Formation of a layered Fe^{III} (hydr)oxide intercalated with dodecanoate

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A layered Fe^{II}-Fe^{III} hydroxide (Green rust, GR) intercalated with dodecanoate has been freeze dried under anoxic conditions and then oxidized by dioxygen to produce the corresponding layered Fe^{III} (hydr)oxide dodecanoate (isomer shift: 0.5003 mm s^{-1}, quadrupole splitting: 0.7523 mm s^{-1} at 80K). The final product (oxGR$_{C12}$) contains no Fe^{III} oxide impurities, and it has the same layer structure as the GR$_{C12}$ (see Fig. 1).

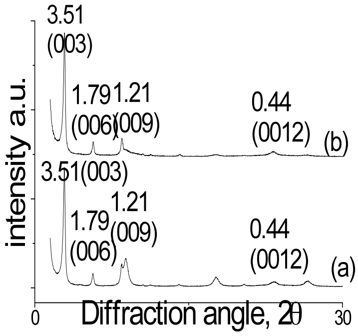

Figure 1, XRD patterns of (a) GR$_{C12}$ (b) oxGR$_{C12}$ resulting from solid-state oxidation. (unit:nm; monochromated Co-Kα radiation (40 kV, 40 mA); randomly oriented powder sample was used.)

The average chemical composition of oxGR$_{C12}$ is Fe$^{III}_{2.8}$O$_{1.8}$(OH)$_{3.8}$(C$_{12}$). Mössbauer spectroscopy shows the presence of a trioctahedral Fe^{III} (hydr)oxide, and the huge variation in quadrupole splitting values of the Fe^{III} doublet reflect dramatic changes of electric field gradient due to the distortion of the octahedral sites which result from the mixture of OH^{-} and O^{2-} ions at the apices of Fe octahedrons. The oxGR$_{C12}$ product is stable in air and water (from pH 3 to pH 8), but it is destroyed in presence of 0.1M HCl and when dodecanoate is exchanged with carbonate. The intercalated dodecanoate stabilizes the Fe hydroxide layers and hinders transformation to Fe oxides. This is the first report describing the formation of a stable layered trioctahedral Fe^{III} (hydr)oxide.

Ab initio electronic structure of Pu(OH)$_4$: Comparison between density functional and multi-reference theories

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Current spectroscopic techniques do not readily allow for the atomic-scale characterization of metal ions and complexes at low concentrations (i.e., $< 10^{-10}$ M). This is problematic for highly insoluble species such as Pu(IV), where little direct information is available on its chemical behavior at environmental conditions. To this end, *ab initio* simulations are potentially useful for gaining insights into Pu complexes in aqueous environments. However, the electronic structure of actinide complexes poses difficulties. Accurate treatments of actinides often require sophisticated correlated wavefunction techniques whose cost grows rapidly with the number of electrons, and are only practical for small systems. Large-scale dynamical simulations of condensed phase phenomena typically rely on density functional theory (DFT); however, current DFT approximations for exchange-correlation (E_{xc}) can yield large errors for actinides due to the presence of localized 5*f*-electrons.

We report benchmark studies for the monomeric Pu(OH)$_4$ complex employing a range of *ab initio* techniques including single-reference approaches (unrestricted Hartree-Fock, UHF; second-order Møller-Plesset perturbation theory, MP2), multi-reference approaches (complete active space self-consistent field method, CASSCF; multi-reference perturbation theory, MRPT) and DFT. We find that single-reference methods such as MP2 provide a reasonable description of ground state geometries and energies, and an explicit inclusion of multi-reference effects involving the Pu 5*f* electrons is not essential. However, DFT with standard approximations for E_{xc} performs poorly for Pu(OH)$_4$. We explore the use of DFT+U as a simple way to improve on the DFT description of on-site Pu 5*f*-electron correlations. Using small hydrated cluster models, Pu(OH)$_4$(H$_2$O)$_n$, we determine an *ab initio* parameterization of DFT+U suitable for the aqueous phase simulation of Pu(OH)$_4$. With this DFT+U parameterization, we carry out periodic, *ab initio* molecular dynamics simulations of Pu(OH)$_4$ in a bulk water environment, in order to determine the aqueous solvation structure around Pu(OH)$_4$.