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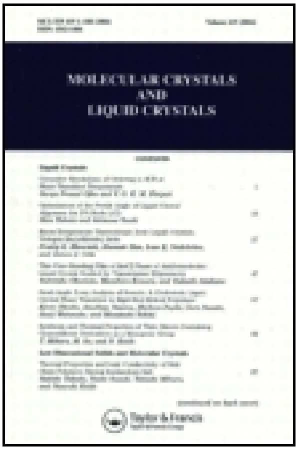

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[Cu-Cr] Layered Double Hydroxides Pillared by CrO_4^{2-} and $Cr_2O_7^{2-}$ Oxometalates

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[Cu-Cr] LAYERED DOUBLE HYDROXIDES PILLARED BY CrO_4^{2-} AND $Cr_2O_7^{2-}$ OXOMETALATES

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Abstract The grafting of CrO_4^{2-} and $Cr_2O_7^{2-}$ oxometalates has been evidenced on [Cu-Cr] layered double hydroxides by a PXRD study under moderate heating and by Infrared spectroscopy.

INTRODUCTION

Among the LDHs[1], hydrotalcite like compounds of general formula: $\left[M^{II}_{1-x}M^{III}_{x}(OH)_2\right]^{x+}\left[X^{m-}_{x/m}.nH_2O\right]^{x-}$ (abbreviated notation: $_x[M^{II}\text{-}M^{III}\text{-}X]$) are known as the most efficient anionic exchangers. They can intercalate between the hydroxylated layers a wide range of anions such as halide, inorganic oxoanions or anionic organic molecules. So far, evidences of pillaring LDH have only been shown for intercalated iso or heteropolyanions, though no grafting has clearly been demonstrated. Moreover such voluminous anions fill almost completely the interlamellar space and prevent high porosity properties. Grafting of the [Zn-Al] and [Zn-Cr] LDH by tetrahedral oxoanions such as SO_4^{2-} and CrO_4^{2-} has been obtained by our research group[1,2]. In order to prepare effective pillared LDH, we have chosen to prepare Cu(II) containing LDH. Layered Cu(II) hydroxides are known to occur naturally with carbonate, chloride and other anions, replacing partially the hydroxyl groups, and so, they are good candidates for pillaring. In consequence, we have studied the pillaring of [Cu-Cr] LDH by CrO_4^{2-} and $Cr_2O_7^{2-}$. The interlamellar contraction under grafting is demonstrated by PXRD.

EXPERIMENTAL

Synthesis of the materials

- Synthesis of [Cu-Cr-Cl] precursor

The sample has been synthesised by the coprecipitation method at a constant pH of 5.5. A mixed solution of 1M $Cu(NO_3)_2.3H_2O$ and 1M $CrCl_3.6H_2O$ is added at a constant

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flow in a beaker containing decarbonated water. Then the LDH is precipitated by a 2M NaOH solution using an automated titrator monitored by the pH controller. The mixture is stirred at room temperature for about 12 hours. Then, repeated washings are performed by suspending the gel into distilled decarbonated water. The recovery is achieved through centrifugations and then the product is left to air-dry at room temperature. The chemical analysis is in agreement with the following composition: $Cu_2Cr(OH)_6Cl.xH_2O$ (with $x \approx 3.0$).

- Synthesis of pillared LDH

The chlorides, initially present in the synthesised compounds can be replaced through exchange by other anions. Practically, the LDH precursor is suspended in an aqueous solution containing a large excess of the anion to be exchanged. The exchange is usually complete after few hours of magnetic stirring at room temperature. The resulting product is then washed and air-dried as previously described for the coprecipitation method. The exchange is controlled by PXRD analysis. The rate of exchange have been analysed in both cases to be 94% and 96% for respectively [Cu-Cr-CrO_4] and [Cu-Cr-Cr_2O_7].

pH of the exchange reaction must be kept in the limits of LDH and anion stability. CrO_4^{2-} are the major anionic species at a pH value > 6.0 meanwhile $Cr_2O_7^{2-}$ is obtained for lower pH values. In consequence, [Cu-Cr-CrO_4] and [Cu-Cr-Cr_2O_7] have been exchanged respectively at pH=8.5 and pH=4.5.

RESULTS AND DISCUSSION

Pillaring of [Cu-Cr] LDH

The [Cu-Cr-Cl] X ray diffractogram (Siemens D501 X-ray diffractometer, Cu Kα) is characteristic of an hexagonal lattice with a rhomboedral symmetry. The refined parameters of the unit cell are a = 3.107 Å and c = 23.054 Å and the basal spacing of 7.68 Å is characteristic of chloride containing LDH phase (Figure 1). The exchange of the oxoanions on [Cu-Cr-Cl] leads in all cases to a lowering of the crystallinity. The number of diffraction lines is very limited (not much than 6 for the chromate and dichromate LDH, including the most intense 00ℓ). The exchange reactions on LDH have been demonstrated to be topotactic reactions, so we probably maintain the hexagonal symmetry for the new LDH. The main structural differences inside the LDH family concerns the stacking of the layers which can be of three types, 1H, 2H or 3R. The poorness of the structural information prevents any identification of the ordering along the perpendicular direction to the planes for our materials. Anyhow, it is possible to give approximated values of the intermetallic and interlayer distances from respectively the 110 and the first observed 001 diffraction lines.

The interlamellar spacings of these new LDH phases are subject to strong variation relative to the storage conditions. We have previously reported distances such as 8.35 Å and 8.08 Å for respectively freshly prepared [Cu-Cr-Cr_2O_7] and [Cu-Cr-CrO_4] (Private communication). Newly prepared compounds exhibit distances of 8.95 Å and 8.42 Å for dichromate and chromate phases respectively. The capability of these phases to intercalate variable amounts of water molecules is moreover confirmed by the different hydration states determined by TGA and chemical analysis. The hydration state is subjected to the equilibrium between the LDH phases and the relative humidity of the ambient atmosphere. These two phases undergo a slow evolution to contracted forms with smaller basal spacings of 7.68 Å and 7.87 Å for respectively the chromate and dichromate phases. These too short distances cannot account for free interlayer oxoanions CrO_4^{2-} and $Cr_2O_7^{2-}$ and are not far from 7.22 Å, the interlayer spacing of $Cu_2(OH)_3MnO_4$ for which MnO_4^- is grafted onto the hydroxylated layer[3]. So, these structural compressions evidence an effective pillaring of the oxoanions on the hydroxylated sheets. This easiness of contraction arises from the specific chemical properties of copper which can give a wide range of lamellar copper hydroxides $Cu_2(OH)_3A$ (A = Cl, ClO_4, NO_3, MnO_4, CH_3COO...)[3] with short interlayer distances. This tendency to the pillaring has also been observed for SO_4^{2-} anion containing LDH[2]. In order to confirm the pillaring of LDH by oxoanions, we have studied the reversibility of the exchange reactions. These phases have been readily exchanged by Cl^- anions in aqueous solution in the presence of an excess of KCl, giving rise to the formation of the easily identified [Cu-Cr-Cl] LDH. Consequently, the oxometalates cannot be consider as permanent pillars in such phases.

Grafting under moderate heating

In order to obtain permanent pillars grafted onto the brucitic layer, the X-ray diffraction spectra of both chromate and dichromate phases have been recorded after heating them 24 hours under air atmosphere. The results are compared to the structural evolution of the [Cu-Cr-Cl] LDH under the same thermal treatment (See Figures 1, 2 and 3).

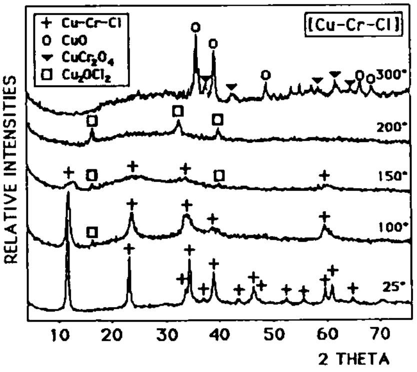

FIGURE 1 Evolution of PXR Diffractograms of $_{0.33}$[Cu-Cr-Cl] LDH with the heating temperature.

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For [Cu-Cr-Cl], in the range of 25°C-150°C, the shift of the 003 diffraction line is in agreement with a strong shortening of the interlamellar distance from 7.68 Å (25°C) to 7.51 Å (100°C) and finally to 7.10 Å (150°C). Such a short distance has not yet been observed for calcined chloride-containing LDH such as [Zn-Al-Cl] and [Zn-Cr-Cl]. It accounts for the removing of the interlamellar water but also for the appearance of stronger interactions between the chloride anions and the hydroxylated sheets. However, the shorter interlayer distance of 5.71 Å encountered for the mineral $Cu_2(OH)_3Cl$ is not reached. In the temperature range of 200°C-300°C, the LDH structure collapses under dehydroxylation and Cu_2OCl_2 crystallises.

The structural evolution of the [Cu-Cr-CrO$_4$] LDH evidences an amorphisation of the phase under dehydroxylation in the same temperature range as the chloride analog. On the other hand, the dichromate containing phases retains the LDH structure at higher temperature (200°C).

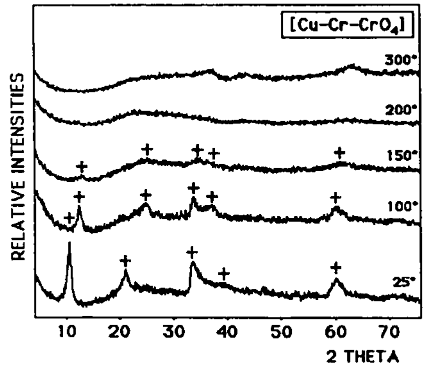

FIGURE 2 Evolution of PXR Diffractograms of $_{0.33}$[Cu-Cr-CrO$_4$] LDH with the heating temperature.

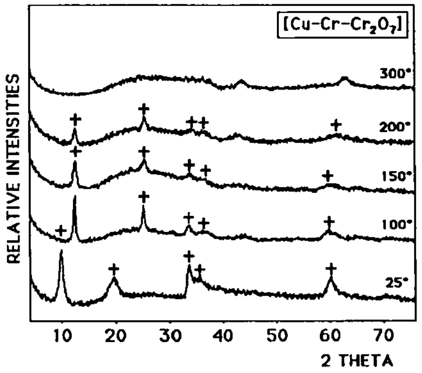

FIGURE 3 Evolution of PXR Diffractograms of $_{0.33}$[Cu-Cr-Cr$_2$O$_7$] LDH with the heating temperature.

The interlayer distance d is modified by temperature to an extent which differs for each one of the products (Figure 4). The change in the interlayer distance for [Cu-Cr-Cl] is typical of a dehydration with a characteristic decrease of the basal spacing over 80°C. When the compound is exchanged by CrO_4^{2-} and $Cr_2O_7^{2-}$, the behaviour is totally different. From room temperature to 80°C, the interlayer distance decreases rapidly from 8.45 Å to 7.30 Å for [Cu-Cr-CrO$_4$] and from 8.95 Å to 7.10 Å for [Cu-Cr-Cr$_2$O$_7$], while only a small decrease is observed in the case of [Cu-Cr-Cl]. Above 80°C, the decrease in the interlayer distance in the case of the exchanged compounds is slower than in that of [Cu-Cr-Cl] but of a comparable amplitude.

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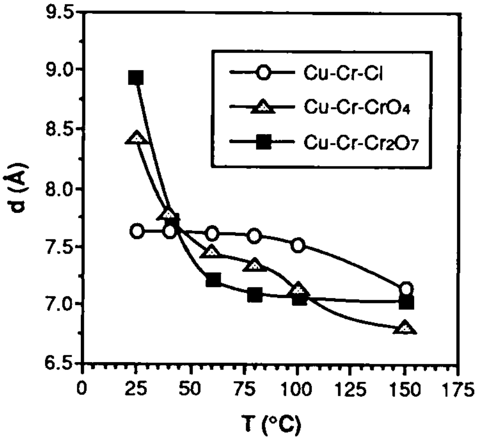

FIGURE 4 Effect of heating on interlayer spacings of [Cu-Cr-X] LDH (X= Cl, CrO_4^{2-} and $Cr_2O_7^{2-}$)

The substantial decrease in the interlayer distance in the case of the two compounds after exchange cannot be explained only by a dehydration process. The strong decrease of the basal spacing to 7.10 Å is irreversible and oxometalates anions cannot be exchanged anymore. These new LDH phases are now really pillared by permanent pillars. These strong compressions of the layers which involved a reticulation of the anions on the hydroxylated sheets by the replacement of an OH linked to the metallic cations are followed by the collapse of the structures above 200°C.

Infrared Analysis

The FTIR spectra (Perkin-Elmer PE16 FTIR spectrophotometer, KBr pellets) of the chromate LDH represented in figure 5 show the stretching vibration bands characteristic of the chromium tetrahedral polyedra in the region from 800 to 1000 cm^{-1}. These bands are broad because of the anisotropy of environment in the interlayer domain. Moreover, they overlap the M-OH bending vibrations of the layers which have been identified on the [Cu-Cr-Cl] IR spectrum.

The structural change under calcination at 100, 150 and 200°C is evidenced on the IR spectra of these three phases. We can notice the appearance of a new band at about 800 cm^{-1} (790 cm^{-1} for the chromate LDH and 820 cm^{-1} for the dichromate one) located near the Cr-O stretching vibration of Cr-O-Cr bridge reported on dichromate species[4]. The band which grows under heating should be identified as the Cr-O stretching band of a grafted chromate onto the layer. Over 200°C, the collapse of the structure leads to an important broadening of the IR vibration bands.

The FTIR spectra of the dichromate and calcined dichromate phases represented in figure 6 lead to the same conclusion. However, we must notice an higher resolution for the uncalcined phase in agreement with a higher order of these anionic species inside the interlayer domain. At 100°C, the growing of the Cr-O symmetric stretching band seems to confirm here again a pillaring phenomenon. This evolution is more important for the 150 and 200°C calcined phases which have shorter interlayer spacings.

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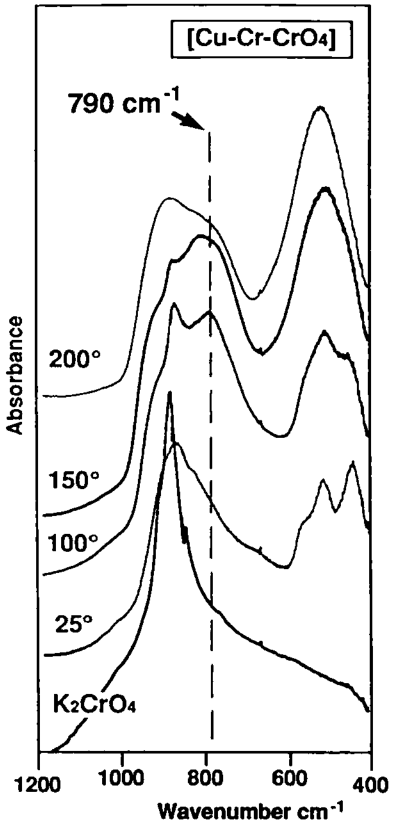

FIGURE 5 Infrared spectra of [Cu-Cr-CrO_4] LDH at different temperatures.

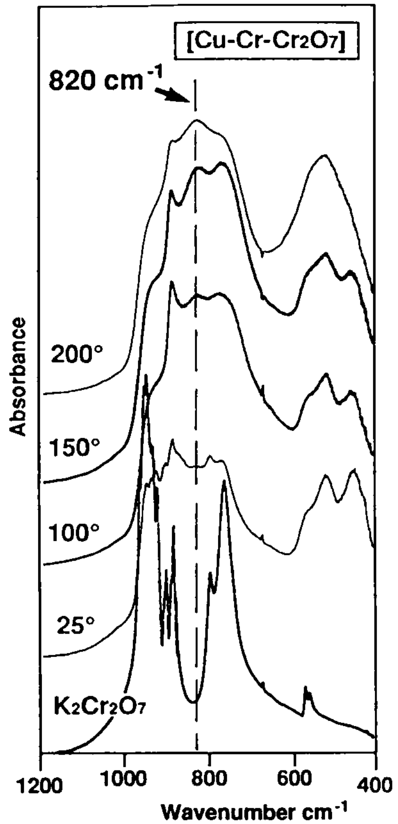

FIGURE 6 Infrared spectra of [Cu-Cr-Cr_2O_7] LDH at different temperatures.

CONCLUSION

This work has evidenced a pillaring phenomenon of CrO_4^{2-} and $Cr_2O_7^{2-}$ oxometalates onto the brucitic layers of [Cu-Cr] LDH. We will carry on our researchs in this way by studying the reticulation of other anions on such compounds at moderate temperatures. We acknowledge the European Community which supports this work, realized under a Brite Euram program.

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