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Interaction of Multivalent Cations with Layered Clays. Generation of Lutetium Disilicate upon Hydrothermal Treatment of Lu–Montmorillonite

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Much interest has been generated in the interaction of multivalent cations, particularly rare earth ions, with clays, in connection with applications such as the preparation of new acid catalysts[1] and radioactive waste isolation.[2]

Diverse structural effects which occur upon air-heating of lanthanide–montmorillonite have already been observed by this research group.[3] For example, in the case of La(III), extended X-ray absorption fine structure spectroscopy (EXAFS) has shown that an important reaction is the deprotonation of the initially hydrated cations and polyoxocation generation.[4]

This paper describes a basic study on the effect of hydrothermal treatments upon montmorillonite saturated with lutetium. Quantitative generation of the phase $Lu_2Si_2O_7$ at temperatures significantly lower than those up to now reported,[5] has been observed. This has great significance for the application of diverse clay-based materials, particularly concerning the use of bentonite as a material for nuclear waste repositories and the design of new acid catalysts.

Of the different montmorillonites employed by us, a sample (MT) from Los Trancos, Almería, Spain, has been utilized as starting material because of its smaller content and structural distribution of Fe, which facilitates solid-state nuclear magnetic resonance measurements. Ion exchange with either Na(I) or Lu(III) has provided two modified smectites, Na–MT and Lu–MT, considered as reference and target samples respectively. Among lanthanides, lutetium has been selected because of its high reactivity according to previous assays. Both samples were treated under a water pressure in the range 8.5–10 MPa (approaching those expected in the projected nuclear waste repositories)[6] and temperatures from 300 to 500 °C for 24 h.

Structural changes occurring in the samples were analyzed studying the long-range order by X-ray powder diffraction (XRD), the chemical environment of the main constituent elements of the lattice by magic-angle spinning nuclear magnetic resonance (MAS-NMR), the microchemical composition by energy-dispersive X-ray (EDX) and the local Lu(III) environment through EXAFS.

From XRD analysis, two different results were observed. Whereas the Na–MT sample was not affected by the hydrothermal treatments even at the higher temperature, the Lu–MT sample was clearly transformed. We have performed our experiments at increasing temperatures and pressures. Under relatively mild conditions, structural modifications affecting the local environment of lanthanide ions had already been observed, but these were not strong enough to be detectable by X-ray diffraction.[4] At 400 °C, along with the reflections of the montmorillonite, a new set of diffraction peaks appears, compatible with the presence of the crystalline phase $Lu_2Si_2O_7$ (Card ASTM No. 34-0509). At 500 °C, a more complicated pattern is obtained which can be explained by the coexistence of SiO_2 and Al_2SiO_5, together with $Lu_2Si_2O_7$. This result implies the development of a lutetium fixation mechanism based on the formation of $Lu_2Si_2O_7$, a crystalline structure described in the literature only at very high temperatures (900–1800 °C).[5]

With respect to the main constituent elements of the lattice, no variation in the ^{27}Al and ^{29}Si MAS-NMR spectra is observed for the Na–MT sample with the hydrothermal treatments. In contrast, there are progressive changes in the ^{27}Al and ^{29}Si signals for Lu–MT as reaction temperatures are raised, in agreement with the X-ray diffraction data. While at 400 °C the ^{29}Si spectrum shows a shoulder centered at –89.5 ppm, ascribable[7] to a lanthanide disilicate with a SiOSi angle $\approx 180°$, both signals undergo substantial modifications at 500 °C. The peak corresponding to tetrahedral aluminum ($\delta = 67$ ppm) has disappeared and several silicon environments with different degrees of condensation[8] from Q^0 to Q^4, were observed.

The reactions that occur under hydrothermal conditions require the aggregation of lutetium cations and must involve a change of the sample microchemical composition. EDX microanalysis has been carried out to check this fact. Hydrothermally treated Na–MT samples exhibit a homogeneous and unchanging composition, corresponding to that of the untreated one. However, the composition of the Lu–MT sample becomes heterogeneous upon treatment, with aluminum free microvolumes showing Si/Al/Lu net peak count ratio compatible with formation of the disilicate.

The local environment of Lu(III) ions in the Lu-MT sample after hydrothermal treatment at 400 °C has been studied with EXAFS, searching for the coexistence of isolated interlamellar lutetium cations and other possible ion species not detectable by XRD, together with the crystalline phase $Lu_2Si_2O_7$. Lu L_{III}-edge ($E = 9244$ eV) spectra of the hydrothermal sample were measured at the SRS (Daresbury Laboratory U.K) in transmission mode,[9] in an "in situ" EXAFS cell.[10] The radial distribution function from the k^2-weighted uncorrected Fourier transform of the EXAFs spectrum[11] shows two well-resolved peaks centered at 1.8 and 3.0 Å approximately. These can be assigned to Lu—O and Lu—Si + Lu—Lu contributions respectively. Data analysis[12] was performed in k and R space using the phase and backscattering amplitude functions obtained from the software provided by

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Table 1. EXAFS Parameters Obtained for the Coordination Shells in Lu–Montmorillonite Hydrothermally Treated at 10 MPa and 400 °C for 24 h[a]

shell	N	R (Å)	$\Delta\sigma^2$ (Å^2 × 10^3)	E_0 (eV)	$Lu_2Si_2O_7$ $N \times R$ (Å)
Lu—O	5.3 ± 0.1	2.21 ± 0.01	7.3 ± 0.5	−9.3 ± 0.2	6 × 2.24
Lu—Si	5.6 ± 0.6	3.44 ± 0.01	9.7 ± 1.6	−0.4 ± 0.7	6 × 3.49
Lu—Lu	1.0 ± 0.9	3.52 ± 0.03	5.0 ± 5.0	−13.0 ± 4.5	2 × 3.53

[a] $\epsilon_\nu^2 = 19.8$; N = coordination number; R = coordination distance; $\Delta\sigma^2$ = Debye–Waller factor (accounting for static and dynamic disorder); E_0 = inner potential (defined in relation with the wave vector k of the ejected photoelectron $k^2 = 0.263\ (E - E_0)$).

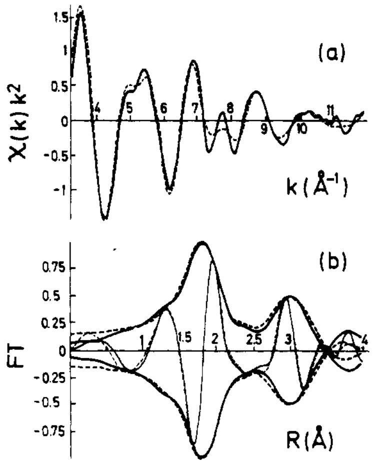

Figure 1. (a) Experimental data (solid line) and best fit (dashed line) of the lutetium-saturated montmorillonite hydrothermally treated at 10 MPa at 400 °C for 24 h. (b) Absolute and imaginary part of the Fourier transform of the curves included in part a.

Rehr.[13] A fairly good reproduction of the experimental unfiltered EXAFS data was obtained with a three-shell fit. Comparative plots of the best fit (dashed line) and experimental data (solid line) in k and R space appear in Figure 1. Fit parameters and standard deviations appear in Table 1, as well as the goodness of the fit ϵ_ν^2. The structural parameters closely resemble those of the Lu-disilicate (also included in Table 1), and the inner potential correction and Debye–Waller factors are similar to others obtained previously.[14] Standard deviations are smaller than 1% for coordination distances, and equal to 2 and 10% for coordination number of Lu—O and Lu—Si contributions respectively. The minor contribution Lu—Lu at 3.52 Å is more indeterminate in coordination number because of the proximity to the major Lu—Si contribution at 3.44 Å. Nevertheless, the set of parameters, the quality of the fit, and the standard deviation show unambiguously the existence of a single environment around Lu(III) ions—that corresponding to a disilicate phase. This information leads to the conclusion that the reaction between the interlamellar Lu(III) ions and the silicate framework can be considered as quantitative.

Systematic investigation of Ln_2O_3–SiO_2 systems had revealed a large number of phases at temperatures near 1000 °C, this limit being imposed by the very slow experimental reaction rate at lower temperatures.[5] Quantitative formation of lutetium disilicate was unexpected at the much lower temperature and extremely short period of time described in this communication and suggests that "chimie douce" methods can extend considerably the experimental reaction conditions of the rare earth silicates, which is particularly important in smectite applications such as those mentioned earlier. The possibility of lanthanide silicate formation had not previously been contemplated because the temperatures of hydrothermal synthesis were well under those of the known phase diagrams of rare earth disilicates at high temepraturе.

With respect to high-level radioactive waste repositories, the structural changes shown in this paper offer an effective mechanism of radionucleide immobilization and directly impact the limitation arising from the longevity of bentonite, the main difficulty predicted up to now.[15]

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Supplementary Material Available: Figures showing the X-ray powder diffraction diagrams for sodium- and lutetium-saturated montmorillonite samples as prepared and after being hydrothermally treated at 400 and 500 °C for 24 h and the ^{29}Si and ^{27}Al MAS-NMR spectra corresponding to the above-mentioned samples (2 pages). Ordering information is given on any current masthead page.

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