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Structural Study of Interlayer Zr Particles in Exchanged and Pillared Beidellite

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ABSTRACT. Zirconia pillared clays (with synthetic beidellite as host material) were prepared by replacing the sodium interlayer cations by zirconium hydroxy polycations, and then heating to stabilize the structure. The pillaring solution was an aqueous solution of zirconyl chloride, but the structure of the polycation which is intercalated remains unknown. From the XRD data, the interlayer spacing was found to be 9 Å in Zr exchanged beidellite and slightly lower (7 Å) after calcination. The local environment of zirconium in solid zirconyl chloride and in the pillaring solution was first examined and then in the ion-exchanged and calcined beidellite. The EXAFS results for zirconyl chloride in the solid state and in aqueous solution, showed that the nearest neighbours and the next-nearest-neighbours environments of Zr are identical in solid and in solution. In the Zr-exchanged beidellite, the Zr cations have the same environment as in the pillaring solution. On the opposite, the mean Zr-O and Zr-Zr distances in the calcined sample are shortened with respect to Zr-exchanged beidellite.

The main interest in clays pillaring is to generate tailor-made structures by controlling the size and population of pillars between the silicate layers. These materials have therefore potential as catalysts in hydrocarbon hydrocracking and for a wide variety of proton catalysed reactions. Among all the pillaring species, Zr is one of the few transition metals known to provide stable pillars. Zirconyl chloride solutions are usually used in the ion exchange step [1] but despite all the work already carried out in this field, the structure of the hydroxy-Zr compounds in the intercalated clay is not clearly established and the transformation into ZrO_2 has not really been evidenced.

Zirconyl chloride octahydrate $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ used to prepare the pillaring solution crystallizes in the tetragonal symmetry ($a = 17.08$ Å and $c = 7.69$ Å) [2]. In the zirconyl unit, four Zr atoms are located at the corners of a slightly distorted square and linked along each edge of the square by two OH groups, one above and one below the plane of the square. Four water molecules are bonded to each zirconium atom and the arrangement of the eight oxygens around Zr is a distorted square antiprism. The Zr-O distances distribution scatters over 0.28 Å and rises at three values, i.e., 2.09-2.13 Å, 2.22-2.23 Å and 2.35-2.37 Å respectively with an average value of 2.24 Å.

The 0.06 M aqueous solution used to perform the ion exchange was prepared from zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98 % Fluka). The Zr-exchanged and pillared beidellite were obtained by replacing the interlayer Na^+ cations of a synthetic beidellite by zirconium hydroxy polycations and calcining at 500 °C [3].

The X-ray absorption experiments were performed at LURE (DCI) on the XAS2 beam line equipped with a Si(311) two-crystal spectrometer. The data were recorded at the Zr-K edge, in the transmission mode, from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (crystal) at room temperature (RT) and 16 K, ZrOCl_2 aqueous solution at RT and Zr-exchanged (ZrEB) and pillared beidellite (PB) at RT and 16 K.

The normalized $k\chi(k)$ spectra [4] are shown in Fig. 1. The Fourier transforms (FT) between 3 and 15 Å⁻¹ of k^3 weighted $\chi(k)$ data recorded from liquid and solid ZrOCl_2 are compared in Fig. 2. Fits of Fourier filtered contributions of oxygen nearest neighbours (NN) and zirconium next-nearest-neighbours (NNN) of Zr were performed in k -space from 3 to 15 Å⁻¹ using theoretical phase shifts and backscattering (BS) amplitudes generated by FEFF6 [5]. The results are presented in Table 1.

Table 1 : Structural parameters deduced from EXAFS

Samples	Zr-O (Å)	N ₁	σ_1 (Å)	Zr-Zr (Å)	N ₂	σ_2 (Å)
ZrOCl_2 (crystal)	2.22 ± 0.02	8 ± 1	0.10	3.57 ± 0.02	1.9 ± 0.5	0.03
ZrOCl_2 (solution)	2.22 ± 0.01	7.9 ± 0.8	0.10	3.58 ± 0.04	1.2 ± 0.8	0.07
ZrEB	2.21 ± 0.01	8 ± 0.3	0.10	3.59 ± 0.02	1.3 ± 0.3	0.07
PB	2.16 ± 0.02	6.1 ± 1.4	0.11	3.38 ± 0.02	1.9 ± 0.6	0.11

Fig.1 : Normalized $k\chi(k)$ spectra from $ZrOCl_2$ crystal at (a) 16 K, (b) RT, (c) aqueous solution at RT, (d) ZrEB at 16 K, (e) PB at 16 K.

Fig.2 : Magnitude of Fourier Transform (FT) of $k^3\chi(k)$ from $ZrOCl_2$ crystal at (a) 16 K, (b) RT, (c) aqueous solution at RT, (d) ZrEB at 16 K, (e) PB at 16 K.

The shape and position of the next neighbour (NN) peak are quite similar for both samples. The value of $2.22 \pm 0.02 \text{ \AA}$ deduced from EXAFS is close to the center of the bond lengths distribution, i.e., $2.24 \text{ \AA}$. The apparent shortening of the mean coordination radius comes from the well-known effect of asymmetric pair distribution ($\sigma^2 > 0.01 \text{ \AA}^2$) which reduces slightly the weight of the longest distances with respect to the shortest ones. Nevertheless, σ^2 is considered to be small enough to use the phase shifts and BS amplitudes extracted from the analysis of the $ZrOCl_2$ spectrum at 16 K in the simulations of the NN contribution in beidellite samples. The peak located at about $3.2 \text{ \AA}$ in the FT (Fig. 2) corresponds to Zr NNN of Zr. Its amplitude is more and more lowered at RT and in the solution. In $ZrOCl_2$ (crystal) each Zr cation has two Zr NNN at $3.57 \text{ \AA}$. This value deduced from simulations is in fair agreement with crystallographic data [2]. Again no major difference between solid and solution is found excepted a small increase of σ in the latter, which indicates a loss of local order. Therefore this preliminary study shows that NN and NNN environments around Zr are identical in the solid and in solution. There is no structural difference between the zirconyl ion present in the solution and in solid $ZrOCl_2 \cdot 8 H_2O$, in agreement with the hypothesis of Fryer et al. [6] on the basis of an electron microscopic study.

Moreover, the FT of $k^3\chi(k)$ data recorded from Zr-exchanged beidellite (ZrEB) (Fig. 2.d.) reveals that the NN distribution is the same as that recorded from the pillaring solution [3]. The values of R , N and σ extracted from the simulations (Table 1) are identical in both to within the uncertainty of the EXAFS method. This result is in agreement with the hypothesis of insertion of the polycation between the silicate layers of the clay. On the opposite, the FT of calcined beidellite (PB) exhibits a clearly visible shift of the NN and NNN peaks towards smaller coordination numbers with respect to the Zr-exchanged one (Fig 2.e.). The results of the simulation of the filtered NN distribution gives 6 oxygen anions at $2.16 \text{ \AA}$ in the calcined sample instead of 8 at $2.21 \text{ \AA}$ in the exchanged one (Table 1). The value of $2.16 \text{ \AA}$ in calcined beidellite is close to the mean Zr-O distance in monoclinic ZrO_2 [7, 8] although the coordination number is slightly lower. The distance of Zr to the Zr NNN is also found to be shorter than in ZrO_2 [8] and the coordination number N_2 remains the same as in the zirconyl ion. More details will be found in ref [3]. These results, which demonstrate the change in the structure of Zr oxide clusters located inside the pillared beidellite can be related to the interlayer spacing decrease from 9 to $7 \text{ \AA}$ observed by XRD before and after calcination respectively in agreement with the results obtained by Ohtsuka et al [9]. This interlayer spacing of $7 \text{ \AA}$ corresponds to about twice the Zr NNN distance. Nevertheless, the size of the cluster becomes too small to reach that of the ZrO_2 unit cell.

In conclusion, the hydrolysis of the zirconyl ion does not infer major changes in the Zr environment. The decrease of the interlayer spacing after calcination of the Zr-exchanged beidellite is related to the change of structure of the ZrO cluster located between the aluminosilicate layers. This study gives thus an additional proof of the transformation of the intercalated polycations into metal oxide particles.

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