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Reactivity of oxalate with ZnAl layered double hydroxides through new materials†

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Reaction of oxalate anion with ZnAl layered double hydroxides (LDHs) gives rise to new LDH phases where either oxalate or aluminum oxalato complexes are intercalated depending on the exchange reaction conditions. Chemical characteristics, structural and spectroscopic data are presented.

Many reactions which use layered double hydroxides (LDHs) intercalated with inorganic or organic anions have recently attracted much attention because of their large fields of application, for example as exchangers,[1] catalysts[2] or electrochemical sensors.[3,4] The LDHs are lamellar compounds with a structure (Fig. 1) derived from that of brucite type $M^{II}(OH)_2$, where trivalent metallic cations replace some of the divalent ones which creates a net positive charge on the layers, $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$. Overall electroneutrality is obtained by the intercalation of anions into the interlamellar spaces, $[A^{y-}_{x/y}\cdot nH_2O]^{x-}$. The LDH generic formula is $M^{II}_{1-x}M^{III}_x(OH)_2A_{x/y}\cdot nH_2O$, abbreviated as $M^{II}M^{III}$-A. According to the fields of application, a great choice of metal composition (M^{II}, M^{III}) or interlayer species (A) is possible.

The main property of these materials is their anionic exchange ability which makes them unique inorganic materials for adsorption of organic and inorganic anions. Utilisation of these properties has been achieved, for example, for purification of waste waters.[5] Moreover recent studies have shown that the LDH sheets can undergo grafting reactions with some inorganic[6,7] or organic anions.[8] Then adsorption and immobilization of chemical pollutants on LDH supports can be envisaged.

Adsorption/desorption processes and reactions at the solid/solute interfaces such as complexation, catalysis, photochemical processes, exchange and hydration reactions are of great importance in environmental chemistry.[9] An example of important surface reactions is the adsorption in soils of acidic organic substances at the surface of hydrous oxides. In order to better understand the adsorption phenomena onto mineral supports and their mechanisms, many studies have been carried out on the adsorption of oxalic acid, one of the carboxylic acid plant by-products which interferes with adsorption of other nutrients such as phosphate. Oxalic acid has been shown to strongly chemisorb onto oxide or hydrous oxide surfaces such as gibbsite,[10] goethite, hematite,[11] rutile and anatase TiO_2.[12,13] Oxalic acid and its anion $C_2O_4^{2-}$ are known to be very strong complexing agents of metal cations. Reactivity of oxalate with LDHs has not been reported so far. This paper deals with the adsorption of oxalate by LDHs *via* anion exchange reactions and its reactivity with the hydroxylated sheets under thermal treatments. We present the preparation and the characterization of two new oxalate containing LDH phases. The cationic components of the layer are Zn^{2+} (for M^{II}) and Al^{3+} (for M^{III}). The particular reactivity of the LDH host structure with oxalate anions under hydrothermal conditions is also reported.

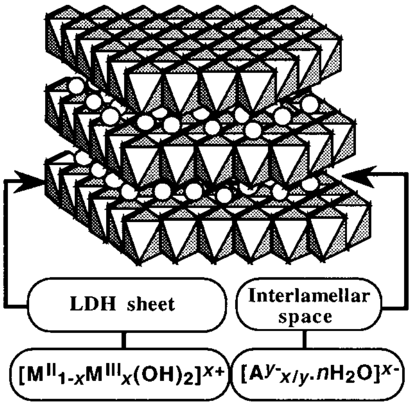

Fig. 1 Structural chemistry of a LDH.

Metal oxalates are interesting precursors to prepare metallic oxide nanoparticles, using controlled thermal treatment. Traversa *et al.*[14] have already reported the interesting influence of oxalate on the thermal decomposition of MgAl hydroxides for the preparation of mixed oxides. Study of the thermal decomposition of the phases prepared here using powder X-ray diffraction, thermogravimetry coupled with mass spectrometry and scanning electron microscopy are also presented.

Experimental

Materials

ZnAl-Cl LDH with the ideal formula of $[Zn_3Al(OH)_8]Cl\cdot 2H_2O$ was used as a precursor for the intercalation studies. This precursor was prepared by coprecipitation at controlled pH as described in the literature.[15] Mixed solutions of $ZnCl_2$ and $AlCl_3$ in the expected Zn^{2+}/Al^{3+} molar ratio, having total cation concentrations of 1 M were used and the pH was maintained during coprecipitation at pH 8.0 by simultaneous addition to the mother solution of 1 M NaOH solution. The synthesis was performed under nitrogen to prevent contamination by carbonate from atmospheric CO_2.

Two methods were used for anionic exchange: standard anionic exchange was carried out at room temperature with a twenty-fold excess of oxalate per Al^{3+}, under nitrogen, for 1 d. The other exchange was performed in an autoclave at 120 °C with a molar ratio anion/M^{III} of 10 : 1 for 4 d. Powdered products were recovered, in all cases, after three washings with carbonate-free water, and dried at room temperature. The compounds obtained by anionic exchange at room temperature are denoted as ZnAl-Ox_{exc} while those obtained under hydrothermal treatment are labelled ZnAl-Ox_{au}.

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Table 1 Chemical compositions of the hybrid and precursor compounds[a]

LDH	Zn^{2+}/M^{3+}	Cl^-/Al^{3+}	H_2O/Al^{3+}
ZnAl-Cl	2.93	1.13	1.9
ZnAl-CO_3	3.04	0.01	2.4
ZnAl-Ox_{exc}	2.90	0.08	1.9
ZnAl-Ox_{au}	3.30	0.03	—
ZnAl-$AlOx_{au}$	1.62	0.03	—

[a] exc = exchanged phase, au = exchanged in autoclave.

For a comparative study, $[Zn_3Al(OH)_8](CO_3)_{0.5}\cdot 2H_2O$ (denoted ZnAl-CO_3) and $[Zn_3Al(OH)_8][Al(C_2O_4)_3]_{0.33}\cdot nH_2O$ (denoted ZnAl-$AlOx_{au}$) were synthesized. The former was prepared by coprecipitation at a constant pH of 10.0 while the latter was obtained under the same conditions as ZnAl-Ox_{au} using $Al(C_2O_4)_3{}^{3-}$ instead of $C_2O_4{}^{2-}$. Potassium trioxalatoaluminate $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ was prepared following a procedure from the literature.[16]

The intercalation of oxalate is evidenced by the chemical analysis data, which indicate the absence of Cl^- in the exchange compounds which retain their initial M^{2+}/M^{3+} ratio (Table 1). The intercalation reactions are also confirmed by X-ray diffraction and FTIR spectroscopy. In the XRD patterns we observe in all cases a shift of the (001) *d*-spacings corresponding to a structural expansion or contraction on replacement of Cl^- by $C_2O_4{}^{2-}$. In the IR spectra the presence of the characteristic bands of oxalate $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ show the presence of $C_2O_4{}^{2-}$ anions in the bulk.

Techniques

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D501 X-ray diffractometer using Cu-Kα radiation and fitted with a graphite scattered beam monochromator. Fourier-transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 16PC spectrophotometer on pressed KBr pellets. Thermogravimetry (TG) was performed with a Setaram TG-DTA92 thermogravimetric analyzer at a typical rate of 5 °C min^{-1} under air atmosphere. Gases evolving from the TG apparatus were analyzed using a mass spectrometer Thermostar 300 from Balzers Instruments. Chemical analyses (Zn, Al, Cr, Cl, H) were performed at the Vernaison Analysis center of CNRS. Scanning electron micrographs were recorded with a Cambridge Stereoscan at the Laboratoire des Matériaux Inorganiques of Techinauv S.A. France.

Results and discussion

Powder X-ray diffraction

Powder X-ray diffraction patterns of hybrid materials and precursors are presented in Fig. 2. An interlayer distance (Table 2) of 0.778(3) nm is calculated for ZnAl-Ox_{exc}. This short value has not been observed before for oxalate-containing LDHs. It is close to that of ZnAl LDH intercalated by $CO_3{}^{2-}$ (ZnAl-CO_3) which has a basal spacing of 0.763(7) nm. The structure of ZnAl-CO_3 is well known;[7] it displays an arrangement of carbonate anions lying parallel to the hydroxylated layers, with their C_3 axis aligned along the *z* axis. By analogy, the similar interlamellar distance measured for ZnAl-Ox_{exc} shows that planar oxalate anions must arrange like $CO_3{}^{2-}$, parallel to the layers (Fig. 3). With a Zn^{2+}/Al^{3+} ratio equal to 3.0 : 1, the ZnAl host structure displays an available surface area per unit charge of 33.3 Å^2 e^{-1}, while the surface of the oxalate anion is 27.0 Å^2. The greater value of the former surface area confirms the possible occurrence of this flat orientation. In this structural model the interlayer surface occupied by the anions is only 41% of the available surface of the sheet. The oxalate groups are then bonded by hydrogen bonding with both adjacent hydroxylated planes *via* the four oxygen atoms. The interlayer space is left for water molecules. Interactions between the host structure and the guest molecules are then very similar to that exhibited by ZnAl-CO_3. This is the first report of a successful intercalation of oxalate anions in LDH using exchange reactions under room temperature conditions.

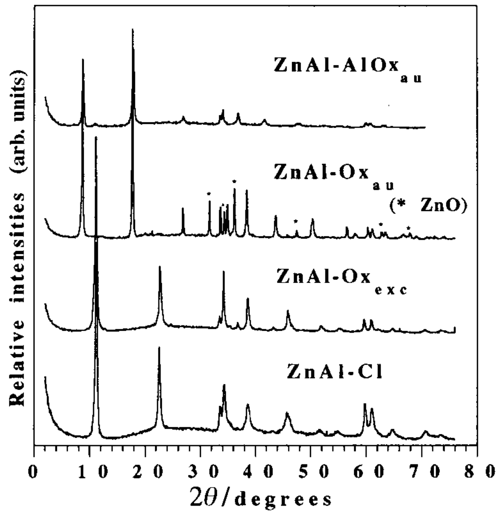

Fig. 2 X-Ray diffractograms of hybrid and precursor LDHs.

Table 2 Powder X-ray diffraction data for precursors and hybrid LDHs

LDH	*a*/nm	*c*/nm	*d*/nm	ss*
ZnAl-Cl	0.3086(4)	2.357(3)	0.786(3)	3R
ZnAl-Ox_{exc}	0.3095(4)	2.333(3)	0.778(3)	3R
ZnAl-Ox_{au}	0.3066(3)	0.9910(9)	0.9910(9)	1H
ZnAl-$AlOx_{au}$	0.3080(3)	2.968(2)	0.989(2)	3R

*ss = stacking sequence.

Intercalation under the same conditions were performed on ZnAl-Cl LDHs with various Zn^{2+}/Al^{3+} ratios (1.0, 2.0, 3.0, 4.0 and 5.0 : 1). XRD patterns of these five phases are displayed in Fig. 4. It appears that intercalation of oxalate in LDHs with a Zn^{2+}/Al^{3+} ratio lower than 3.0 : 1 leads to a mixture of LDH phases with a distribution of basal spacing. For a Zn^{2+}/Al^{3+} ratio equal to or greater than 3.0 : 1, the interlayer oxalate content allows a distribution of the anions in a planar configuration between the hydroxylated planes as discussed previously while when the charge density increases the interlayer space cannot accommodate a greater amount of anions which are then forced to stand in a tilted position.

The exchange reaction performed in an autoclave gave rise to a different LDH phase, namely ZnAl-Ox_{au} (Fig. 2). The interlayer space increased from that in the chloride precursors to 0.9910(9) nm. Meyn *et al.*[17] have reported a ZnAl-Ox LDH (Zn^{2+}/Al^{3+} = 2.0 : 1) with a similar basal spacing of 0.99 nm. They performed an anion exchange on a nitrate LDH precursor

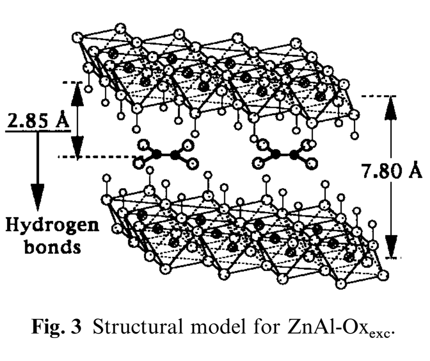

Fig. 3 Structural model for ZnAl-Ox_{exc}.

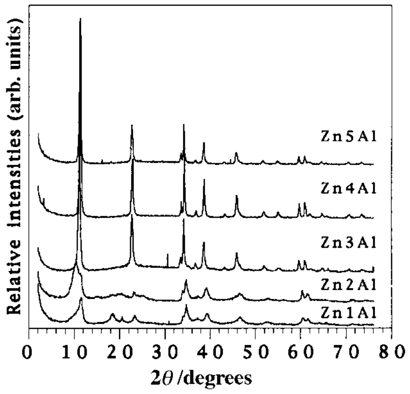

Fig. 4 PXR diffractograms of ZnAl-Ox_{exc} with various Zn^{2+}/Al^{3+} ratios.

for 2 d at 65 °C. They proposed, only on the basis of the basal spacing value, an orientation of the oxalate groups perpendicular to the sheets as for the series of alkali mono- and di-acid salts.

The exchange conditions that we use lead to a LDH phase with an unusually high crystallinity. However, if the use of autogenous pressure conditions provide phases with high crystallinity it leads in all cases to the formation of ZnO, zincite. Attempts to obtain pure phases with the same crystallinity were, unfortunately, unsuccessful.

When X-ray diffractograms for ZnAl-Ox_{exc} are indexed and refined as for the chloride precursors in a hexagonal lattice with a 3R stacking sequence (ss) of the sheets (Table 2), the best indexing for ZnAl-Ox_{au} is obtained in a 1H stacking mode. Values of refined *a* and *c* parameters are listed in Table 2. This is the first time that a 1H stacking sequence has been reported for a synthetic LDH. The basal spacing calculated from the first d_{001} indicates that the interlayer structure is different from that of ZnAl-Ox_{exc}. A simple model where oxalate anions are no longer lying flat in between the layers but are in a tilted orientation, as proposed by Meyn *et al.*[17] does not appear so obvious. Indeed, on the diffractogram of ZnAl-Ox_{au} the inversion of intensity of the two first (00l) diffraction lines must be taken into account. This has been observed for LDH containing heavy interlayer molecular species such as chromate or vanadate in MgAl LDH,[18,19] and has been related to the increase in electron density in (00l) planes at a $d_{bs}/2$ distance of the layers. Traversa *et al.*[14] reported a MgAl LDH-containing oxalate with a Mg^{2+}/Al^{3+} ratio of 1:2 which displays a powder X-ray diffractogram with the same intensity inversion between the (003) and (006) diffraction lines. The occurrence of such a phenomenon for ZnAl-Ox_{au} has two possible origins, one is the decrease in Zn^{2+} content in the layers. This should involve the creation of unoccupied octahedral sites in the plane as in the gibbsite $Al(OH)_3$ phase and explain the presence of zincite on X-ray patterns. The second reason would be the presence of heavier oxalate species intercalated after reaction with some of the metallic cations from the sheets. Indeed oxalate can react with Zn^{2+} or Al^{3+} to form respectively the anionic oxalato complexes $Zn(C_2O_4)_2^{2-}$ or $Al(C_2O_4)_3^{3-}$, the latter being preferentially favoured thermodynamically. However, it appears clearly that, under hydrothermal exchange conditions ZnAl-Ox_{au} is obtained *via* a mechanism of dissolution and reconstruction of the LDH structure which changes the chemical composition of the layers and leads to a new interaction of the host with the oxalate anions.

In order to better characterise the structure of this phase, we carried out, for comparison, the intercalation of $Al(C_2O_4)_3^{3-}$ in ZnAl-Cl using the same preparation conditions, exchange between LDH and potassium trioxalatoaluminate[10] $K_3[Al(C_2O_4)_3]\cdot 3H_2O$. This phase, denoted ZnAl-$AlOx_{au}$ presents a diffractogram (Fig. 1) quite close to that of ZnAl-Ox_{au}, with the series of characteristic LDH diffraction lines, an interlamellar distance of 0.989(2) nm (Table 2) and an intensity inversion between the two first diffraction lines. However, some differences should be noted: ZnAl-$AlOx_{au}$ has a much lower crystallinity than ZnAl-Ox_{au}, it adopts a 3R stacking sequence and no ZnO is formed during preparation.

Infrared spectroscopy

IR spectroscopy is an appropriate technique in order to better understand the structure of ZnAl-Ox_{au} because molecular vibrations of the oxalate anion are very sensitive to the symmetry of the organic anion and to the nature of interactions between $C_2O_4^{2-}$ and its surroundings, through hydrogen or coordination bonds.[20,21] For the sodium oxalate salt the D_{2h} symmetry of $C_2O_4^{2-}$ gives rise to a simple feature in the COO stretching region with two very intense bands, the $\nu_{as}(COO^-)$ (1638 cm^{-1}) and $\nu_s(COO^-)$ (1321 cm^{-1}) bands while for $C_2O_4^{2-}$ in other oxalato complexes the stretching vibrations decompose into a higher number of active IR bands, at least four bands due to the bidentate coordination mode of the anion to the metallic cations.

The FTIR data of ZnAl-Ox_{exc} and ZnAl-Ox_{au} are displayed in Fig. 5 and Table 3 with that of $Na_2C_2O_4$ and $K_3Al(C_2O_4)_3\cdot 3H_2O$. The higher crystallinity of ZnAl-Ox_{au} over ZnAl-Ox_{exc} is evidenced by the high resolution of the lattice vibrations which appear in the wavenumber range 400–650 cm^{-1}. The large and intense band centered at 800 cm^{-1} observed in the IR spectrum of ZnAl-Ox_{exc} is characteristic for LDHs of the MOH stretching band in LDHs. This band has strongly decreased for ZnAl-Ox_{au}. This arises when LDH displays a high ordering of the interlayer domains, with a low content of water molecules and strong interactions between interlayer anions and layer hydroxyl groups or for LDH with inorganic anions grafted onto the layers.[7]

Compared to $Na_2C_2O_4$, ZnAl-Ox_{exc} displays $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ bands shifted about 25 cm^{-1} to lower energy but $\Delta(\nu_{as}-\nu_s)$, characteristic of the bending mode of oxalate,[22] is similar to that of the sodium salt, so the symmetry of $C_2O_4^{2-}$ is probably the same in both compounds. For ZnAl-Ox_{au}, the $\nu_{as}(COO^-)$ band appears in the same position as that for $Na_2C_2O_4$ but $\nu_s(COO^-)$ (1321 cm^{-1}) is split into two bands (1307 and 1286 cm^{-1}) and three new bands are observed, a $\nu_s(COO)$ stretching band at 1427 cm^{-1} and two $\nu(CO)$ bands at 1040 and 948 cm^{-1}. Such changes account for a fundamental modification of the symmetry of $C_2O_4^{2-}$ which is no longer, in ZnAl-Ox_{au}, in a D_{2h} configuration. No such infrared spectrum for oxalate has been reported in the litera-

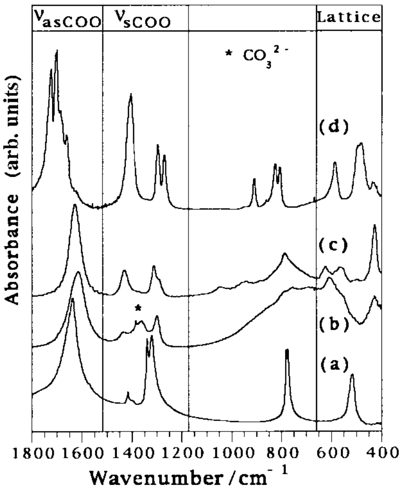

Fig. 5 FTIR spectra of $Na_2C_2O_4$ (a), ZnAl-Ox_{exc} (b), ZnAl-Ox_{au} (c) and $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ (d).

Table 3 IR data of precursors and hybrid LDHs

LDH	ZnAl-Ox$_{exc}$	ZnAl-Ox$_{au}$	$Na_2C_2O_4$	$K_3[Al(C_2O_4)_3]·3H_2O$
$\nu_{as}(COO^-)/cm^{-1}$	1617	1631	1638	1722–1701, 1680–1659
$\nu_s(COO^-)/cm^{-1}$	1434, 1364,[a] 1293	1427, 1307–1286	1321	1406, 1293–1265
$\nu(CO)/cm^{-1}$		1040–948		906, 822–801
	793	786	781	

[a] Contamination by carbonate.

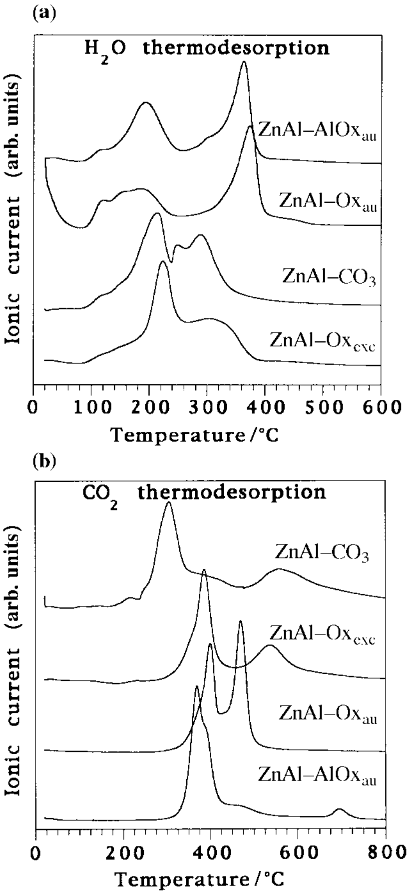

Fig. 6 Thermodesorption of H_2O (a) and CO_2 (b) for oxalate and carbonate containing LDHs.

ture; the nearest feature is found in part of the IR spectrum of $K_3Al(C_2O_4)_3·3H_2O$. Indeed for the aluminum oxalato complex (Table 3) the $\nu_s(COO^-)$ vibrations are split into a single band (1406 cm^{-1}) and a doublet (1293 and 1265 cm^{-1}) and three bands are observed in the ν(CO) region at 906, 822 and 801 cm^{-1}.

For ZnAl-Ox$_{au}$, the IR study is in agreement with structural models in which the hydroxylated layers are strongly affected

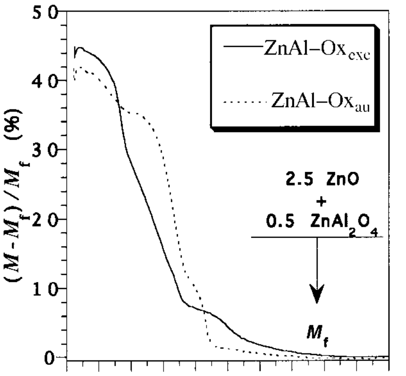

Fig. 7 TG of ZnAl-Ox$_{exc}$ and ZnAl-Ox$_{au}$.

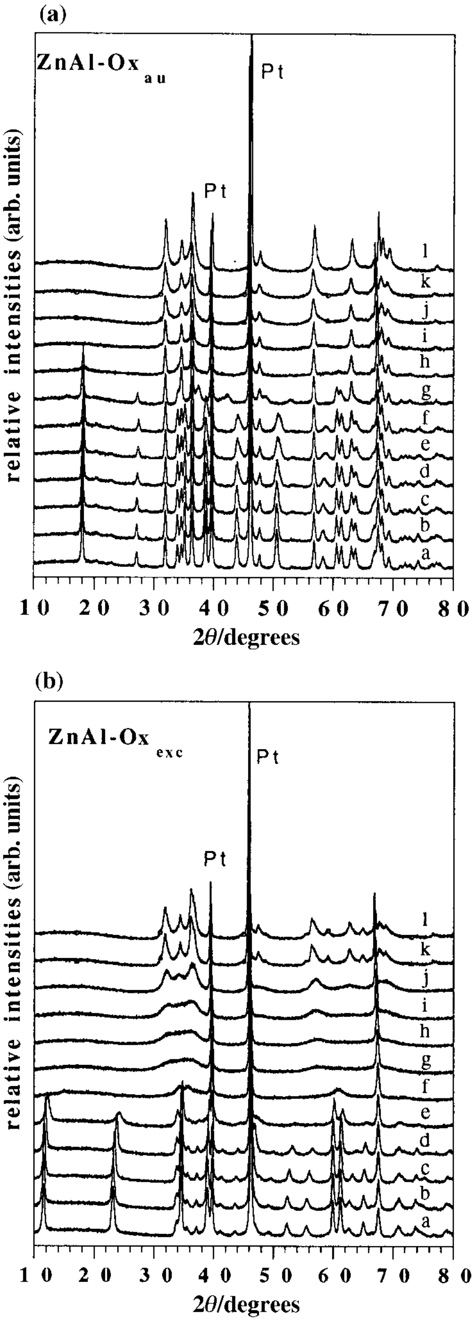

Fig. 8 (a) XRD of ZnAl-Ox$_{au}$ *versus* temperature: 30 °C (a), 50 °C (b), 70 °C (c), 90 °C (d), 110 °C (e), 150 °C (f), 250 °C (g), 350 °C (h), 450 ° (i), 650 °C (j), 850 °C (k), 1050 °C (l). (b) XRD of ZnAl-Ox$_{exc}$ *versus* temperature: 40 °C (a), 60 °C (b), 80 °C (c), 100 °C (d), 120 °C (e), 200 °C (f), 300 °C (g), 400 °C (h), 550 °C (i), 750 °C (j), 950 °C (k), 1050 °C (l).

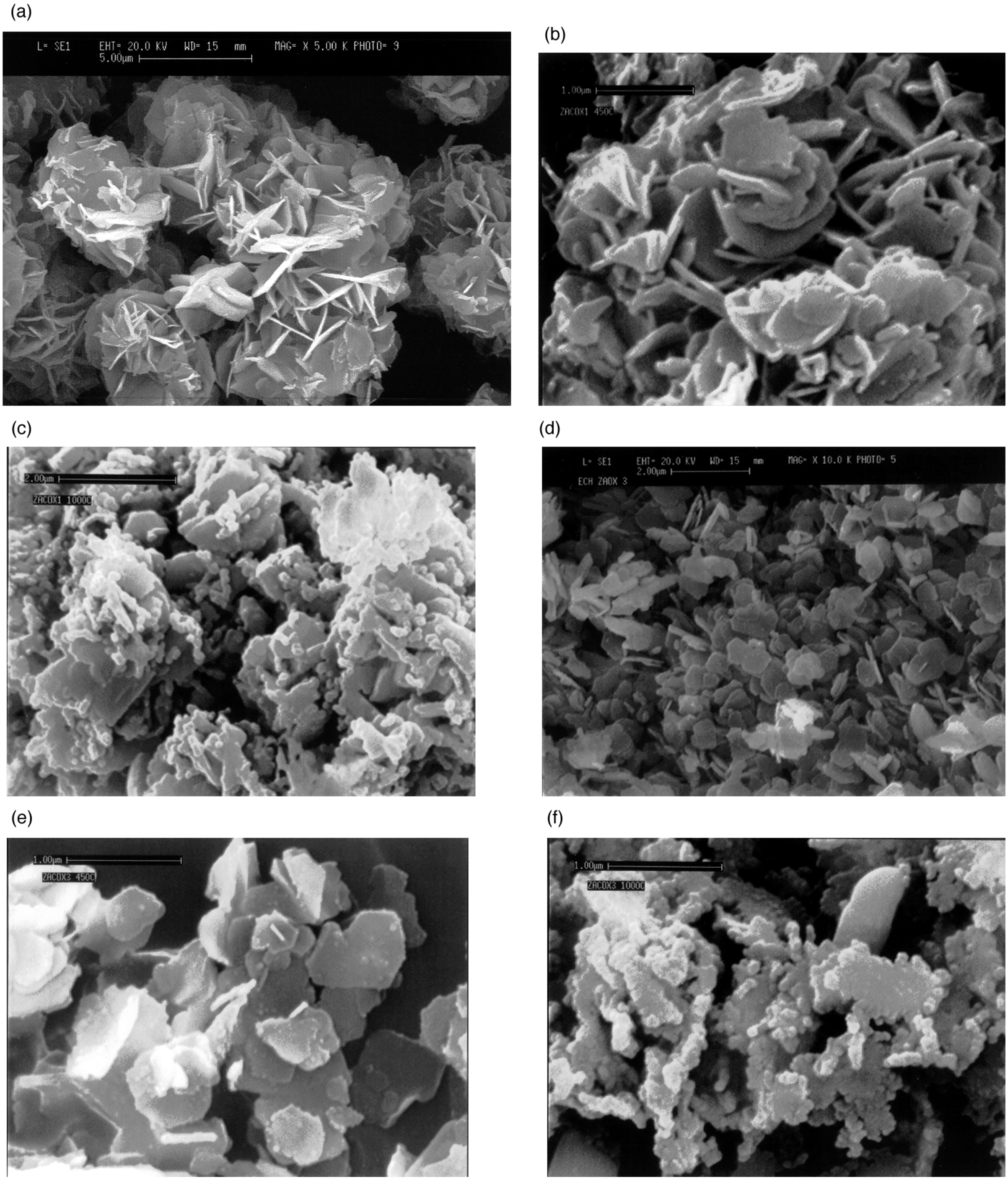

Fig. 9 SEM micrographs of ZnAl-Ox_{exc} (a) and ZnAl-Ox_{au} (d) and phases calcined at 450 °C [(b) and (e)] and 1000 °C [(c) and (f)].

by the intercalated anions and the $C_2O_4^{2-}$ anions are covalently bonded to metallic cations either with metals of the layers or with metals extracted from the layers and intercalated as anionic oxalato complexes.

Thermal behaviour

Thermogravimetry coupled to mass spectrometry. Fig. 6(a) and (b) present the thermodesorption of gases (H_2O and CO_2) evolved during TG analysis of ZnAl-Ox_{exc}, ZnAl-Ox_{au}, ZnAl-CO_3 and ZnAl-$AlOx_{au}$ and measured using a coupled mass spectrometer. The thermal decomposition of oxalate-containing LDH phases involves the thermodesorption of water molecules and carbon dioxide. Water molecules are evolved in the temperature range of 100 to 400/420 °C depending on the LDH, from desorption of intercalated water molecules and from decomposition of hydroxyl groups. In all the LDHs containing oxalate, the organic anion decomposes into CO_2 and evolution of carbon monoxide, typically observed during the decomposition of metal oxalate, was not seen. The H_2O thermodesorption curves reveal close similarity between, on one hand, ZnAl-Ox_{exc} and ZnAl-CO_3 and between ZnAl-Ox_{au} and ZnAl-$AlOx_{au}$ on the other hand. For the two last compounds the dehydroxylation occurs in a well defined step, at higher temperatures between 300 and 400 °C, simultaneously with the first CO_2 thermodesorption event. Fig. 6(b) confirms these analogies. It shows for ZnAl-Ox_{exc}, the decomposition of oxalate in carbonate, and a final step of CO_2 elimination similar for both ZnAl-Ox_{exc} and ZnAl-CO_3. The decomposition of oxalate–LDH in a carbonate phase was reported by

Traversa *et al.*[14] for MgAl but a mechanism with a CO thermodesorption was proposed. On the other hand, ZnAl-Ox_{au} and ZnAl-$AlOx_{au}$ display the same initial step of oxalate decomposition, the various thermal events being restricted on shorter ranges of temperature. The thermal decompositions result for all compounds in the formation of a mixture of zinc and aluminium oxides.

The thermal behaviour of ZnAl-Ox_{exc} and ZnAl-Ox_{au} confirm that differences between these two LDH phases do not arise from different orientations of the oxalate anions in the interlayer domains, but more certainly from different types of interaction between the host lattice and guest molecules.

The TG traces for ZnAl-Ox_{exc} and ZnAl-Ox_{au} are displayed in Fig. 7. The mass losses are calculated in % mass of the residual molecular weight which is similar in both cases and equal to that of a mixture of 2.5 ZnO and 0.5 $ZnAl_2O_4$. Because the chemical composition of the calcined derivatives is the same in both cases, such an unusual property allows one to quantify the amount of organic part whatever the water content of ZnAl-Ox_{exc} and ZnAl-Ox_{au} is. If the total mass loss is nearly the same for the two materials, the remaining mass to be lost at 300 °C, the temperature before organic decomposition occurs, is much lower for ZnAl-Ox_{exc} (15.23%) than for ZnAl-Ox_{au} (29.44%). The former phase has a higher hydration state and undergoes a greater mass loss in a lower temperature range than does ZnAl-Ox_{au} which shows a higher thermal stability.

X-Ray diffraction. Investigation of the thermal behaviour of ZnAl-Ox_{exc} and ZnAl-Ox_{au} was completed by XRD analysis of samples heated from room temperature to the final decomposition step at 1050 °C. Fig. 8(a) and (b) display the patterns of both LDH–oxalates. Great differences are observed between the materials. The higher thermal stability of ZnAl-Ox_{au} observed in the TG study is confirmed by XRD. Indeed ZnAl-Ox_{au} retains the LDH structure up to 250 °C, while ZnAl-Ox_{exc} collapses at a temperature of 150 °C. In the temperature range where the LDH structures are stable, we do not observe any contraction of the basal spacing as usually seen for highly hydrated LDH. We conclude that the interlayer distances in both phases are controlled by the structure of the anion and its interaction with the sheets. Moreover because the dehydroxylation occurs before or during the oxalate decomposition we would not observe the structural transformation of ZnAl-Ox_{exc} in hydroxylated ZnAl-CO_3 as shown for MgAl LDH.[18,19] The ZnAl host structure appears less thermally stable than MgAl. The amorphous intermediate state remains over a large range of temperature from 150–550 °C for the first compound. In the case of ZnAl-Ox_{au} crystallization of ZnO and $ZnAl_2O_4$ occurs after decomposition of the organic matter.

Scanning electron microscopy. The SEM photomicrographs of ZnAl-Ox_{exc} and ZnAl-Ox_{au} as prepared and calcined at 450 and 1000 °C are presented in Fig. 9. The hexagonal platelets are clearly observed for both untreated phases. Homogeneity in shape and dimension of the crystallites is seen. The main difference arises from the way that crystallites are aggregated. ZnAl-Ox_{exc} displays a 'sand rose' morphology whereas the hexagonal plates of ZnAl-Ox_{au} are totally dispersed. This is the effect of preparation conditions (temperature and pressure). For both materials the initial morphology is retained up to 450 °C, a temperature which corresponds to the formation of intermediate amorphous metallic oxides. The micrographs recorded for the samples calcined at 1000 °C are quite similar because thermal decomposition leads, in both cases, to the same mixture of ZnO and spinel $ZnAl_2O_4$. On these micrographs the two oxides are well distinguished, large crystallites of ZnO with small attached spherical particles of $ZnAl_2O_4$.

Conclusion

This work shows that new LDH phases intercalated by oxalate or aluminium oxalate, not yet reported in the literature, are obtained by reactions between oxalate salts and a chloride LDH. In one type, the oxalate anion is in a horizontal arrangement between the layers, like carbonate in LDH, and another highly crystallized LDH type is intercalated by an anionic aluminium oxalato complex obtained *via* an extraction of Al^{3+} from the sheets by the oxalate anions. The mechanism of formation of these phases is not obvious. The most probable mechanism is a dissolution–reconstruction mechanism where some of the M^{3+} is complexed by $C_2O_4{}^{2-}$ as $M(C_2O_4)_3{}^{3-}$ while a LDH host structure is reconstructed with a probably lower Zn^{2+}/Al^{3+} molar ratio as evidenced by the presence of ZnO. Simultaneously or in a final step $M(C_2O_4)_3{}^{3-}$ would be intercalated. This leads to the trapping of oxalate anions in the host structure up to 250 °C.

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