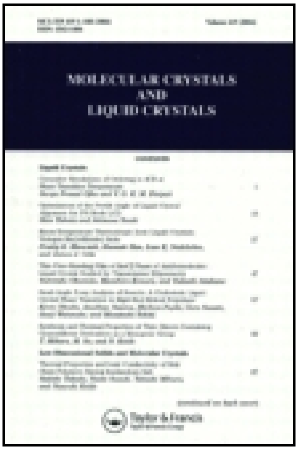

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First EXAFS Characterisation of a Grafting Process in Layered Double Hydroxides

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First EXAFS Characterisation of a Grafting Process in Layered Double Hydroxides

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In this work the grafting process occurring during thermal treatments on [Ni-Al] based LDHs intercalated with CrO_4^{2-} or $Cr_2O_7^{2-}$ oxoanions is investigated.
The irreversible decrease of the basal spacing evidenced by PXRD measurements strongly suggests the occurrence of a grafting process.
EXAFS measurements are performed at very low temperature (8K) at the K-edge of the Cr atom of the intercalated anionic species. The radial density patterns clearly show the grafting of CrO_4^{2-} or $Cr_2O_7^{2-}$ anions on the brucitic sheets by the appearance of a new feature at about 3.40 Å on the compounds calcined at 150°C.

Keywords: layered double hydroxides ; anionic clays ; grafting ; EXAFS.

INTRODUCTION

Layered Double Hydroxides (LDHs) consist of positively charged brucite-like $M(OH)_2$ layers separated by interlamellar counteranions and water molecules. The chemical composition of such lamellar compounds is :
$[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}\ [X^{q-}_{x/q}\ .nH_2O]^{x-}$, (abbreviated notation: $[M^{II}\text{-}M^{III}\text{-}X]$) where M^{II} and M^{III} represent divalent and trivalent metallic cations, and X^{q-} is the charge-balancing interlayer gallery anion.

In LDHs, interlamellar species are generally tied onto layers by Van der Waals-like interactions. By appropriate post-synthesis treatments such phases can be stabilised by creating stronger bonds between anions and layers. This grafting reaction is a route to obtain pillared lamellar solids which can be tailored with the size and the charge of interlamellar anions. Of interest is the potential utility for shape-selective adsorption and catalysis. In this work, we have focused on the intercalation of chromate and dichromate oxoanions in [Ni-Al] based LDHs. These compounds are synthetised by the anionic exchange method from a chloride precursor prepared by coprecipitation[1,2].

RESULTS AND DISCUSSION

X-Ray Diffraction

We have realised powder X ray diffraction measurements (PXRD) on all phases prepared at room temperature and calcined at various temperature in order to study the effect of moderate thermal treatments.

At room temperature, [Ni-Al-Cl] phase has a quite poorly organised structure (Fig. 1(a)) but the first two (00l) harmonics are well defined and evidence the lamellar character of this compound. After a 24h heating treatment the structure is well conserved at 200°C and subsists until 250 or 300°C with a great decrease in the crystallinity. The weak contraction of interlayer distance *d* (Fig. 1(b)), directly related to the (00l) harmonics position, corresponds to the elimination of interlamellar water molecules

PXRD patterns of [Ni-Al-CrO_4] and [Ni-Al-Cr_2O_7] exchanged phases show an increase in the basal spacing and a decrease in the crystallinity in comparison with the precursor. The thermal stability is improved with a maintenance of the lamellar LDH structure up to 300°C for the chromate and 350°C for the dichromate. Moreover there is a strong and irreversible decrease in the basal spacing *d* from room temperature to 100°C (Fig. 1(b)) that can not be just due to dehydration.

On the other hand we also observe a disappearance of exchange properties.

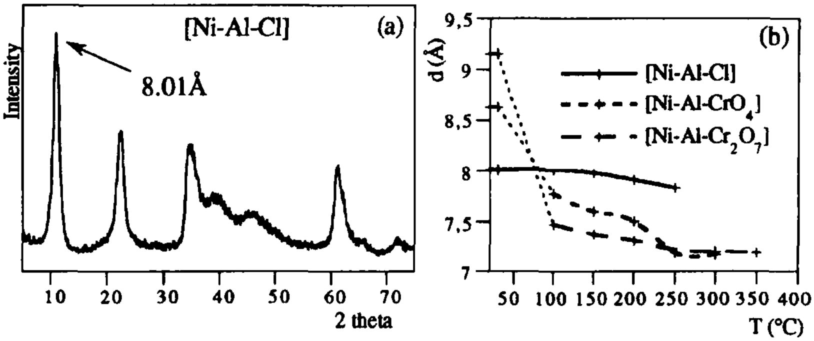

FIGURE 1 (a) [Ni-Al-Cl] diffraction pattern.
(b) Thermal evolution of interlayer spacing.

These phenomena can be explained by a grafting process of CrO_4^{2-} or $Cr_2O_7^{2-}$ anions onto [Ni-Al] hydroxilated layers : the creation of strong bonds between intercalated oxoanions and layers induces a contraction of the interlayer space and these anions, acting as pillars, have a thermal stabilisation effect on the structure.

EXAFS

Because of the low crystallinity of these LDHs, the study of their fine structure involves the use of EXAFS, sensitive to local environment rather than a long range order.

In the case of hydrotalcite-like phases, the target atoms can be either the metallic cations of the hydroxylated layers or the anion itself or an element belonging to the anionic species.

Radial distributions are described by pointing the peaks position with no corrected distances (NC) for phase shift.

Ni K-edge

Spectra of LDH compounds prepared at room temperature are constituted of two main peaks : the first one, at 1.5 Å NC, corresponds to the first O shell coordination surrounding the absorbing atom, and the second one, at 2.7 Å NC, to the first metallic neighbours.

We have seen by PXRD a decrease in the crystallinity from the chloride precursor to the exchanged LDH compounds whereas the radial distributions are very similar whatever the intercalated anion. The exchange of the Cl^- ions by CrO_4^{2-} or $Cr_2O_7^{2-}$ inside the interlamellar domain does not affect the Ni K-edge EXAFS spectra which does not seem to be sensitive to what happened between two sheets. This can be explained by the distance between Ni atoms and intercalated anions (about 4 Å) and probably by the great static and thermal structural disorder of the free anions into the interlayer space.

A calcination at 150°C does not induce sensitive modification of the radial distributions, and the grafting can not be seen. This is not really surprising because the intense second peak is in the domain where modifications are expected (3.4 Å).

Cr K-edge

The radial distributions of exchanged phases are shown on Fig. 2.

The tetrahedral oxygen environment of the Cr atom in chromate or dichromate is represented by the first sharp peak at 1.22 Å NC. Modelisations indicate that the Cr-O distance is 1.66 Å, which is consistent with the distance in K_2CrO_4. After a 24 h calcination at 150°C this first peak (Fig. 2) is not affected, so the first coordination shell of chromium has a good thermal stability.

Very low temperature experiments on the [Ni-Al-CrO_4] 25°C sample allow to see two different peaks in the 2 - 3.5 Å NC domain (Fig. 2), whereas radial distributions realised at room temperature exhibit only one wide peak. When a k^3 weighted Fourier transform (FT) is performed, relative intensities of electronic density maxima do not change. So we can think that these peaks are not due to the response of heavy atoms, but to atoms whose atomic number is close to oxygen :

- the first one, at 2.42 Å NC must correspond to atoms of the interlayer domain because the nearest atoms constituting the sheet are too far (about 3.3 Å) from Cr to be concerned.

- the second one, at 2.94 Å NC can correspond both to interlamellar entities or sheet hydroxyls when we consider we must add 0.4-0.5 Å because of the phase shift. The latter hypothesis should be the good one because hydroxyls have a better defined position than free species of the interlayer.

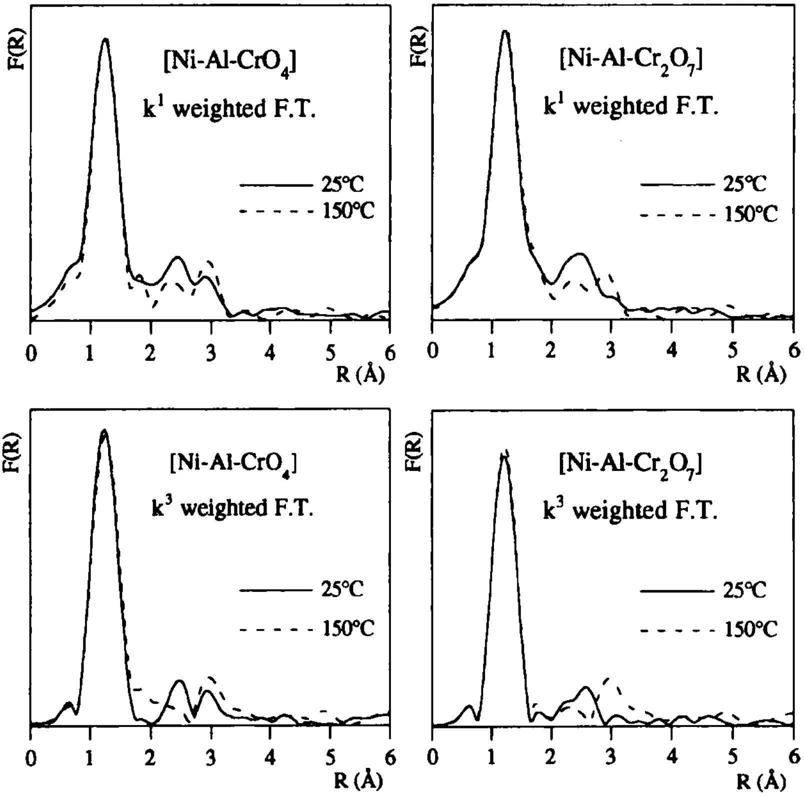

FIGURE 2 k^1 and k^3 Fourier transformed measured at 8K at the Cr K-edge in exchanged phases no heated and heated at 150°C.

A 150°C heat treatment modify the shape of the radial distribution in the same 2 - 3.5 Å NC domain :

- the important loss of intensity of the peak at 2.42 Å NC corresponds to departure of water molecules and confirms that this signal is due to light atoms (oxygen).

- the intensity of the second peak clearly increases and a k^3 weighted FT exalts its relative intensity as it usually occurs for heavy backscatterers. A k^3 weighted FT on the untreated phase does not show the same trend. Modelisations performed on this peak confirm the presence of a combination of both Ni and Al atoms at 3.42 Å.

We can note the same evolution for the [Ni-Al-Cr_2O_7] phase with an intense peak at 3.92 Å NC on the k^3 weighted FT of the calcined compound. Modelisations give a distance Cr-Ni/Al = 3.39 Å.

These values are consistent with the expected distance Cr-Ni or Cr-Al when an oxygen atom becomes the apex of both a CrO_4 (or Cr_2O_7) tetrahedron and an octahedron of the brucite-like sheet.

CONCLUSION

PXRD and Ni K-edge EXAFS studies highlight the thermal stabilisation effect of chromate or dichromate anions on the LDH structure. Moreover we observe a strong and irreversible decrease in the basal spacing and a complete loss of anionic exchange properties for the calcined phases. These clues strongly support a grafting process.

Very low temperature EXAFS results about exchanged phases at the Cr K-edge clearly evidence the grafting of CrO_4^{2-} or $Cr_2O_7^{2-}$ anions onto the hydroxylated sheets by the appearance of a new feature on the radial distribution at about 3.0 Å NC on the compounds heated at 150°C. Simulations confirm the presence of Ni and Al atoms at 3.40 Å which is the expected distance for grafted chromate or dichromate species.

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