Effect of Surface Modification on the Interlayer Chemistry of Iron in a Smectite Clay

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A hydrophobic nanostructured composite has been created through the addition of an organic monolayer to the external surface of a smectite clay. This film inhibits the free exchange of water in to and out of the interlayer located between the aluminosilicate sheets of the clay. The effect of the presence of such a monolayer, which is formed from octadecyltrimethoxysilane, on iron(III) cations exchanged into the clay interlayer has been examined using X-ray absorption spectroscopy. Mild hydrothermal conditions have been used to increase the rate of potential reactions involving the ferric ions. The addition of the organic coating results in partial reduction of the iron to the ferrous state, a process that is furthered by hydrothermal treatment of the hydrophobic clay. In contrast, the iron in the simple ion-exchanged clay aggregates into small iron−oxygen clusters but is not reduced. These results are discussed in the context of the reduction potential of iron(III) and the susceptibility of that iron to hydrolysis in aqueous solution.

Introduction

The creation of composite materials that combine organic and inorganic species in one matrix has been of considerable recent interest.[1] Within this broad realm of potential materials and architectures, there has been a focus on the nanostructures that can be created by organic modification of clay minerals. These investigations have been driven by the recognition that a clay provides a preengineered nanostructure. Addition of an organic modifier with dimensions similar to that found in clays leads directly to a nanostructured composite. In this paper we examine how organic modification affects other components within clay minerals. Specifically we monitor the fate of ferric ions within an organically modified smectite clay using X-ray absorption spectroscopy (XAS).

Smectite clays consist of crystalline sheets of aluminosilicate that are negatively charged.[2,3] These sheets have a 2:1 structure, with a central layer of aluminum in octahedral coordination with oxygen. These Al−O layers are sandwiched between two layers of silicon that is tetrahedrally coordinated with oxygen. Although the ideal aluminosilicate is electrically neutral, random substitutions for the aluminum and silicon result in a net negative charge within the sheet. Typical substitutions include Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+}. To balance this negative charge, cations such as sodium, potassium, or calcium are located in an amorphous interlayer located between the sheets. The interlayer also includes water molecules, some of which are complexed to the interlayer cations. Clay particles are composed of alternating sheets and interlayers. For smectite clays, the bulk of the negative charge is located in the central aluminum octahedral layer. Therefore the Coulombic forces between the sheet and the interlayer cations are low enough to permit the replacement of the interlayer cations with other positively charged species.

The modification of a clay mineral by the addition of an organic material can be divided into two general categories. The first encompasses those modifications in which the original interlayer cations are replaced with a positively charged organic species. The traditional addition of quaternary ammonium species or other cationic surfactants represents the most common modification in this category. Another example is the creation of multilayer structures through sequential addition of a cationic polymer and exfoliated clay sheets, which is a formal equivalent of cationic exchange.[4] The added organic material may itself incorporate a metallic species. The introduction of metalloporphyrins into montmorillonites in order to create new catalytic materials represents such a modification.[5,6]

The second category comprises the addition of a neutral organic material to a smectite clay. In these modifications charge balance is usually maintained by

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the cations present in the native mineral. Examples include the creation of polymer–clay composites, either through addition of the polymer directly[7] or by polymerization of a monomer intercalated within a clay.[8] Often the added polymer can interact with the cations within the interlayer. Association between sodium ions and the oxygen atoms in poly(ethylene oxide) has been observed when solid electrolytes are formed through addition of the polymer to a smectite clay.[9] The inclusion of crown ethers[10] or porphyrins[11] in clays also leads to the formation of cationic–organic species that incorporate the interlayer cations.

Most additions of uncharged organic compounds to clays occur within the interlayer. The presence of organic moieties in this location normally perturbs the overall structure of the interlayer and the coordination environment of the cations located therein. In this paper we examine a different type of organic modification, one that occurs at the surface of the clay, rather than in the interlayer. This approach is driven by the fact that an inherent feature of clay minerals is their interaction with water.[2] To preserve the structure of the interlayer while adding an organic film to the clay's exterior, we have used a method that deposits a monomolecular film on the external surface of the clay. This monolayer is formed from octadecyltrimethoxysilane, OTS, in a manner similar to monolayers formed from the related alkyltrichlorosilanes.[12,13] This system, which has been developed to create coatings that prevent the free exchange of water in to and out of the clay,[14] uses a nonpolar solvent to minimize migration of water out of the clay during the deposition process. Our method contrasts with the typical deposition procedure for alkoxysilanes, which utilizes aqueous or protic solvents.[15] When additional water is present, the clay, which is naturally hydrophilic, can swell, changing the interlaminar (d_{001}) spacing between the sheets of aluminosilicate. In our method the original spacing in an ion-exchanged clay is preserved upon addition of the coating.[16] Similar methods have been employed to graft chlorosilanes onto clay surfaces using nonaqueous conditions.[17] We use a trialkoxysilane in place of the corresponding trichloro compounds since chloride, a byproduct from the reaction of the latter species, complexes with transition-metal cations located within the interlayer.[14,18] Because the alkoxysilanes are not as reactive as the trichlorosilanes, an organic acid catalyst that is soluble in nonpolar solvents is used to facilitate the reaction. The resultant composites are extremely hydrophobic.

Our previous results have indicated that this type of organic modification, in addition to preserving the overall structure of the clay, does not perturb the coordination of the exchanged, interlayer cations within the smectite.[14,16,18] There is evidence from those studies, however, that the presence of the monolayer can alter the chemistry of the interior cations. For this reason we have created a system that favors the occurrence of direct interactions between the exchanged cation and the organic component of the composite. The interlayer cations originally present in bentonite, a smectite clay, have been exchanged for iron(III) prior to addition of the organic film. The standard reduction potential of iron(III) to the ferrous ion is 0.77 V,[19] indicating a thermodynamic preference under standard conditions for the ferrous state. Therefore, the potential redox chemistry within these composite systems is more likely for iron than for metals with lower reduction potentials.

To increase the rate of any reaction that may occur, we used mild hydrothermal processing. The three types of manipulations employed in these studies, ion exchange, surface modification, and hydrothermal treatment, are shown in Scheme 1. The valence and coordination of the iron cations was monitored using X-ray absorption spectroscopy (XAS).[20] Since each element has a specific X-ray absorption edge, XAS is an excellent probe of the structure and electronic properties of a metal atom or ion within a complex system. The X-ray absorption near-edge structure (XANES) provides information on the electronic state of the atom. The extended X-ray absorption fine structure (EXAFS) is a representation of the local coordination around the absorbing atom.

Experimental Section

The Ca^{2+} form of bentonite, a form of montmorillonite (bentolite L, Southern Clay Products, Gonzales, TX), and ferric chloride (Mallinckrodt) were used as received. The clay had been treated by the manufacturer to remove most the iron present in the natural material. The surfaces of the ion-exchanged clays were coated with octadecyltrimethoxysilane, $CH_3(CH_2)_{17}Si(OCH_3)_3$ (OTS, Aldrich). The silane was distilled and stored under dry nitrogen prior to use.

The general preparation of ion-exchanged clays has been described elsewhere.[21] The bentonite clay (2.0 g) was placed in an aqueous solution of ferric chloride (0.1 M, 200 mL) and stirred for 18 h. After allowing the exchanged clay to settle, the bulk of the supernatant was decanted. The remaining clay was washed with deionized water (80 mL) and centrifuged. This procedure was repeated three times. Approximately 70 mL of the water above the clay after the final centrifugation were removed. The remaining water was used to form a slurry that was then transferred to a large Petri dish. The exchanged clay was dried in air, after which the clay platelets were ground into a powder using a mortar and pestle. A yellow-orange powder was isolated (1.6 g, 80%).

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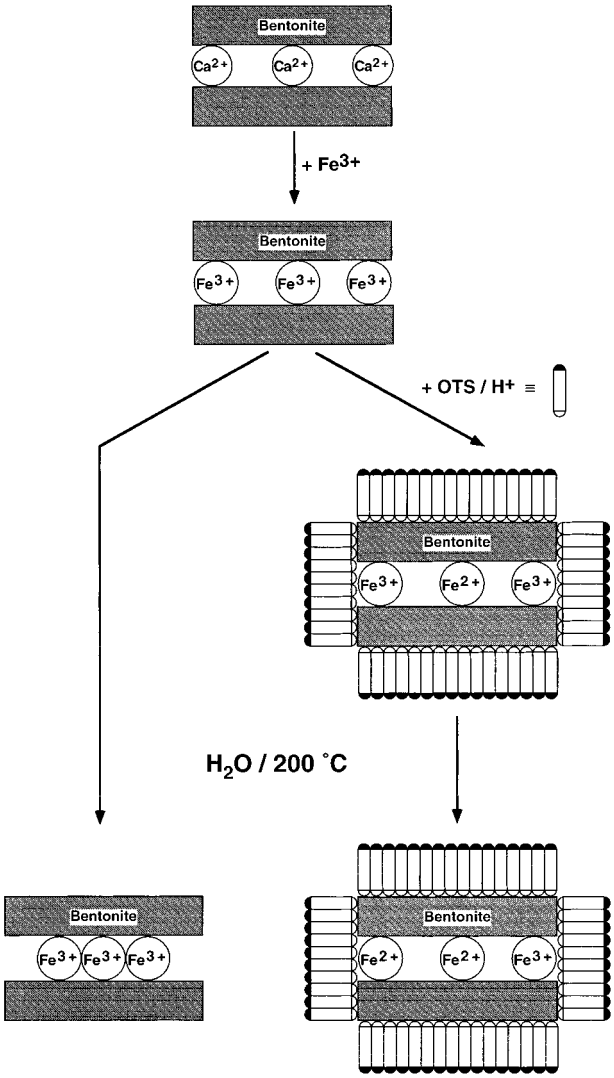
Scheme 1. Reaction Scheme for the Ion-Exchange, Surface Modification, and Hydrothermal Treatment of Bentonite Clay



The clay (0.8 g) and silane (1 mL) were added to anhydrous heptane (40 mL). The mixture was stirred for 24 h at room temperature under a dry nitrogen atmosphere. A catalyst, 3-indolepropionic acid (Aldrich, 0.01 g), was added for the reaction of the trimethoxysilane with the clay surface. The samples were collected by centrifugation, washed three times with anhydrous heptane (50 mL) to remove any unreacted silane, and dried at room temperature. The resultant powder is hydrophobic and slightly purple in color. The isolated yield was 1.0 g. The process for the formation of the surface coatings is based on previous work on self-assembled monolayers.[12,13]

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 to 200 °C. The bomb was maintained at 200 °C and 15.5 bar (calc) for 20 h, after which the samples were cooled radiatively to room temperature. After hydrothermal treatment the iron(III)-exchanged clay is bright orange. The exchanged clay with monolayer present becomes brown upon exposure to hydrothermal conditions but remains hydrophobic and floats on water.

X-ray absorption spectra for the iron clay samples were obtained in both fluorescence and transmission modes at the National Synchrotron Light Source (NSLS) on beamline X10C. The beamline was equipped with a Si[220] double-crystal monochromator. Harmonics were rejected by use of a mirror. Fluorescence spectra were collected using a Lytle detector that was purged with Ar gas. A 3-absorption-lengths filter of manganese was placed between the sample and the ionization chamber of the detector to minimize artifacts caused by scattering of the incoming X-ray radiation. Calibration of the edge energies was monitored through the simultaneous acquisition of the transmission spectrum of an iron metal foil. The calibration is precise to 0.3 eV. The energy of the maximum in the derivative spectrum from the reference was assigned to 7112 eV. This energy also serves as the origin for the wavevector of the electron, k. Each reported spectrum is an average of at least two scans.

XAS spectra for ferrous oxide (FeO) and ferric oxide (α-Fe_2O_3) were obtained at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 4-3 using a Si[220] double-crystal monochromator. Spectra were acquired in transmission mode. Harmonics were rejected by detuning of the monochromator. Energy calibration was monitored by taking the spectrum of iron foil immediately prior to or following the acquisition of the XAS spectrum of the oxide. The calibration for these two spectra is precise to 0.5 eV.

The data were analyzed using XAMath, a package for the reduction of XAS spectra that was developed at Argonne National Laboratory.[22] Analyses of the EXAFS data were performed using theoretical phase shifts and scattering amplitudes from FEFF 3.25.[23] The scale factor for the scattering amplitude was determined for Fe-bentonite, assuming octahedral coordination, and then used for all other samples and coordination shells.

Results

XANES. The near-edge, XANES spectrum from the iron K edge for the four samples in this study are compared with the corresponding spectra from two representative iron standards, α-ferric oxide (α-Fe_2O_3) and ferrous oxide (FeO), in Figure 1. The iron in both of these minerals is octahedrally coordinated with oxygen. The edge for ferrous oxide is approximately 4−4.5 eV below that of the ferric mineral. The position of the edge and features in the spectrum for the original iron(III)-exchanged clay, Fe-bentonite, match well with those obtained from the ferric standard. These observations indicate that the iron retains its oxidation state and near-neighbor coordination upon exchange into the clay interlayer. The intensity of the edge is approximately 3 times that found for the native clay.[24] Hydrothermal treatment of Fe-bentonite (Scheme 1) results in changes in the shape of the absorption edge, and a slight shift to lower energy of approximately 0.7 eV. In contrast to these uncoated samples, the Fe-bentonite that has an organic coating formed from OTS has a markedly different XANES spectrum from the original ion-exchanged clay. The observed edge is located approximately 1.6 eV below that of the uncoated Fe-bentonite. Hydrothermal processing of the OTS-coated clay lowers the energy of the absorption edge by 2.8 eV relative to the original Fe-bentonite sample. The shift of the edge to lower energy after addition of the

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(24) The intensity of the Fe K edge from the native clay is approximately the same as that of a clay which had been exchanged with Cu(II). This result suggests that the iron in the original clay is not exchangeable and therefore probably located in the aluminosilicate sheet, rather than in the interlayer. The energy of the edge demonstrates that this lattice iron is in the +3 oxidation state.

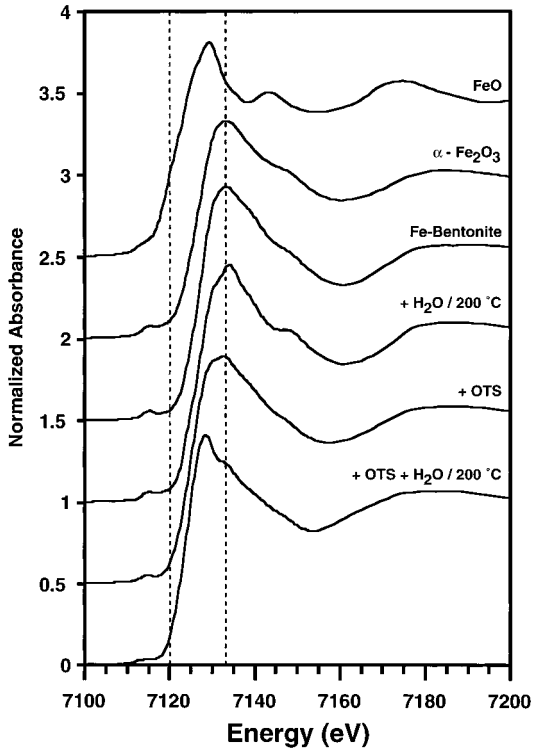

Figure 1. Normalized X-ray absorption near-edge (XANES) spectra for ferrous oxide (FeO, transmission), hematite (α-Fe_2O_3, transmission), iron(III)-exchanged bentonite (Fe-bentonite, fluorescence), hydrothermally processed Fe-bentonite (+ H_2O/200 °C, fluorescence), hydrophobic Fe-bentonite created by the addition of octadecyltrimethoxysilane (+OTS, fluorescence), and hydrophobic Fe-bentonite after hydrothermal treatment (+OTS + H_2O/200 °C, fluorescence). The offset between successive spectra is 0.5.

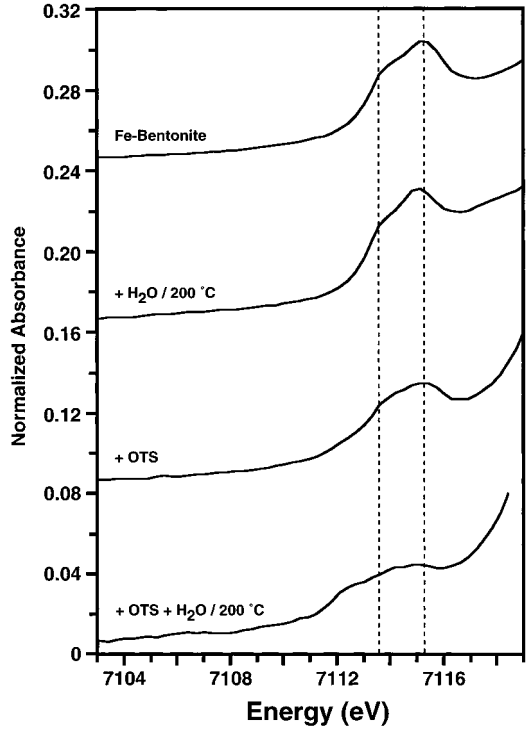

Figure 2. Preedge region in the XANES spectra for iron(III)-exchanged bentonite (Fe-bentonite, fluorescence), hydrothermally processed Fe-bentonite (+H_2O/200 °C, fluorescence), hydrophobic Fe-bentonite created by the addition of octadecyltrimethoxysilane (+OTS, fluorescence), and hydrophobic Fe-bentonite after hydrothermal treatment (+OTS + H_2O/200 °C, fluorescence). The offset between successive spectra is 0.08.

monolayer and exposure to hydrothermal conditions is only approximately two-thirds of the shift expected upon reduction of iron(III) to the +2 oxidation state.

The energy of an absorption edge (XANES) is generally a function of both the valence of the element of interest and the identity and orientation of the coordinating ligands. In the systems examined here, we expect iron only to be bound to a single element, oxygen. This supposition, combined with the fact that both isolated ferrous and ferric species prefer octahedral coordination,[25] suggests that the changes in edge energy reflect a change in the average valence of the iron. Confirmation for this conclusion is found by examining the 1s−3d transition in the preedge region of the spectra (Figure 2). The shape and location of this transition in Fe-bentonite are similar to those found for iron(III) in octahedral coordination.[26] The doublet feature arises from transitions into the t_2 and e subsets of the 3d orbitals.[27,28] Hydrothermal treatment lowers the intensity of the transition, but the general shape is maintained. When OTS is added, the transition becomes even weaker and broadens, although the energy at which it appears is the same as the original Fe-bentonite. However, when the Fe-bentonite is treated with OTS and exposed to hydrothermal conditions, the onset of the transition moves to lower energy. The 3d feature in this sample mirrors that of ferrous ions in an octahedral environment.[26]

The overall position of the absorption edge, as well as that for the preedge 3d transition, indicate that the iron is initially exchanged into the clay as a ferric species. The cation remains in the +3 oxidation state when exposed to water at 200 °C. There is some reduction of the iron upon initial addition of the organic film. Hydrothermal conditions further this reaction, but do not apparently reduce all of the iron(III) present in the clay.

EXAFS. The extracted EXAFS data and radial structure functions for the four iron-bentonite samples are shown in Figures 3 and 4. The presented Fourier transforms do not include the effect of the phase change upon absorption and scattering of the outgoing electron. Features in the radial structure functions will be referred to as a function of r', the length scale in the non-phase-corrected Fourier transform. We will describe actual atomic distances in terms of r, which includes the effect of the phase change upon X-ray absorption and scattering.

Whereas the EXAFS data for the Fe-bentonite coated with OTS are similar to those from the ion-exchanged starting material, the two hydrothermally treated samples have distinct EXAFS spectra. The radial structure functions show that for all but the hydrothermally treated Fe-bentonite, the EXAFS is dominated by a single coordination sphere. The hydrothermal Fe-

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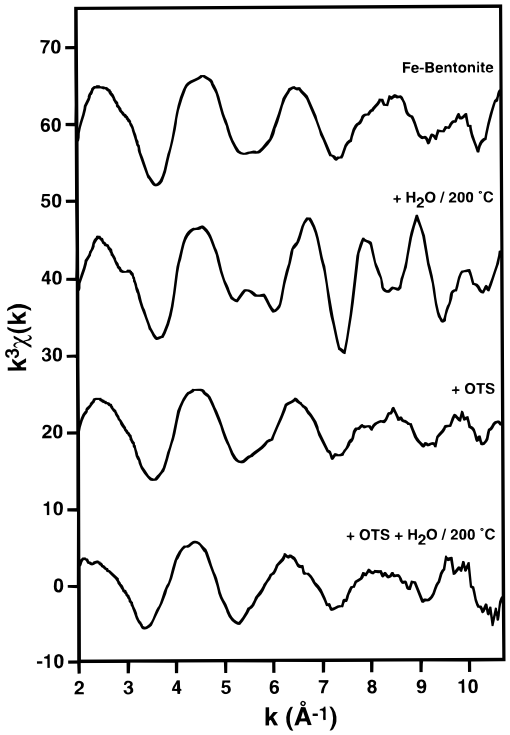

Figure 3. k^3-weighted extended X-ray absorption fine structure (EXAFS) for iron(III)-exchanged bentonite (Fe-bentonite), hydrothermally processed Fe-bentonite (+H_2O/200 °C), hydrophobic Fe-bentonite created by the addition of octadecyltrimethoxysilane (OTS), and hydrophobic Fe-bentonite after hydrothermal treatment (+OTS + H_2O/200 °C). All spectra were acquired in fluorescence mode. The offset between successive spectra is 20.

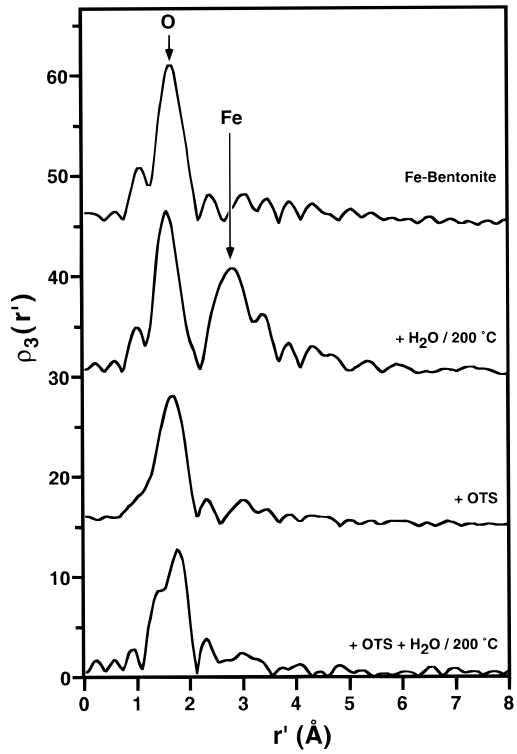

Figure 4. Radial structure functions derived from the EXAFS of the four clay samples shown in Figure 3. The offset between successive spectra is 15.

Table 1. Fitted Parameters for the Fluorescence XAFS Spectra of Iron in Bentonite[a]

sample	coordinating element	n	r	σ^2	E_0
Fe-bentonite	O	6	2.01	0.010	12.4
+200 °C/H_2O	O	5.4	1.96	0.010	9.6
	Fe	5.5	2.95	0.012	9.1
+OTS	O	5.4	2.02	0.012	11.0
+OTS and 200 °C/H_2O	O	5.1	2.06	0.011	9.4

[a] The estimated errors in coordination numbers (n) and radial distance (r) are ±20% of n and ±0.02 Å, respectively. The scale factor was determined assuming $n = 6.0$ for Fe-bentonite. This scale factor was used for both oxygen and iron coordination. Windows for Fourier transforms of $k^3\chi(k)$: forward 2.0 to 10.7 $Å^{-1}$, inverse 1.3 to 2.2 Å. The data were fit in the range from 2.5 to 10.3 $Å^{-1}$.

bentonite is alone in showing significant coordination beyond the first shell.

The results of fitting the first coordination shell are shown in Table 1. There are, within experimental error, approximately the same number of oxygen atoms surrounding each iron cation. These coordination numbers are consistent with octahedral coordination. However, the distance between the iron and oxygen vary considerably. Hydrothermal treatment of Fe-bentonite results in a contraction of the average Fe−O bond distance by approximately 0.05 Å. While addition of the organic film to the exchanged clay does not apparently induce a significant change in bond length (2.01 vs 2.02 Å), exposure to hydrothermal conditions results, unlike in the hydrophilic clay, in an increase in bond distance. This change is consistent with a reduction of the iron from iron(III) to iron(II).

Table 1 also includes fitting data for an additional coordination shell observed with the hydrothermally processed Fe-bentonite. Comparison of the radial distributions from k^2- and k^3-weighted data demonstrate that this shell is from an element with a relatively high atomic number, Z, which in these systems must be iron. The radial structure function for this sample in the region from $r' = 2.26$ to 3.6 Å shows two peaks. In fitting the data, we find two additional coordination shells, one at $r = 2.95$ Å, the second at $r = 3.42$ Å.

These features are assigned to iron−iron interactions. Although inclusion of the second iron shell at 3.42 Å does result in a statistically significant improvement in the quality of the fit, there is a certain amount of ambiguity regarding the disorder and energy parameters. The best fit to the data for the further iron shell has $\sigma^2 = 0.003 \pm 0.003$ and $E_0 = 20.9 \pm 10$ eV. Since the theoretical reference did not include any disorder in the calculation, such a small σ^2 parameter appears unphysical. The energy parameter, E_0, is also suspect because of its high value. For these reasons, the estimated errors in the parameters for the last iron coordination shell are significantly larger than for the inner oxygen and iron coordination spheres. Nevertheless, we can rely on the qualitative conclusion that there is some detectable iron at a distance of approximately $r = 3.4$ Å.

On the basis of the stability of the clay framework, we do not expect that the exchanged iron has substituted for aluminum or silicon within the lattice. In addition, the iron initially present in the lattice remains in place.[29] Even if hydrothermal processing were to favor introduction of iron directly into sites within the clay sheet, the iron would have to be located in

adjacent sites in order to generate the aggregated features observed in the Fe-bentonite exposed to hydrothermal conditions. We conclude that the coalescence of iron in the hydrothermally treated sample has occurred in the disordered, fluid environment of the interlayer.

Principal Component Analysis. The positions of the absorption edges for these four samples, combined with the variations in bond distance, indicate that there are at least three distinct species among the four iron samples. In addition, because the positions of the edges for the two samples with the organic coating are intermediate between those of authentic ferric and ferrous species, there are probably mixtures of iron environments within these specimens. Unfortunately, the original EXAFS data only extend to 10.7 $Å^{-1}$, due to a glitch at that wavevector in the incoming X-ray beam. Therefore the number of degrees of freedom in the Fourier filtered data for the first coordination shell, $\Delta k = 8.7$, $\Delta r = 0.9$, is at most 8.[30,31] Since the ΔE parameter must be included because of the potential change in the valency of the iron, the number of parameters necessary for each shell is 4. As a result, it is not possible through fitting of the EXAFS data to distinguish, within a single sample, between different types of coordination in the first shell of iron. In fact, we do not obtain a statistically significant improvement in the fit to the data when a second coordination environment is included in the overall first shell.

To aid in determining which of these samples contain more than one iron species, we have used the techniques of principal components analysis (PCA) on both the XANES and EXAFS data.[32−34] Although this approach is limited in this study by the small number of spectra available, several qualitative conclusions can be drawn. First, analyses of both the XANES and EXAFS data suggest that there are three distinct iron species in these samples. For the extracted EXAFS spectra, this conclusion is based on the entire range of unfiltered data. Therefore the effects of coordination shells more distant than the first are explicitly included. We deduce that the alterations in the spectra are not simply the result of reduction of ferric cations to ferrous ones, since the observed changes in the XAS spectra are not merely the superposition of two different species.

We have used uniqueness tests[32] to determine which of these spectra contain samples in common. From this analysis it is apparent that the hydrothermally treated Fe-bentonite is unique, a conclusion amply supported by its distinctive radial structure function. We also deduce that the Fe-bentonite with the monolayer present shares species with both the coated clay after hydrothermal treatment and the original Fe-bentonite. However, the latter two samples do not have iron environments in common. This result suggests that despite our inability to detect mixtures through analysis of the EXAFS data for the first coordination sphere, the addition of the monolayer does result in a mixture of iron species. Hydrothermal processing of this sample then results in further conversion of the Fe(III) to the ferrous state.

The conclusion that the Fe-bentonite after addition of the monolayer is a mixture of the species located in this type of clay after hydrothermal treatment and in the original ion-exchanged clay must be reconciled with the positions of the absorption edges. The XANES data suggest that both the samples coated with OTS contain mixtures of ferrous and ferric species. Principal-component analysis is a linear method. Consequently, under certain conditions a linear combination of two real species can appear as a single component. In the spectra presented here, the lattice iron(III) presumably remains in the +3 oxidation state and at the same concentration in all samples. Its presence is therefore masked in the PCA analysis. Nevertheless this species contributes to the observed spectra. These considerations do not affect the conclusion that there are at least three distinct iron species present in the various clay interlayers.

Discussion

We have demonstrated that organic modification of a clay can affect the speciation of the interlayer ion. In addition, the presence of the monolayer changes the reaction path followed by the cation upon hydrothermal treatment. Each of the XAS spectra from the iron-containing clays is unique. Even in the case where XANES spectra are similar for the Fe-bentonite before and after hydrothermal treatment, the EXAFS from these two samples differ dramatically.

The changes in the observed XANES and EXAFS spectra, together with the results of principal component analysis, indicate that there are at least three iron species in the interlayers of these deceptively simple systems. We can combine the above results into a qualitative picture of the iron environments present in the four samples. The first species is an individual ferric ion coordinated to oxygen. This moiety probably is the only one present in the interlayer of the original Fe-bentonite. It is also present in the Fe-bentonite after addition of the OTS monolayer and possibly at a low level in the modified clay after hydrothermal processing. The second species is an isolated ferrous ion, found in the mixtures present in the OTS-modified clay both before and after hydrothermal treatment. The third moiety is an aggregated ferric species, which appears only in the hydrothermally treated Fe-bentonite. The iron(III) in the lattice, whose structure remains unperturbed in all four samples, provides a constant background in each of the spectra. To aggregate in the hydrothermally processed Fe-bentonite, ferric cations must have sufficient freedom to move within the gallery, suggesting that the iron is not strongly bound to the interlayer surface. The results observed here are consistent with iron in an aqueous environment. Similar behavior was observed previously for uranyl ions that had been exchanged into bentonite.[16]

The chemistry of iron(III) and iron(II) are consistent with our proposed structures. Aqueous ferric species

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are prone to hydrolysis.[25,35] This hydrolysis can lead to complexes such as $Fe(OH)^{2+}$ or $Fe(OH)_2^+$, which have been proposed as the species in the interlayer of a ferric-exchanged smectite.[36] Our experiments cannot distinguish these moieties, which can be considered as isolated cationic complexes, from iron(III) that is complexed only with water. The observed aggregation in the Fe-bentonite after exposure to hydrothermal conditions is similar to that found during the formation of hematite, Fe_2O_3, from ferric chloride in aqueous solution.[37] Both the changes in the radial structure function and the Fe−Fe distances agree well with this study on hydrothermal formation of ferric oxides. In contrast, ferrous ions remain as independent entities in aqueous solution.[25]

Although the differences in the speciation of iron between the two hydrothermally treated samples can be explained in terms of fundamental aqueous iron chemistry, there remains the possibility that the presence of the monolayer has more of an effect than simply facilitating the reduction of the metal. The original ion-exchanged clay is hydrophilic and readily swells upon exposure to an excess of water. However, addition of the monolayer results in a hydrophobic substrate. Indeed, the coated clay continues to float on water even after hydrothermal treatment. The monolayer prevents the free exchange of water in to and out of the interior of the clay and therefore suppresses swelling of the clay. In contrast, absorption of water by the clay will occur during hydrothermal processing of the uncoated Fe-bentonite. The resultant lower concentration of water in the interlayer of the hydrophobic clay could inhibit hydrolytic reactions, in a direct application of LeChatlier's principle. Despite the overall excess of water during hydrothermal processing of the surface-modified clay, there may not be a large amount of water actually between the clay sheets. In addition, the reduced exchange of interlayer water with the bulk may have a significant effect on the acidity of the interlayer environment. These effects may be significant because changes in pH exert a considerable influence on the redox behavior of iron.[38]

As noted above, under standard conditions, ferrous ions are thermodynamically more stable than ferric ones, a fact reflected in the high standard reduction potential of iron(III). Our results suggest that reduction occurs fairly easily in the clay systems studied here. Appreciable amounts of iron(II) form in the clay upon addition of the organic monolayer. The susceptibility of iron to reduction correlates well with these results. Cations with lower standard reduction potentials are expected to be more likely to remain in the oxidation state in which they were originally introduced into the clay. For example, we have found that the oxidation states of lead(II), copper(II), or uranium(VI) in the form of uranyl, UO_2^{2+}, do not change when OTS monolayers are added to ion-exchanged clays containing these metals.[14,16,18] The standard reduction potentials for these species are −0.13 (to Pb(0)), 0.16 (to Cu(I)), and 0.27 (to UO_2), respectively.[19] Exposure of the hydrophobic clays containing these cations to hydrothermal or thermal conditions leads to reduction of only the latter two species.[16,18]

In these experiments our focus has been on the fate of the iron species. However, any observed reduction requires a corresponding oxidation. In these systems the organic monolayer is the most likely reductant, because it is the most reducing species present. Unfortunately, at this stage we cannot eliminate the possibility that the organic catalyst, the methanol formed as a result of deposition of the organic coating, or residual heptane solvent serve as the reducing agent. The type of reduction observed here has been proposed as the complement to the transformation of the organic species in clay-catalyzed oxidations. Reductions of both iron and copper have been invoked in synthetic reactions utilizing ion-exchanged clays.[39,40]

The hydrolysis of iron(III) represents an implicit ion exchange within the clay. Any reduction of the net charge on the iron requires another cation in the interlayer to maintain the charge balance, because the charge within the aluminosilicate sheets of the bentonite is fixed. Hydrolysis results in an effective decrease in the charge on the metal through addition of negatively charged hydroxyl or oxo moieties. Presumably, the protons generated by the hydrolytic mechanism become the cationic species within the interlayer. Similarly, the reduction of iron requires the addition of another cation or the removal of an anion to preserve electric neutrality. Further work is necessary to determine the mechanism of iron reduction and the details of charge balance within the clay interlayer.

For these experiments the hydrothermal treatments are used to apply a reactive stress to the materials while minimizing the potential for dehydration of the clay. However, mild hydrothermal conditions are often used for the synthesis of clays and zeolites.[41−45] In particular, when forming large-pore aluminosilicates such as the MCM series of catalysts, an organic surfactant template is usually employed during the hydrothermal synthesis.[46] Our results indicate the possibility of a redox interaction of the template with other reactants.

The hydrophobic monolayers on the surfaces of our ion-exchanged clays have been demonstrated to affect the speciation of the iron in the interlayer. This influence may result from either direct or indirect interactions between the organic components and the iron. In a direct interaction, the organic film or products from its decomposition react directly with the ferric ions. Our observation of iron reduction only in the surface-

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modified samples strongly suggests that such a direct interaction does occur. The oxidation half-reaction occurs at the organic species. In an indirect interaction, the monolayer does not participate in a chemical reaction with the iron. Instead, the presence of the organic coating, and the consequential inhibition of free exchange of water in to and out of the interlayer, result in a subtle interplay between the monolayer and cation. In the original ion-exchanged clays, the ferric ions aggregate upon hydrothermal treatment, presumably through a hydrolytic mechanism. This aggregation does not appear when the hydrophobic clay is exposed to water at elevated temperatures, suggesting that the siloxane film also indirectly alters the chemistry of the iron. However, the presence of some ferrous iron in the organo–clay nanocomposite prior to heat treatment may also inhibit aggregation. Additional experiments will be required to determine why the iron does not coalesce within the hydrophobic clay and the role of indirect interactions in the observed interlayer chemistry.

Conclusions

This paper has analyzed the changes that occur to ferric ions upon organic surface modification of smectite clays. Depending on the conditions to which the clay is exposed, the iron(III) within the interlayer either reduces or aggregates. Although these composite systems are fairly complex, incorporating at least two inorganic components, the aluminosilicate sheet and the cation, as well as organic materials, the behavior of the iron can be explained through application of a few fundamental chemical concepts. The combination of the known redox and aqueous chemistries of Fe(III) and Fe(II) is sufficient to explain our observations. Our results indicate that the creation of hybrid organic–inorganic systems based on clays can affect other components within layered aluminosilicates.

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