent oxygen planes of both the layer and the oxalate, and l_{anion} (0.21 nm) is the size of the pseudo-octahedral anion along the $C3$ axis. With a mean experimental d value of 0.99 nm, we calculate a guest–host distance of 0.285 nm characteristic of strong hydrogen interactions. The structure can then be described as a pillared layer structure (Fig. 5) where MOx_3^{3-} pillars are distributed in the interlayer approximately 0.9 nm apart from each other and strongly attached to the layers, even if they are not covalently bonded.

The LDH phases containing the copper oxalato anion display similar basal spacings as the ones observed for the $M^{\text{II}}M^{\text{III}}\text{-MOx}_3^{3-}$ systems (Table 3). Edwards and co-workers (15) reported, on the basis of IR and Raman data, that the structure of this anion is based on the formula $[\text{CuOx}_2(\text{H}_2\text{O})_2]^{2-}$. It has a square-planar structure of two oxalate ligands around Cu^{2+} plus two axial water molecu-

les. The orientation of the complex between the plane is probably analogous to the former cases. A structural difference is observed for the tetrahedral BeOx_2^{2-} anion. The shorter observed basal spacing (0.907 nm) for ZnAl- BeOx_2^{2-} can only be explained by orientation of the tetrahedral anion with its $C2$ axis parallel to the c direction.

A common feature on all the X-ray patterns is that the second (001) diffraction line becomes more intense than the first one. This is typical of an increase of the electron density in the midplane of the interlayers due to the presence of the heavy metals. As expected, the inversion is not observed for the BeOx_2^{2-} -containing phase.

The vibration bands of the oxalato anions are very sensitive to the interactions with the host layers, as shown on the IR spectra (Figs. 2 and 3) and as mentioned in a previous study on intercalation of AlOx_3^{3-} in ZnAl LDH (2). The asymmetric C–O vibrations of the ligand appears particularly affected, with values between 1600 and 1800 cm^{-1} . We observed a change in the relative intensities of the asymmetric C=O vibrations, ν_7 and ν_1 . The ν_1 band is the

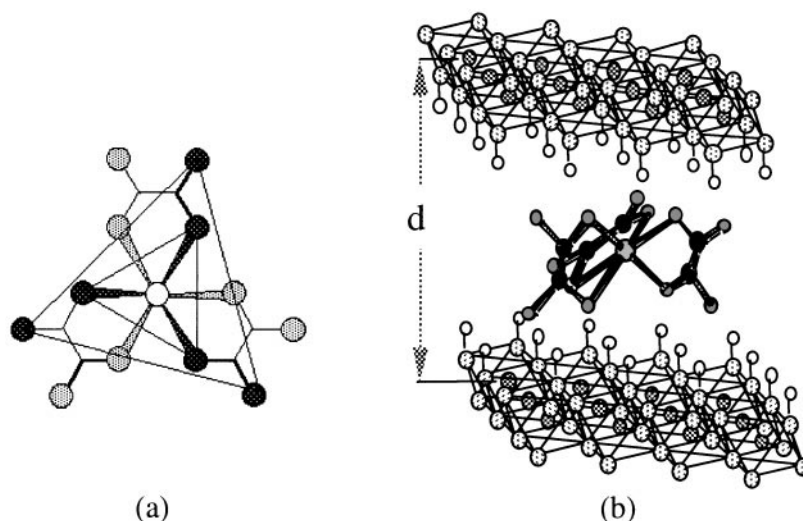


FIG. 4. Structural models of (a) the oxalato complexes (black and gray circles correspond respectively to front and back atoms) and (b) the exchanged LDH.

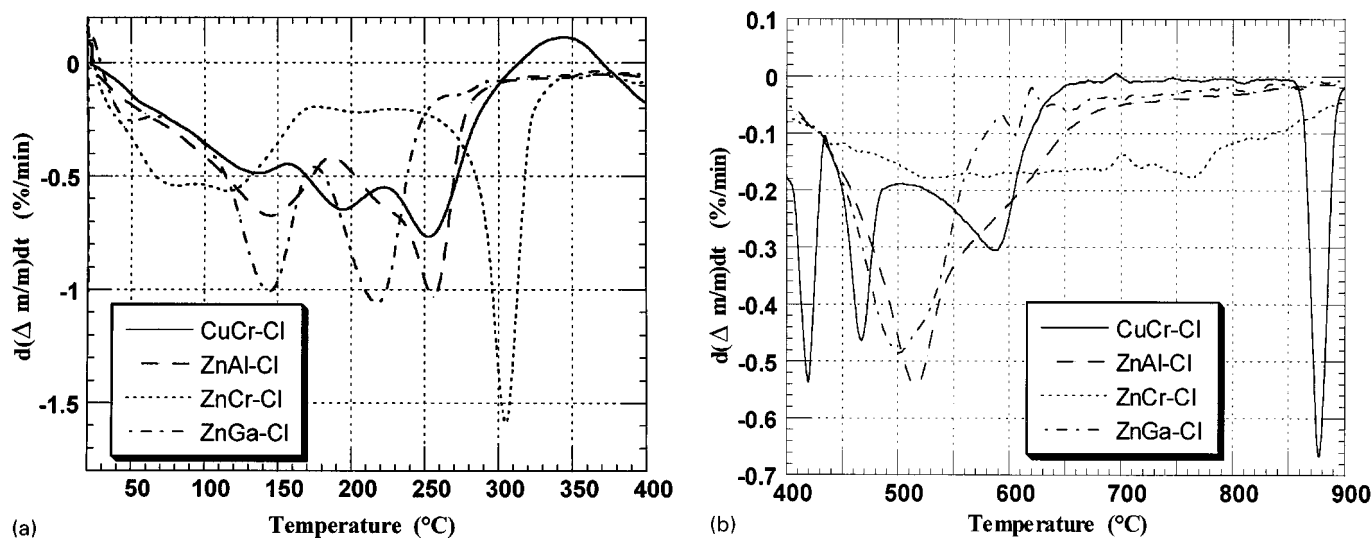


FIG. 6. DTG curves for LDH precursors.

most intense for the intercalated anions and shifts from 1680 cm^{-1} for the tris-oxalato aluminium salt to 1762 , 1715 , and 1710 cm^{-1} , respectively, for CuCr-, ZnCr-, and ZnAl-host layers. The stronger the hydrogen interactions between oxygen of C_2O_4 and OH planes are, the higher the shift to a low-energy value is. The symmetric stretching band, $\nu_s(\text{C}=\text{O})$, remains at nearly the same position. On the other hand, the intercalation leads also to a great broadening of the lattice vibrations ($400\text{--}700\text{ cm}^{-1}$) of the LDH matrix compared to the spectra of the precursors. This is due to the compact stacking of the layers induced by the strong interactions with the interlamellar species.

In the cyanide complexes ($\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, $\text{Co}(\text{CN})_6^{3-}$, $\text{Mo}(\text{CN})_6^{3-}$) the metallic cations displays an octahedral symmetry, the complexes have a larger size compared to the oxalato complexes. Their intercalation in MgAl- (16–18) results in an increase of the basal spacing from 0.78 nm for the LDH precursor to 1.07 nm for the intercalated products. Kikkawa and co-workers (15) concluded that the anionic complexes were oriented with their

C6 axes parallel to the stacking direction. The oxalato complexes containing LDHs prepared in this study display a very similar structure.

Thermal Behavior of the Precursors and Exchanged Phases

Thermogravimetry Analysis of the Precursors

The thermal decompositions of the four LDH precursors are plotted as DTG curves in Fig. 6a and 6b. Quantitative data processing of these curves is listed in Table 4. In all cases, two steps of dehydration are observed: the dehydration of water molecules, physisorbed at the external surface of the crystallites, and the dehydration of intercalated water molecules more strongly attached to the network via stronger hydrogen bonds. The temperature ranges and the temperatures of maximal decomposition rate of these two events are quite similar for all precursors except for ZnCr-Cl which allows de-intercalation of bulk water molecules at very low temperature (117°C). The dehydration processes

TABLE 4
Thermal Decomposition Steps of the LDH Precursors

LDH	Dehydration		Dehydroxylation	
	Step 1 ^a	Step 2 ^a	Step 1 ^a	Step 2 ^a
ZnAl-Cl	20-85/50	85-175/144	175-300/217	–
ZnGa-Cl	20-80/48	80-187/145	187-230/216	230-310/256
ZnCr-Cl	20-97/77	97-175/117	237-350/304	–
CuCr-Cl	20-84/55	84-157/135	157-222/194	222-345/253

^aT1-T2/T3 with T1-T2, decomposition thermal range; T3, temperature of maximal decomposition rate.

TABLE 5
Temperature of Crystallization of Derived Oxides

LDHs	Crystallization temperature (°C)	
	MO	$M^{II}M_2^{III}O_4$
ZnAl-Cl	240	580
ZnGa-Cl	-	-
ZnCr-Cl	340	340
CuCr-Cl	250	300

depend greatly on the nature of the metallic cations. The thermal stability of the phases increases with the temperature at which the dehydroxylation starts in the order CuCr-Cl < ZnAl-Cl < ZnGa-Cl < ZnCr-Cl, with a shift of

about 80°C from the least stable to the highest stable compound.

At temperatures higher than 400°C, the chloride anion is evolved following various mechanisms according the matrix, involving either evaporation of HCl or sublimation of metal chloride. However, the decomposition of CuCr-Cl involves an additional step related to the formation of the intermediate Cu_2OCl_2 , while for ZnCr-Cl, ZnAl-Cl, and ZnGa-Cl the continuous loss arises from the contribution of the slow sublimation of zinc chloride. In the temperature range of 400 to 600°C, a mixture of amorphous but reactive divalent and pre-spinel metal oxides of catalytic interest (19, 20) is formed. Crystallization of the derived oxides, MO and $M^{II}M_2^{III}O_4$ spinel phases, begins above 600°C at different temperatures (Table 5) according the matrix.

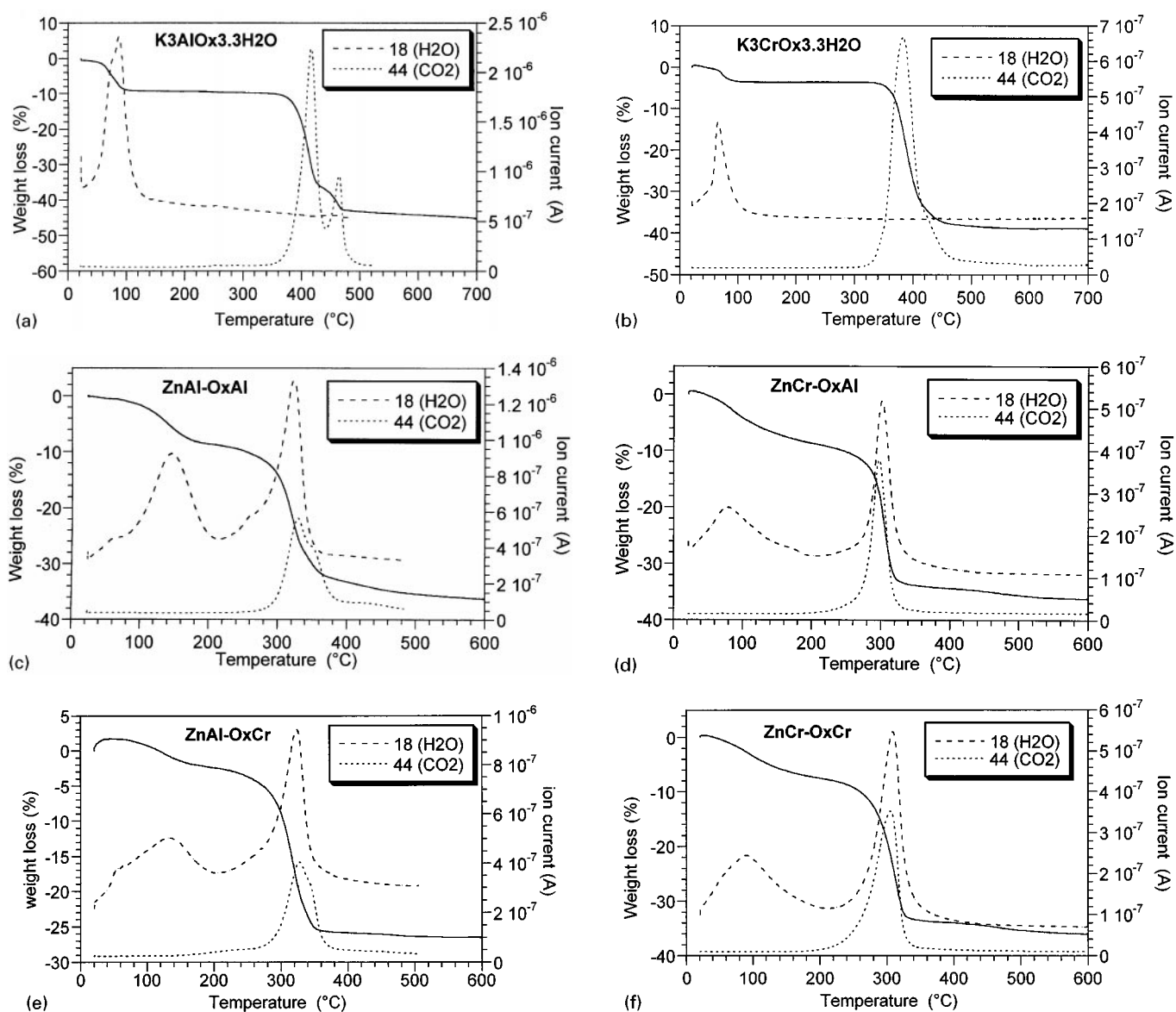


FIG. 7. TG/SM curves of (a and b) precursor salts, (c and d) AlOx, and (e and f) CrOx-containing LDHs.

TABLE 6
Spinel Phases Obtained from Calcination of Oxalato Complexes Containing LDHs

LDH	AlOx ₃ ³⁻	CrOx ₃ ³⁻	GaOx ₃ ³⁻	FeOx ₃ ³⁻	CuOx ₂ ²⁻
ZnAl-	ZnAl ₂ O ₄	ZnAl _{1.5} Cr _{0.5} O ₄	ZnAl _{1.5} Ga _{0.5} O ₄	-	ZnAl ₂ O ₄ + CuAl ₂ O ₄
ZnGa-	-	-	ZnGa ₂ O ₄	-	-
ZnCr-	ZnCr _{1.5} Al _{0.5} O ₄	ZnCr ₂ O ₄	-	ZnCr _{1.5} Fe _{0.5} O ₄	ZnGa ₂ O ₄ + CuAlO ₄
CuCr-	CuCr _{1.5} Al _{0.5} O ₄	CuCr ₂ O ₄	-	CuCr _{1.5} Fe _{0.5} O ₄	CuCr ₂ O ₄

Thermogravimetry Analysis Coupled with Mass Spectrometry of the Oxalato Complexes Containing LDHs

Under air atmosphere, the hydrated potassium oxalato metal salts decompose in three steps following Eqs. [1], [2], and [3]:

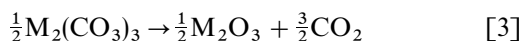
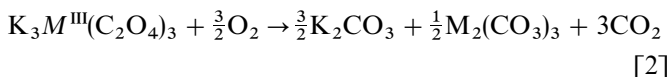
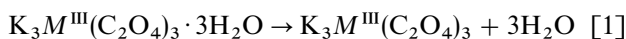


Figure 7a and 7b display the thermograms of K₃AlOx₃·3H₂O and K₃CrOx₃·3H₂O coupled with the mass spectrometry signals corresponding to masses 18 and 44, respectively, H₂O and CO₂. The decomposition of the oxalate ligands occurs in two separate events for the former compound, between 350 and 500°C, while for the latter compound the decomposition begins at lower temperature (320°C) following a single continuous thermal phenomenon.

When [AlOx₃]³⁻ and [CrOx₃]³⁻ are intercalated in ZnAl- and ZnCr- LDHs, the decomposition of both complexes occurs simultaneously with the dehydroxylation of the host structures. When the mineral matrix is ZnCr-, evolution of both CO₂ and H₂O occurs at the same temperature (300°C), while for ZnAl-dehydroxylation begins at 50°C lower than the combustion of the oxalate ligands. In this case the anion undergoes a decomposition in two steps, as observed for K₃AlOx₃·3H₂O. The decomposition is probably an oxidative pyrolysis induced by the water molecules evolved under dehydroxylation. In the case of ZnCr- the decomposition of the oxalato complexes is probably assisted and increased by the oxidative action of the intralayer chromium cations. It then results in a one-step reaction and does not involve intermediate carbonate compounds.

The total decomposition of LDHs leads to a mixture of divalent metal oxide and spinel phases. If the starting LDH is the formula [M_{1-x}^{II}M_x^{III}(OH)₂][M^{III}Ox₃]_{x/3}·nH₂O, then the composition of the mixed oxides obtained after calcination is (1 - 5x/3)M^{II}O + (2x/3)M^{II}(M_{3/2}^{III}M_{1/2}^{III})O₄ (Table 6).

X-ray diffraction shows that a single spinel phase is obtained, corresponding to a solid solution between M^{II}M^{III}O₄· and M^{II}M₂^{III}O₄·. When M^{III} = M^{III}, the decomposition leads to 33% more spinel in the oxide mixture. Solid solutions of spinel in combination with two divalent or two trivalent metals are then obtained.

If one compares the thermograms of the oxalato exchange products and the precursors, the major difference arises in the temperature range from 200 to 400°C. While for the precursor the dehydroxylation and the loss of chloride are two well-separated thermal events, in the exchange phases both decomposition processes occur jointly. For the ZnAl- matrix, the decomposition occurs at 60°C higher than the dehydroxylation step in the ZnAl-Cl precursor. Because of the higher stability of the ZnCr- network (300°C), the dehydroxylation meets the complex decomposition. In the case of ZnAl- this delay of dehydroxylation is due to the stabilization of the matrix by the oxalato pillars through strong hydrogen interactions.

CONCLUSION

The intercalation of a large series of tris-oxalato and bis-oxalato metallates in four-layered double hydroxydes (ZnAl-, ZnCr-, ZnGa-, and CuCr-) has been obtained by anion-exchange reactions. The strong interactions between the anionic complexes and the host structures lead to pillared-like layered structures with basal spacings lower than 1 nm and internal galleries with limited sizes. As shown by the TGA/SM analysis, the thermal decomposition of the host structure is induced by the pyrolysis of the anionic complexes, at lower temperatures than for the chloride precursors. The chemical combination of the guest and host through the intercalation of oxalato complexes in LDHs is a very promising way to prepare precursors to obtain mixtures of finely divided oxides with a desired composition of the spinel phase. This study evidences a new means to prepare catalysts with tunable metal content.

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