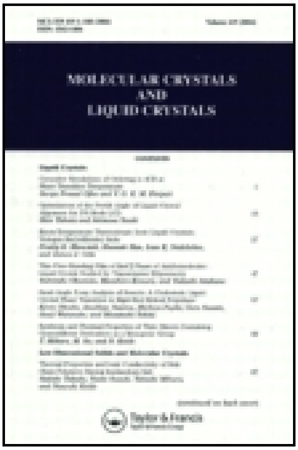

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Synthesis, Thermal and Chemical Behaviour of New Tartrate Intercalated [Zn_3Al] and [Zn_2Cr] Layered Double Hydroxides

V. Prevot [a], C. Forano [a] & J. P. Besse [a]

[a] Université Blaise Pascal, Laboratoire des matériaux inorganiques, UPRES-A 6002, 63177, Aubière Cedex, France

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Synthesis, Thermal and Chemical Behaviour of New Tartrate Intercalated [Zn_3Al] and [Zn_2Cr] Layered Double Hydroxides

V. PREVOT, C. FORANO, J.P. BESSE
Université Blaise Pascal, Laboratoire des matériaux inorganiques, UPRES-A
6002, 63177 Aubière Cedex France

Tartrate anion has been intercalated in [Zn_3Al] and [Zn_2Cr] LDHs. The preparations using either coprecipitation, anionic exchange or reconstruction methods are described. The structural characterization, the thermal evolution and the chemical stability of these phases are studied by PXRD, FTIR, TGA and DTA. Results are presented here.

Keywords LDH; tartrate; thermal treatment; organic-inorganic hybrid material.

INTRODUCTION

Actually organic-inorganic hybrid materials receive considerable attention owing to their very large field of application as catalysts, catalyst supports, electrochemical sensors or sorbent for organic pollutants. Ionic exchangers intercalated by organic entities form one type of the hybrid materials. For this familly of hybrid compounds, the optimization of the chemical and thermal stability needs an increase of the interactions between the organic units and the inorganic surfaces which can be represented in the optimal situation by the grafting. For this study, Layered Double Hydroxide materials (LDHs) described by the $[M^{II}M^{III}(OH)]A^{m-}{}_{x/m}nH_2O$ formula are chosen as inorganic host structures for their high anionic exchange capacities and their layer reactivities. Tartrate, with its two carboxylate groups and its two condensable OH groups appears to be an appropriate guest molecule for the preparation of new stable hybrid LDHs. Intercalation of tartrate anion in LDH and thermal treatements of the hybrid phase are presented here. This study concerns two different LDH phases $[Zn_3Al(OH)_8](C_4H_4O_6)_{0.5}\ nH_2O$ and $[Zn_2Cr(OH)_6](C_4H_4O_6)_{0.5}\ nH_2O$ noted more simply [Zn_3AlTar] and [Zn_2CrTar].

EXPERIMENTAL

The different materials are made via three different methods: anionic exchange on LDH precursor, direct coprecipitation[1] and reconstruction of the LDH phase from calcined LDH derivatives. [Zn_3AlCl], [Zn_3AlTar], [Zn_2CrCl] and [Zn_2CrTar] were coprecitated at the constant pH values respectively 8.0 and 5.5 for the [Zn_3Al] and [Zn_2Cr] LDHs from chloride salts. [Zn_3AlCO_3] was coprecipitated at pH = 9.0.

Tartrate exchange were performed on the chloride LDH precursors. Echange on [Zn_2Cr] was realized at pH = 5.5. The reconstruction method was carried out on the [Zn_3AlCO_3] calcined at 673K. For exchange and reconstruction an excess of 10 equivalent tartrate anion over Al^{3+} content was used. All the preparative procedures were performed with deionized water, under stirring and nitrogen atmosphere. And the precipitate were recovered from their mother liquors by repeated centrifugation-washing cycles.

RESULTS AND DISCUSSION

[Zn_3AlTar]

Only the anionic exchange on the precursor [Zn_3AlCl] has given a pure and well cristallized phase [Zn_3AlTar]. The dianion tartrate was fully intercalated. Indeed the basal spacing (d_{003}) of the precursor, 0.78 nm, increases to 1.22 nm after the exchange, as also reported by MEYN and Co[2]. Exchange was also confirmed by IR spectroscopy. Carboxylate ν_s and ν_{as} stretching vibrations, at 1380 and 1620 cm^{-1} appear on the spectra beside the absorpion bands of the hydroxide layers, M-O and O-M-O between 400-800 cm^{-1}. For all the coprecipitations, whatever the conditions of pH, temperature or excess of anion, the LDHs obtained present a poor cristallinity and allways coexist with an important amorphous phase. The reconstruction method, reported in the litterature as an alternative synthetic pathway for hybrid LDH materials[3], gave no conclusive result, no LDH phase was obtained and ZnO is present in all the cases, whatever the calcination temperature of the precursor. While, with the same conditions, in presence of Na_2CO_3, we succeed to obtain the [Zn_3AlCO_3] phase.

For these two last methods, the complexing nature of the tartrate seems to prevent the LDHs synthesis from happening.

[Zn_2CrTar]

Like for the [Zn_3AlTar], only the exchange reaction has given good results with a 100% exchange either at room temperature or in an autoclave at 120°C. Intercalation has been confirmed by X rays diffraction (XRD) and infrared spectroscopy (IR). The chemical compositions for the various LDH phases were obtained by elemental analysis and are given in Table I, water content was confirmed by thermogravimetry analysis (TGA).

The experimental M^{II}/M^{III} ratio is near to the initial value of the starting salt solutions, thanks to the right coprecipitation pH value. The anion excess is explained by adsorption of the anion on the LDH surface. For both [Zn_3AlTar] and [Zn_2CrTar], all the diffraction lines were indexed in the hexagonal lattice with a $R\bar{3}m$ rhomboedral symmetry.

TABLE I Chemical compositions of the hybrid and precursor compounds

	Zn^{2+}/Al^{3+} or Zn^{2+}/Cr^{3+}	Anion/Al^{3+}	$nH_2O:Al^{3+}$
[Zn_3AlCl]	2.95	1.2	2.5
[Zn_3AlCO_3]	3.04	0.9	2.4
[Zn_3AlTar]	2.73	0.66	2.5
[Zn_2CrCl].	1.8	1.1	3.1
[Zn_2CrTar]	1.7	0.62	2.2

Thermal evolution

We have already reported[4] the grafting of oxoanions (SO_4^{2-},CrO_4^{2-}, $Cr_2O_7^{2-}$, SiO_4^{4-}) on [Zn_3AlCl] and [Zn_2CrCl] LDH by moderate thermal treatments. For the grafting of organic molecules on LDH, in order to prepare new stable hybrid materials, tartrate seems to be the right candidate because of both carboxylate and hydroxy functions of potential reactivities for a grafting process. Moreover, the tartrate is known for giving stable complexes of transition metals. So the thermal stabilities of [Zn_3AlTar] and [Zn_2CrTar] were studied. For [Zn_3AlTar] (Fig1), a structural transition was observed between 333K and 353K, which involves an interlamellar distance contraction of 0.25 nm. We note that the LDH structure is maintained up to 523K, this is an unusual high thermal stability for a

LDH organic nanocomposite; such phases usually display a structural collapse at around 513K.

Similar results were observed for [Zn_2CrTar] with a basal spacing contraction of the same magnitude of 0.272 nm at 343K. The refined parameters of these phases calcined at the different temperatures (Fig2) show that no modification of both ν_s and ν_{as} COO^- stretching band and δ_{COH} characteristic of the tartrate molecule are observed after the transition. This result was confirmed by the ^{13}C CPMAS NMR spectroscopy (Fig 3), the chemical shifts for the carboxylate or the hydroxy carbons are the same for both the untreated and heated phases, respectively 183 ppm and 75 ppm. So it seems clear that the structure of the guest molecules is not affected by the contraction process.

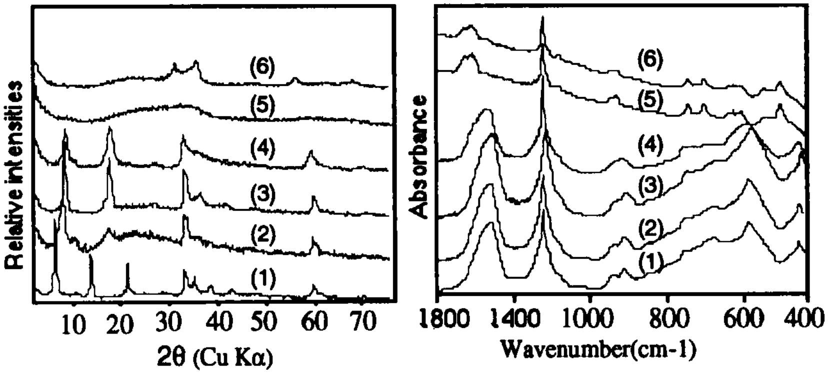

FIGURE 1 and 2 XRD patterns and IR spectra of [Zn_3AlTar] phase calcined at different temperatures:(1)- 293K, (2)-343K, (3)-393K, (4)-473K, (5)-573K, (6)-625K.

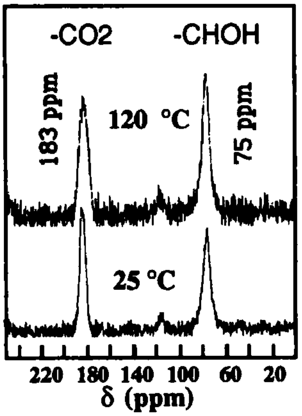

FIGURE 3 CPMAS ^{13}C NMR of untreated and calcined [Zn_3AlTar] LDH.

LDH	a (nm)	c (nm)	d (nm)
$[Zn_3AlTar]$	0.3079	3.671	1.224
$[Zn_3AlTar]_c$	0.3078	2.912	0.971
$[Zn_2CrTar]$	0.3099	3.672	1.224
$[Zn_2CrTar]_c$	0.3091	2.856	0.952

TABLE 2 Refined cell parameters and basal spacing of the tartrate LDH phases.

Chemical stability

In order to study the chemical stability of both $[Zn_3AlTar]$ phases, we have performed two reactive tests: back exchange by CO_3^{2-} and rehydration. LDH, as basic layered hydroxides, are known to display a very high affinity for carbonate. For the original $[Zn_3AlTar]$ a total exchange is observed which leads to a $[Zn_3AlCO_3]$ LDH phase with an interlamellar distance of 0.76 nm. By contrast, for the calcined phase, noted $[Zn_3AlTar]_c$, we have observed only a partial exchange, the XRD pattern shows the coexistence of both $[Zn_3AlCO_3]$ and $[Zn_3AlTar]_c$.

We have tried to rehydrate the $[Zn_3AlTar]_c$ in deionized water, to see if the structural transition was reversible. But, it was impossible to come back to the initial phase with the d = 1.22 nm, in all rehydration conditions either at room temperature and pressure or in a 393K autoclave.These tests have confirmed that after contraction a great strengthening of the interactions between the guest molecules and the host structure is obtained. This leads to an increase of the thermal and chemical stability.

Structural models

All the experimental results agree with structural features for both $[Zn_3AlTar]$ phases where the anions are not grafted at all to the layers but display only different hydrogen bonding with the host matrix. If distances relative to the layer thickness (0.21 nm) and to the hydrogen bond domains between guest and host (0.27 ± 0.01 nm) are subtracted to the basal spacing[5], the distances of the Van der Waals interlayer domains, fully occupied by the anions, are calculated to be 0.474 and 0.221 nm respectively for $[Zn_3AlTar]$ and $[Zn_3AlTar]_c$. Comparison with the size of the tartrate anion (0,471 nm) leads us to conclude that these values are in agreement respectively with a perpendicular and a flat orientation of the tartrate in the internal galleries. Then, the structural transition at about 343K is probably due to a reorientation of the organic anion around the central C_2-C_3 bond, in the interlamellar space. This reorientation leads to a net decrease of the internal micropore size and occurs simultaneous with the expulsion of interlayer water molecules as confirmed by the DTG curves of both phases. We put forward the structures in figure 4.

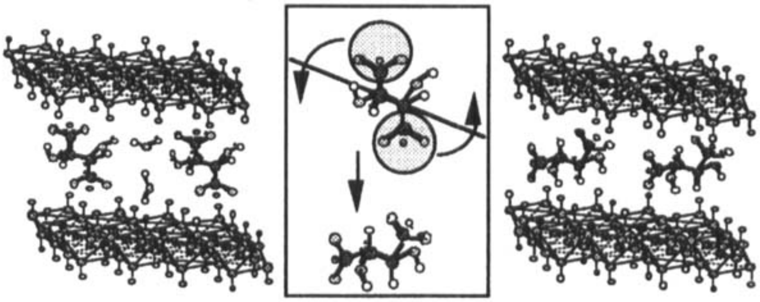

FIGURE 4 Model for the reorientation into the layers of the tartrate.

CONCLUSION

During this study, we have great stressed upon the different method of synthesis and their different results. For the phase [Zn_3AlTar], a moderate heating did not give prominence to a grafting but to a reorientation of tartrate into the interlamellar space at about 343K. This reorientation endows the phase with stability upon 523K, this proves that we have optimized the interactions between organic anions and inorganic host.

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