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XAFS Study of Structural Evolution During Calcination of Two Zinc-Chromium Based Lamellar Double Hydroxides

A. Ennaqadi, M. Khaldi, A. de Roy, C. Forano and J.P. Besse

Laboratoire de Physico-Chimie des Matériaux, URA 444 du CNRS, 63177 Aubière Cx, France

Abstract. Two [Zn-Cr^{III}] Lamellar Double Hydroxides respectively intercalated by chloride and sulphate anions were prepared and two series of samples were obtained by heating these two compounds at increasing temperatures. At temperatures higher than 200°C these compounds become ill-organized materials. The lamellar structure collapses at about 300°C leading to highly divided amorphous oxides. A spinel-like phase and zinc oxide crystallise at high temperatures. The EXAFS study at Zn and Cr K-edges shows clearly the presence of a pre-spinel organisation in the ill-organized samples at intermediate temperature range. The XANES spectra at Cr K-edge evidence the formation of small amounts of Cr^{VI} which disappears at higher temperatures. These behaviours are observed at slightly different temperatures for both sulphate and chloride intercalated precursors.

1. INTRODUCTION

Lamellar Double Hydroxides (LDHs) are based on brucite-like M(OH)₂ layers containing mixed M^{II}, M^{III} metallic cations.

The general formula:

gives prominence to the positively charged main layers separated by charge balancing interlamellar domains of solvated X anionic species; we shall use the short notation [M^{II}-M^{III}-X]. These materials display a broad spectrum of potential applications and one of the main fields of research is their use as catalysts and precursors of catalysts [1,2]. By controlled calcination, they lead to highly divided amorphous oxides. It is therefore necessary to characterise accurately their thermal evolution.

In previous works [3-4] we studied, the [Zn-Cr-Cl] and [Zn-Cr-SO₄] LDHs. These compound were prepared by the coprecipitation methods [5] with a x=1/3 trivalent metal ratio. Crystal structures were studied by the Rietveld method on PXRD data. The thermal evolution of these precursors was also followed by Thermo-Gravimetric, Differential Thermal Analysis, Infra-Red spectroscopy and Powder X-Ray Diffraction (PXRD) measurements. At low temperatures (20-300°C), the LDH structure evolves with changes in the basal spacing and stacking sequence of the layers. At high temperatures (more than 800°C) well crystallised ZnO and a ZnCr₂O₄ spinel-like phase are obtained. The intermediary temperature domain from 300°C to 450°C displays very ill-organised materials.

In this paper we give some XAFS results on the temperature related structural evolution of these compounds. Samples were heated overnight in air at thirteen different temperatures up to 1030°C and characterised at room-temperature. XAFS transmission mode measurements at Zn and Cr K-edges, were performed at the LURE, EXAFS IV station on DCI ring. Absorption data was processed with the software written by A. Michalowicz. [6-8] In this short report, experimental data is only given for some selected calcination temperatures of the [Zn-Cr-SO₄] precursor.

2. EXAFS CHARACTERISATION

2.1 Zn K-edge

The absorption was measured in the 9600-10600 eV range with a 2 eV step. The k³ χ(k) radial distributions of selected samples at zinc K-edge are reported in Figure 1. The [Zn-Cr-SO₄] precursor displays two main peaks; the first one corresponds to the six oxygen atoms of hydroxyl groups octahedrally surrounding the zinc

Figure 1: k³ χ(k) Radial distribution at zinc K-edge

atoms and the second one to the six nearest metallic cations in the LDH main layer. By heating at 360°C a quasi amorphous oxysulphate is obtained; as the LDH structure collapse, the second peak disappears and the first peak shifts to a lower distance, very close to the one observed in zinc oxide and shorter than in the ZnCr_2O_4 spinel-like phase obtained at 1100°C from ZnO and Cr_2O_3 . However the global shape of radial distribution is similar to ZnCr_2O_4 .

2.2 Cr K-edge

The absorption was measured in the 5930-6930 eV range with a 2 eV step. The $k^3 \chi(k)$ radial distributions at chromium K-edge are reported in Figure 2. For the $[\text{Zn-Cr-SO}_4]$ precursor, the two main peaks correspond respectively to the same neighbouring atoms as at Zn K-edge. The 360°C heated sample radial distribution looks very close to the one of the ZnCr_2O_4 phase. On the opposite to the behaviour observed at Zn K-edge, the position of the first peak corresponding to Cr-O distances remains constant.

Figure 2: $k^3 \chi(k)$ Radial distribution at chromium K-edge

Figure 3: XANES spectra at chromium K-edge

3. XANES CHARACTERISATION

The measurements were performed at the Cr K-edge (5980-6020 eV with a 0.5 eV step). For all of the samples, the K-edge displays the same global shape consistent with octahedrally surrounded Cr^{III} moieties. Compared with the calcined samples, the white band of the LDH precursor (6009.5 eV) is observed at a lower energy (≈ 2 eV). A remarkable feature is the presence of a small pre-peak at 5994.2 eV for all samples since dehydroxylation of LDH layers (200°C) which disappears at higher temperatures (500°C). This pre-peak is obviously related to the presence of small amounts of Cr^{VI} in this temperature range.

4. CONCLUSION

The EXAFS study of the $[\text{Zn-Cr-SO}_4]$ Lamellar Double Hydroxides is consistent with the early formation of a pre-spinel short-range organisation in the ill-organised materials obtained at 300 - 450°C. Such structural relationship between lamellar atacamite and spinel-like structure was reported elsewhere [9]. Mainly in the same temperature range, the formation of small amounts of Cr^{VI} is evidenced by the XANES study; at higher temperatures only Cr^{III} remains. The $[\text{Zn-Cr-Cl}]$ phase displays a similar behaviour under thermal treatment but the sulphate intercalated material displays a higher thermal stability.

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