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Nanoscale Encapsulation: The Structure of Cations in Hydrophobic Microporous Aluminosilicates

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Abstract: Hydrophobic microporous aluminosilicates created by the modification of zeolites and clays are currently being investigated as storage media for hazardous cations. Addition of an organic monolayer to the surface of an aluminosilicate after introduction of an ion into the zeolite or clay reduces the interaction of water with the material. The resultant systems are approximately 20 times more resistant to leaching of the stored ion than the unmodified ion-exchanged materials. XAS spectra demonstrate that byproducts from the organic modifier can complex with the encapsulated cation. This complexation can result in a decreased affinity of the cation for the aluminosilicate matrix. Changing the organic modifier eliminates this problem. XAS spectra also indicate that the reactivity and subsequent speciation of the encapsulated ion alters upon application of the hydrophobic layer.

1. INTRODUCTION

Microporous aluminosilicates, including clay minerals and zeolites, are ion-exchange materials [1, 2]. In their most common forms, they have the ability to incorporate cationic species within their matrices. Because of this property, microporous aluminosilicates have been proposed as storage media for hazardous waste. In this paper we use XAS to examine the structure of cations held within smectite clay minerals and to determine how modification of the surface of the clay affects the coordination of the stored cation.

Figure 1: Structure of smectite clay minerals and schematic representation of ion exchange and organic encapsulation of ions within a smectite.

The structure of smectite clays is illustrated in Figure 1. They consist of aluminosilicate sheets which contain a central section of octahedrally coordinated $\text{Al}^{3+}$ that is sandwiched between two layers of tetrahedrally coordinated $\text{Si}^{4+}$ [3]. Random substitutions, generally of $\text{M}^{2+}$ for $\text{Al}^{3+}$ and $\text{Al}^{3+}$ for $\text{Si}^{4+}$, result in a net negative charge in the lattice. This charge is balanced by cations in the interlayer between the sheets. The interlayer cations can be replaced by ion-exchange techniques with other positively charged species. For this study...
we have replaced the cations originally present in a clay, usually sodium, calcium, and potassium, with cationic metal species, including copper(II), nickel(II), lead(II), and uranyl (UO$_2^{2+}$). The clay used for these experiments is bentonite, a form of montmorillonite.

Clays are naturally hydrophilic. This affinity for water, however, also facilitates the leaching of any hazardous species stored within the mineral. In order to isolate the cationic species within the clay interlayer, we have modified the surfaces of ion-exchanged smectite clays using alkylsilanes of the form RSiX$_3$, R = C$_2$H$_5$, C$_{13}$H$_{27}$, X = Cl, -OCH$_3$ (Figure 1). The organosilanes bind covalently to the surface of the clay mineral and render the mineral hydrophobic. The presence of this coating inhibits the exchange of external water, and accompanying cations, into and out of the interlayer.

2. EXPERIMENTAL SECTION

The general preparation of ion-exchanged clays has been described elsewhere [4]. The Ca$^{2+}$ form of bentonite was used as received (bentonite L, Southern Clay Products, Gonzales, Texas). The surfaces of the ion-exchanged clays were coated with octadecyltrimethoxysilane, CH$_3$(CH$_2$)$_{17}$Si(OCH$_3$)$_3$ (OTS, Aldrich), and ethyltrichlorosilane, CH$_3$CH$_2$SiCl$_3$ (ETS, Aldrich). The silanes were distilled and stored under dry nitrogen prior to use. The clay (1 g) and silane (1 mL) were added to anhydrous hexane (40 mL). The mixture was stirred for 24 h at room temperature under a dry nitrogen atmosphere. 3-indolepropionic acid (0.01g) was added as a catalyst for the reaction of the trimethoxysilane with the clay surface. The samples were collected by centrifugation, washed three times with anhydrous hexane (25 mL) to remove any unreacted silane, and dried at room temperature. The process for the formation of the surface coatings is based on previous work on self-assembled monolayers [5, 6].

Hydrothermal processing of the clay samples was performed in a sealed stainless steel Parr high pressure bomb (4746) with a Teflon® insert that contained clay (250 mg) and deionized water (10 mL). The bomb was placed in a Lindberg crucible furnace and heated at 1° per minute to 200 °C. The bomb was maintained at 200 °C and 15.8 kg/cm$^2$ (calc) for 20 hours, after which the samples were cooled radiatively to room temperature.

X-ray absorption spectra were obtained at the National Synchrotron Light Source (NSLS) on beamlines X23A2 and X10C, and at the Stanford Synchrotron Radiation Laboratory (SSRL) on station 4-3. The beamlines were equipped with either a $<220>$ (SSRL and X10C) or $<311>$ (X23A2) double-crystal Si monochromator. Harmonics were rejected on X10C by use of a mirror and at SSRL by detuning the monochromator to approximately 50% of the maximum X-ray intensity. Fluorescence spectra were collected using a Lytle detector that was purged with Ar gas. An appropriate 3 absorption lengths filter was placed between the sample and the ionization chamber of the detector. Calibration of the edges was maintained through simultaneous acquisition of the transmission spectrum of a reference material. The position of k = 0 Å$^{-1}$ was defined as the maximum in the derivative spectrum from the reference. Analysis of the EXAFS data was performed using theoretical phase shifts and scattering amplitudes from FEFF 3.25 [7].

3. RESULTS AND DISCUSSION

Figure 2 shows the near edge spectra (XANES) and radial structure functions for copper(II) ions in the interlayers of bentonite (Cu-bentonite) before and after addition of organic monolayers formed from ethyltrichlorosilane (ETS) and octadecyltrimethoxysilane (OTS). The clays that result from addition of these two coatings are hydrophobic. However, the two silanes have distinct effects on the local coordination of the copper ion. In the original Cu-bentonite, the resolved shoulder in the Cu K edge at 8988.5 eV, which corresponds to the 1s - 4p transition, is indicative of a copper ion in a square planar environment [8, 9]. The EXAFS data indicate that the coordinating species are oxygen atoms, presumably from water molecules contained within the interlayer of the clay. The XANES and radial distributions after addition of OTS are identical to those of the original Cu-bentonite. In contrast, when ETS is used to form the monolayer, the XANES spectrum shifts approximately 1.5 eV to lower energy. At the same time the first coordination sphere in the radial distribution separates into two distinct peaks. The peak at r' = 1.55 Å (not-phase corrected) in the radial structure function reflects the continued ligation of the copper by oxygen atoms. That at r' = 1.96 Å apparently indicates the replacement of approximately half of the coordinating water molecules by chloride ions, Cl$^-$. The EXAFS fitting parameters for these three systems are summarized in Table I.

This change in the local coordination affects the ability of the clay-monolayer system to retain the interlayer ion. In leach tests the hydrophobic clay created using OTS is approximately 20 times more effective than the original Cu-bentonite in retaining the copper ion [10]. The clay modified with ETS is slightly worse than the original Cu-bentonite in keeping the copper within the aluminosilicate matrix. We believe that this behavior is a direct result of the complexation of chloride anions with the copper cation. The reaction of an alkyltrichlorosilane, RSiCl$_3$, with the clay surface and the water adsorbed there, forms siloxane bonds, -Si-O-Si-, and hydrochloric acid, HCl. Replacement of two or more neutral water molecules with negative chloride anions from the acid results in a complex that is no longer positively charged. The chlorinated copper species are easily leached from the mineral, since the coulombic forces which normally hold the cation in place are no longer effective. Similar behavior, both in the changes to the XAS spectra and in resistance to leaching, is observed when nickel(II), lead(II), or uranyl (UO$_2^{2+}$) cations are used in place of copper in these systems. The positive charge in the interlayer, formerly located on the copper species, is probably now centered on protons (H$^+$) from the HCl.
Figure 2: (A) X-ray absorption near edge spectra (XANES) and (B) radial structure functions (not phase corrected) for copper(II) in the interlayer of bentonite: (1) ion-exchanged clay (——), (2) after formation of a monolayer from octadecyltrimethoxysilane (C_{18}H_{37}Si(OCH_{3})_{3}, ----), and (3) after formation of a monolayer from ethyltrichlorosilane (CH_{3}CH_{2}SiCl_{3} ----). The range for the forward Fourier transform was Δk = 1.8 - 13.0 Å⁻¹.

Table I: Parameters for the First Coordination Shell in the Fluorescence XAS Spectra of Copper(II) in Bentonite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>n</th>
<th>r (Å)</th>
<th>σ² x 10^3</th>
<th>E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu - bentonite</td>
<td>O</td>
<td>4.0</td>
<td>1.92</td>
<td>4.5</td>
<td>8.7</td>
</tr>
<tr>
<td>Cu - bentonite + C_{18}H_{37}Si(OCH_{3})_{3}</td>
<td>O</td>
<td>4.1</td>
<td>1.92</td>
<td>4.5</td>
<td>8.6</td>
</tr>
<tr>
<td>Cu - bentonite + C_{2}H_{5}SiCl_{3}</td>
<td>O</td>
<td>2.1</td>
<td>1.93</td>
<td>6.4</td>
<td>8.7</td>
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<tr>
<td></td>
<td>Cl</td>
<td>2.0</td>
<td>2.26</td>
<td>6.0</td>
<td>8.4</td>
</tr>
</tbody>
</table>

*The estimated errors in coordination numbers (n) and radial distance (r) are ± 20 % of n and ± 0.02 Å respectively. The scale factor for FEFF was determined assuming n = 4.0 for Cu - bentonite. Windows for Fourier transforms of k²χ(k): forward-1.8 to 13.0 Å⁻¹, inverse-0.7 to 2.35 Å. The data were fit in the range from 2.5 to 12.5 Å⁻¹.*
Hydrothermal Processing

In order to simulate the effects of long term storage on these materials, as well as the effects of extreme conditions which may occur in a geologic repository, we have subjected both hydrophobic and hydrophilic clays that contain uranyl (UO$_2^{2+}$) cations to hydrothermal processing [11]. Figure 3 shows the near edge spectra and radial distributions for uranyl in bentonite before and after such treatment. Figure 3 also shows the XAS spectra from a uranyl-bentonite after both addition of an organic monolayer, formed from OTS, and exposure to hydrothermal conditions. For the simple uranyl-bentonite, the XANES and radial structures are unchanged after hydrothermal processing. The two peaks in the radial distribution between $r' = 1$ and 2.5 Å reflect the presence of two axial oxygen atoms, which are directly bound to the uranium, and approximately 5 equatorial oxygen atoms from water molecules which are complexed to the uranyl species. The spectra of a uranyl-clay after application of an organic monolayer but prior to hydrothermal treatment (not shown) are identical to those of the uranyl-bentonite. However, when the monolayer is present, exposure to hydrothermal conditions shifts the absorption edge approximately 3 eV to lower energy. This shift is confirmed by a lowering of the energy parameter in the EXAFS fits by 3.5 eV. At the same time, the axial and equatorial features of uranyl have essentially disappeared from the radial structure function, to be replaced by a single peak centered at $r' = 1.8$ Å. Simultaneously, a uranium-uranium correlation appears at $r' = 4$ Å. These changes are consistent with the reduction of uranium to the +4 oxidation state, and the aggregation of the uranium into small, disordered UO$_2$ particles. We cannot rule out the possibility that the shoulder in the radial distribution at $r' = 1.42$ Å indicates the continued presence of a small amount of unmodified uranyl cations. We have observed a similar reduction of Cu(II) upon the heating of Cu(II)-bentonite that has been modified by OTS.

Figure 3: (A) X-ray absorption near edge spectra (XANES) and (B) radial structure functions (not phase corrected) for uranyl (UO$_2^{2+}$) in the interlayer of bentonite: (1) ion-exchanged clay (---), (2) after hydrothermal processing at 200 °C (---), and (3) after hydrothermal processing of the modified uranyl clay created using octadecyltrimethoxysilane (C$_{18}$H$_{37}$Si(OCH$_3$)$_3$, .--.). The range for the forward Fourier transform was $\Delta k = 1.0 - 11.0$ Å$^{-1}$.

4. CONCLUSION

These experiments have demonstrated the utility of XAS in evaluating how surface modification affects the chemical and physical structure of ions held within the interlayers of clay minerals. XAS has also illuminated the reductive processes which
can occur within these interlayers when hydrophobic clays are subjected to hydrothermal processing. The latter results can serve as models for the interactions which occur in nature between ions, clay minerals, and organic compounds.

Acknowledgments

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