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Study of Lanthanum Local Structure in Montmorillonite

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SUMMARY: The local structure of the interlamellar lanthanide ions in montmorillonite upon heating is studied. The analysis of the EXAFS data has been carried out using two model environments, that of La^{3+} aquocomplex and that of the lanthanum oxide. The information thus obtained is crucial in elucidating the intercalation mechanism and demonstrates the important role that XAFS techniques can play in the knowledge of the location and environment of the exchangeable ions in layered silicates.

Keywords: rare earth, montmorillonite, intercalation mechanism, EXAFS

1. INTRODUCTION

Smectites and their pillared derivatives inserted with trivalent lanthanide ions have recently attracted much attention as catalysts[1]. In addition, La^{3+} simulates Am^{3+} in studies of the interaction of the latter with clay minerals, in which the determination of the interaction mechanism upon heating is important for the design of safe repositoires for high level nuclear wastes. The storage of these wastes in continental or marine repositoires usually involves a clay bearing packing materials that act as a barrier.

Previous studies have shown the usefulness of X-ray absorption techniques to inform about local structure around lanthanum ions in cation exchanged montmorillonite[2]. The aim of this work is to determine the location and environment of the interlamellar lanthanide cations in a montmorillonite upon heating. Herewith we report on the accurate results of the full analysis of the EXAFS spectra of three La-montmorillonite samples.

2. EXPERIMENTAL

Trancos (Almería, Spain) montmorillonite was used to prepare the lanthanum saturated sample following the method described elsewhere[2]. The sample thus obtained was studied air-dried at room temperature (untreated sample) and after submitting it to thermal treatments at 300 °C and 700 °C.

X-ray absorption measurements (La L_I and L_{III} edges) spectra of the samples were measured at the SRS (Daresbury U.K.) at Station 8.1 using a double crystal Si(111) monochromator, in transmission mode at room temperature. Data analysis was carried out by fitting in k- and R- space[3]. Phase shift functions and backscattering amplitudes for La-O contributions were obtained from experimental spectrum of $La(NO_3)_3$ solution measured in a specially designed liquid cell[4]. Mckale tables were used to calculate the same functions for La-La contribution[5].

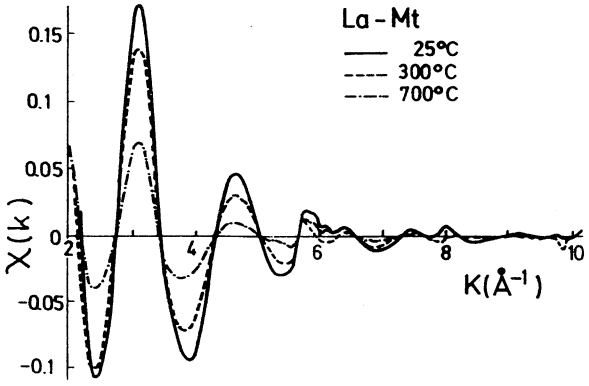

Fig 1. La L_{III} edge EXAFS spectra of La(III)-montmorillonite after heating 6 h in air at 25°C (——); 300°C (----); 700°C (-.-.-).

3. RESULTS AND DISCUSSION

Figure 1 shows raw La L_{III} edge EXAFS data of the three La-montmorillonite samples. Data quality is very good up to k= 10, the higest value before L_{II} edge. A marked decrease in intensity is induced by the thermal treatments, that can be due either to a diminution in the coordination number or to a new arrangement of the coordination polyhedra around the La^{3+} ions. Previously only qualitative approaches[2] have been made because no good fit could be attained using theoretical references. We have obtained a new experimental reference from $La(NO_3)_3$ water solution for La-O contribution which has decreased the uncertainity in the La-O shells. Nevertheless, these results can be submitted to further revision since there is a controversy concerning coordination number of water molecules in the La^{3+} aquocomplex[6].

Three coordination environments have been proposed for La^{3+} ions: the aquocomplex, for which the most reliable parameters are 9.13 water molecules at 2.58 Å[7], the tricapped trigonal prism appearing in the hydroxide $La(OH)_3$ (3 oxygen at 2.55 Å and 6 O at 2.59 Å), and the monocapped octahedron appearing in La_2O_3 (3 O at 2.38 Å, 1 O at 2.45 Å and 3 O at 2.72 Å[8]).

Table I. Coordination parameters for La-exchanged montmorillonites submitted to thermal treatments at increasing temperatures.

Sample	Shell	N	R(Å)	$\Delta\sigma^2$(Å^2)	E_o(eV)
Untreated*	La-O (MOD.I)	10.00	2.58	0.0039	-0.50
Heated 300°C**	La-O (MOD.I)	9.29	2.58	0.0100	-0.13
Heated 700°C***	La-O_1 (MOD.II)	2.09	2.36	0.0050	0.45
	La-O_2 (MOD.I)	4.23	2.61	0.0001	-1.00
	La-O_3 (MOD.II)	2.51	2.86	0.0000	-1.00
	La-La (MOD.II)	0.90	4.01	0.0090	-2.00

*Δk= 2.17-9.58; ΔR= 0.5-4.0 **Δk= 2.13-9.80; ΔR= 0.0-4.0 ***Δk= 2.14-9.70; ΔR= 0.2-4.0
Estimated standard deviations are R±0.005Å, N±0.2, $\Delta\sigma^2$±0.0008, E_o±0.50

Since the two distances appearing in the hydroxide are very similar (ΔR=0.04 Å) the polyhedra can be approximated by 9 oxygens at 2.58 Å (average distance) thus being similar to the local environment in the aquocomplex. This environment will be called MODEL I, and is represented by 9 La-O bonds at 2.58 Å. The oxide can be approximated by two shells at 2.39 Å and 2.72 Å with coordination number 4 and 3 respectivley (MODEL II).

As discussed before on the basis of the XANES spectra of L_I edge[2], in the untreated sample the coordination

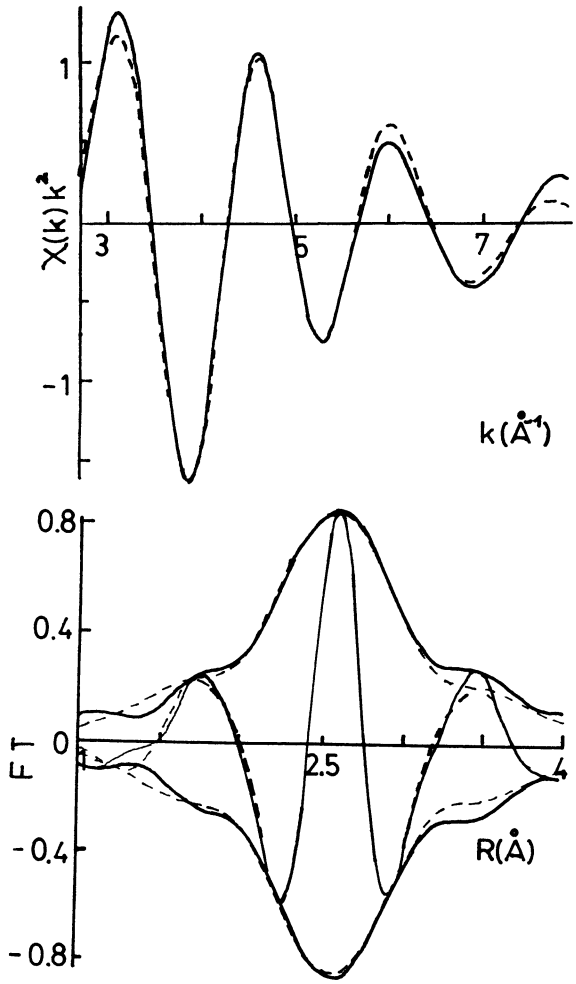

Fig. 2.(a) Fourier fitered experimental data (solid line) and best fit (dashed line) of the untreated sample. (b) Absolute and imaginary part of Fourier transform of the curves included in part (a), corrected for La-O phase shift.

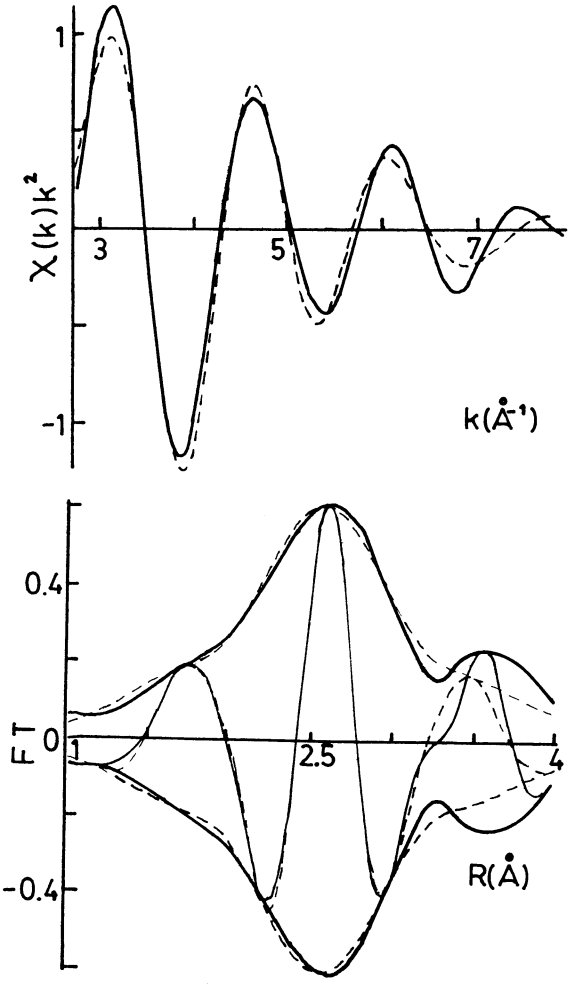

Fig. 3.(a) Fourier filtered experimental data (solid line) and best fit (dashed line) of the 300°C heated sample. (b) Absolute and imaginary part of Fourier transform of the curves included in part (a), corrected for La-O phase shift.

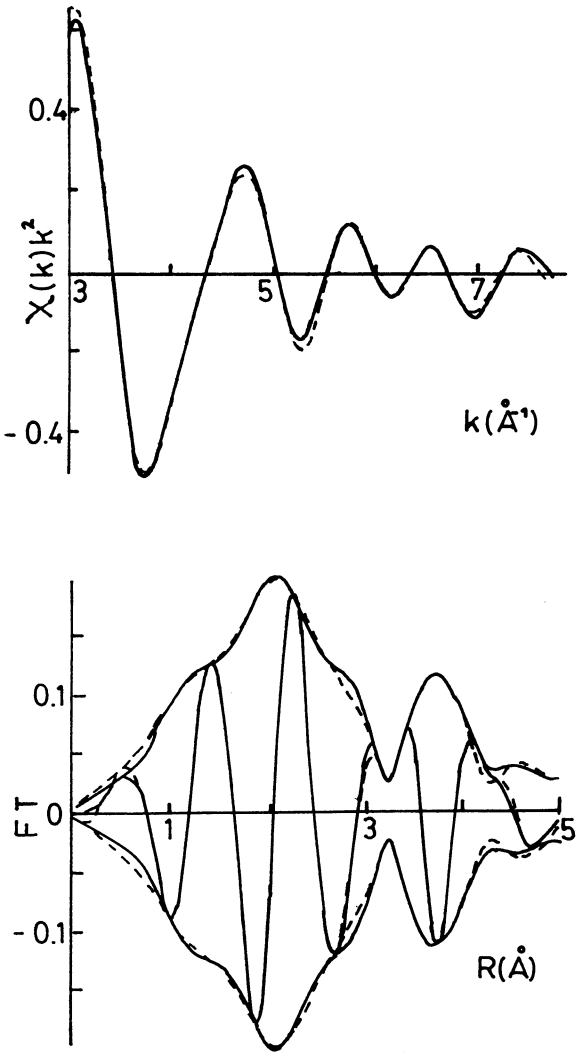

Fig. 4.(a) Fourier filtered experimental data (solid line) and best fit (dashed line) of the 700°C heated sample. (b) Absolute and imaginary part of the uncorrected Fourier transform of the curves included in part (a).

environment is expected to be similar to the hydroxide or the aquocomplex (MODEL I), while the sample treated at 700°C approach the structure of La_2O_3 (MODEL II). Following this hypothesis we have carried out the analysis of the three samples and fit parameters and filtering ranges are included in Table I. Comparative plots in k and R spaces of the best fit (dashed line) and experimental EXAFS function (solid line) for the three samples appear in Fig. 2, 3 and 4.

The local environment in the first two samples is similar to that of the hydroxide, although a small decrease is observed in coordination number for the second sample. The poorer quality of the fit, the higher Debye-Waller value and the appearance of a second peak in the FT spectrum point to the existence of additional contributions of smaller intensity.

Using the same MODEL, (I), to fit the spectra of the sample heated at 700 °C the coordination number obtained is 3.5. Since this result is not possible for La^{3+} and taking into account that the XANES spectra resemble that of La_2O_3, we have considered the possiblity that the species have undergone geometrical transformation under the thermal treatment. The best fit is obtained for a mixture of both environments, these represented by Model I and II, being the ratio aproximately 1:1. Thus MODEL I is represented by La-O_2, while La-O_1, La-O_3 and La-La stands for MODEL II (oxide-like).

This strategy has shown to be very useful in the study of a wider set of samples, that formed by four thermally treated La-montmorillonite samples submitted to *in situ* treatments in an EXAFS cell under He at room temperature and 125 °C. The full analysis of the eight spectra is the subject of a wider paper.

From the results above we would like to stress two main facts: the change in the coordination polyhedra around La^{3+} ions and the appearance of La-La bonds induced by the heating at high temperature. Both aspects suggest the existence of polymerized species in the 700°C heated sample.

4 CONCLUSIONS

The analysis of EXAFS data supports the hypothesis that the the heating at temperatures up to 700°C of La-saturated montmorillonite causes deprotonation of interlamellar hydrated La^{3+} ions, resulting in polyoxocations.

In addition to the structural information obtained for the samples studied, it is the aim of this contribution to demonstrate that XAFS techniques (both EXAFS and XANES) can give new insight in the understanding of the geometrical structures of the cation exchanged clays.

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