CHARACTERIZATION OF MONTMORILLONITE SURFACES AFTER MODIFICATION BY ORGANOSILANE

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Abstract—X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), surface area measurements, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were used to examine the surface properties of organosilane-modified smectite-type aluminosilicate clays. Organic modified clays derived from the reactions of montmorillonite (containing 93–95% montmorillonite from a bentonite, <1% quartz, and 4–6% opal CT) with octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$) and octadecyltrimethoxysilane [$C_{18}H_{37}Si(OMe)_3$] are highly hydrophobic. Surface loadings of the modified clays depend on the organosilane and the solvent, and they range from 10 to 25 wt. %. The organic species are probably adsorbed to the outer surfaces and bound to the edges of the clay via condensation with edge–OH groups. Encapsulation of montmorillonite with $C_{18}H_{37}SiCl_3$ and $C_{18}H_{37}Si(OMe)_3$ resulted in a hydrophobic coating that acts like a "cage" around the clay particles to limit diffusion. Basal spacings of the organic modified clays remain at ~15 Å upon heating to 400°C in N_2, whereas those of unmodified clays collapse to ~10 Å. A considerable reduction in surface area (by 75–90%) for organic modified clays is observed, which is consistent with the existence of a surface coating. The solvent used can affect the amount of organic silane coated on the clay particles, whereas the difference between the products prepared using $C_{18}H_{37}SiCl_3$ and $C_{18}H_{37}Si(OMe)_3$ in the same solvent is relatively small. The carbon and oxygen K-edge NEXAFS spectroscopy of the modified montmorillonite surfaces showed that surface coatings on the outside of the clay particles exist. The encapsulating system may allow for economical remediation and storage of hazardous materials.

Key Words—Clay-Organic Interactions, Montmorillonite, Organic Coating, Silane, Surface Modification.

INTRODUCTION

The reactivity of silanol groups towards organic molecules has been extensively studied for silica and porous glass surfaces (Hair and Hertl, 1969; Hair, 1977). Surface–OH groups are predominant in these materials and produce organo-mineral derivatives. Various methods have been employed to increase the number of surface–OH groups on mica (which is nearly devoid of active surface sites), which act as anchoring points for additional surface–OH groups. For example, increased coverage by silanes on mica was attained by (1) pre-treatment with water and hydrochloric acid for octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$) coverage (Carson and Granick, 1990), (2) prehydrolysis of alkyltrialkoxysilanes followed by monolayer self-assembly (Kessel and Granick, 1991), (3) pre-treatment with water vapor plasma (Parker *et al.*, 1989, 1990), and (4) a combination of (2) and (3) (Wood and Sharma, 1994). The objective of the acid pre-treatment is to remove octahedral cations, each of which leaves behind two additional Si-OH groups (Rausell-Colom and Serratosa, 1987). Kaolinite, with edge–OH groups estimated at ~10%, was examined also by direct reaction with silane in solvent (Braggs *et al.*, 1994). Sepiolite, with a comparatively larger –OH content, was examined for direct grafting either with

or without cohydrolysis utilizing acid (Ruiz-Hitzky and Fripiat, 1976; Fernandez and Ruiz-Hitzky, 1979; Hermosin *et al.*, 1982). Phenyl-derivatives of sepiolite were also made using this latter method (Aznar *et al.*, 1992).

Direct grafting reactions with montmorillonite were investigated by Berger (1941), Deuel *et al.* (1950), and Gieseking (1949). However, plate-like clay surfaces (as opposed to fibrous clays, such as sepiolite) have –OH groups only at the edges of individual particles and at relatively low contents (Rausell-Colom and Serratosa, 1987). Only limited amounts of organics, therefore, can be covalently linked and, when excess amounts are present in the interlayer, they are presumed to be hydrolysis products retained by adsorption forces (Rausell-Colom and Serratosa, 1987). Surface coverage studies of silanes on montmorillonite are scant, but the utility of this mineral for many applications is high. One attractive property is that they can be converted from hydrophilic to hydrophobic forms when exposed to appropriate organic reagents (Thomas, 1982). Traditional methods for the preparation of hydrophobic clays involve treatment with quaternary ammonium cations that contain one long chain hydrocarbon tail. Such organoclays have been effectively used as sorbents for various organic pollutants (Cowan, 1963; Roberts, 1964; Mortland *et al.*, 1986; Boyd *et al.*, 1988; Hermosin and Cornejo, 1993; Srinavasan and Folger, 1994).

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Smectite clays are especially useful because of their high cation exchange capacity and the ability of the interlayer to swell easily. Recently, the effect of silane surface modification on the interlayer chemistry of iron in a montmorillonite was examined by X-ray absorption spectroscopy (Wasserman *et al.*, 1998). In our study, surface modification to increase hydrophobicity involves the reaction of a smectite with a reactive organosilane of type R_nSiX_3, where n is an integer, R is a long-chain hydrocarbon, and X is either Cl or a methoxy group. In addition, the surface properties of the clay are examined by X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

EXPERIMENTAL

Materials

Bentolite L, a Ca^{2+}-rich montmorillonite, was purchased from Southern Clay Products Inc., Gonzales, Texas. This clay has a cation exchange capacity of 80 meq/100 g and contains 71.7% SiO_2, 15.7% Al_2O_3, 3.6% MgO, 1.7% CaO, 0.3% Fe_2O_3 and TiO_2, 0.2% Na_2O, and 0.16% K_2O, and was previously treated by the manufacturer to remove most of the iron content. It is at least 93–95% montmorillonite obtained from a bentonite. The supplier has determined that the impurities are <1% quartz and 4–6% opal CT. Octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$) at 95% purity and octadecyltrimethoxysilane [$C_{18}H_{37}Si(OMe)_3$] at 90% purity were obtained from Aldrich (Milwaukee, Wisconsin) and distilled under vacuum prior to use. High purity solvent-grade methylene chloride and n-hexane were used as received from J.T. Baker (Phillipsburg, New Jersey).

Organosilane-modified montmorillonite clays were prepared by reactions of the clay with $C_{18}H_{37}SiCl_3$ in hexane ($C_{18}H_{37}SiCl_3$-hex) or in methylene chloride ($C_{18}H_{37}SiCl_3$-met), and with $C_{18}H_{37}Si(OMe)_3$ in the presence of p-toluene sulfonic-acid catalyst in hexane ($C_{18}H_{37}Si(OMe)_3$-hex). The reactions were performed at a weight ratio of 1:1:30 for clay:silane:solvent in a closed system for 2–3 d. The HCl gas liberated from the reaction with $C_{18}H_{37}SiCl_3$ was released periodically in the process. The modified clays were isolated by filtration followed by rinsing with reaction solvent several times to remove any unreacted silanes, and then air dried. Other solvents tested include chloroform, n-heptane, and cyclohexane, which also resulted in hydrophobic coatings, but only the products derived from using methylene chloride and hexane are discussed here.

XRD data were obtained from a Rigaku D/Max-2400V diffractometer using CuKα radiation at a scan rate of 0.5°2θ/min. The samples were heated under N_2 for 2 h at 200, 400, and 600°C, respectively, prior to XRD analysis. Thermal analysis was performed on an SDT 2960 from TA Instruments. Samples were heated at a rate of 5, 10, and 15°C/min under N_2 flow (100 ml/min). For thermal-stability measurements, the samples were heated on the TGA apparatus to either 200, 400, or 600°C and held at that temperature for 10 min. Nitrogen BET surface areas (Brauner *et al.*, 1938) were measured on an Autosorb-6 sorption analyzer from Quantachrome (equilibrium method); samples were outgassed for ~15 h at room temperature under vacuum. The NEXAFS experiments were performed on the U1 beamline of the National Synchrotron Light Source, Brookhaven National Laboratory, Brookhaven, New York. The spectra were obtained by measuring the intensity of electron yield and recorded using a channeltron electron multiplier located near the sample holder. All NEXAFS spectra were recorded with the photon beam at the normal incident angle with respect to the sample surface. To reduce the intensity contribution from low-energy secondary electrons from the subsurface regions, the entrance of the channeltron was biased to repel these electrons by a negative voltage of 100 eV. The sample powders were pressed into stainless-steel sample holders of ~1.3 cm in diameter and 0.1 cm in depth. All samples were pressed under identical conditions to ensure the same surface exposure to the beam. The NEXAFS spectra of carbon K-edge (275–335 eV) and oxygen K-edge (510–590 eV) were monitored as a function of the incident X-ray photon energy using the electron yield method, which is sensitive to the few topmost atomic surface layers of the substrates. All samples were corrected against a reference sample (boron nitride) and the data are calibrated so that the differences in intensity can be ascribed to the type of coating.

RESULTS AND DISCUSSION

Thermal analysis

Thermal gravimetric analysis was used to examine the amount and stability of organic coatings on the clays. In Figure 1, the weight loss below 160°C corresponds to loss of surface and interlayer H_2O. Weight loss at 500–550°C is assumed to be related to decomposition of the silane. The wt. % silane loading is summarized in Table 1. The silane coated on $C_{18}H_{37}SiCl_3$-met at 24.8% is significantly larger than those for $C_{18}H_{37}SiCl_3$-hex (10.7%) and $C_{18}H_{37}Si(OMe)_3$-hex (14.8%). Irreversible dehydroxylation of the unmodified clay occurs at 670°C. This peak is evident in $C_{18}H_{37}SiCl_3$-hex and at near background in $C_{18}H_{37}Si(OMe)_3$-hex, but it is not evident in $C_{18}H_{37}SiCl_3$-met. This trend of decreasing hydroxyl weight loss follows an increased loading of silane, and may be a direct correlation if direct grafting is dependent upon these hydroxyl groups. However, Morris *et al.* (1990) determined from X-ray analysis that octa-
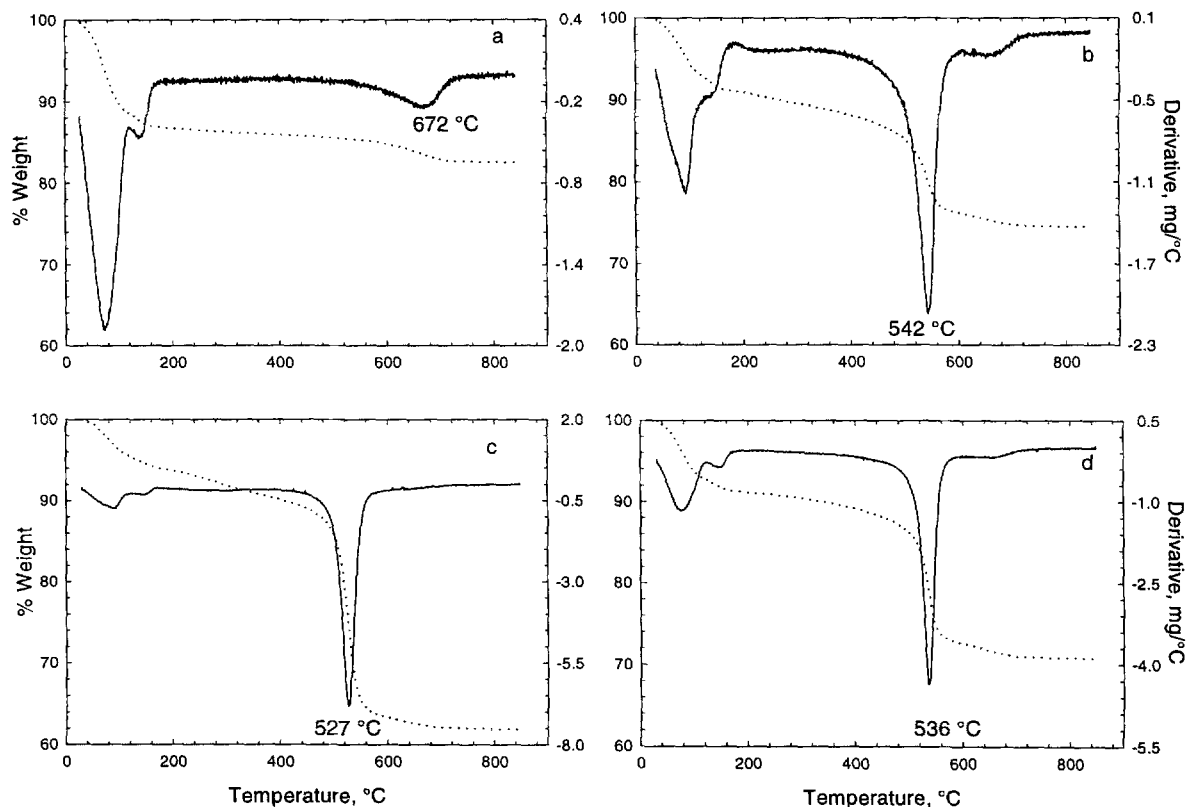
Figure 1. Thermal gravimetric analysis (TGA) and derivative curves of (a) unmodified montmorillonite and montmorillonite modified with silanes: (b) $C_{18}H_{37}SiCl_3$-hex, (c) $C_{18}H_{37}SiCl_3$-met, and (d) $C_{18}H_{37}Si(OMe)_3$-hex as discussed in the text.

hedral-sheet hydroxyls are inaccessible to silanes and, because of the size of the $C_{18}H_{37}SiCl_3$ molecule, only the edge hydroxyl sites will probably react. Morris *et al.* (1990) determined that 3.3% of all Al atoms in a montmorillonite are surface or edge Al Brønsted–OH sites.

The methylene chloride solvent used in the preparation of $C_{18}H_{37}SiCl_3$-met is not only more polar than hexane, but it is also more hygroscopic. Because water may participate in the reaction, it becomes a significant

factor in the hydrolysis and subsequent deposition. Octadecyltrichlorosilane is highly susceptible to hydrolysis and pre-crosslinking. If care is not taken to exclude water until the appropriate time, a three-dimensional network ("gelslug") can settle on a substrate (Wood and Sharma, 1994; Kessel and Granick, 1991). The use of surfaces with a large degree of functionality can mask the gelslug, but this is not the case for montmorillonite. Thus, a significant amount of the 24.8 wt. % silane coverage on $C_{18}H_{37}SiCl_3$-met clay

Table 1. Comparison of BET surface area with wt. % silane coverage.

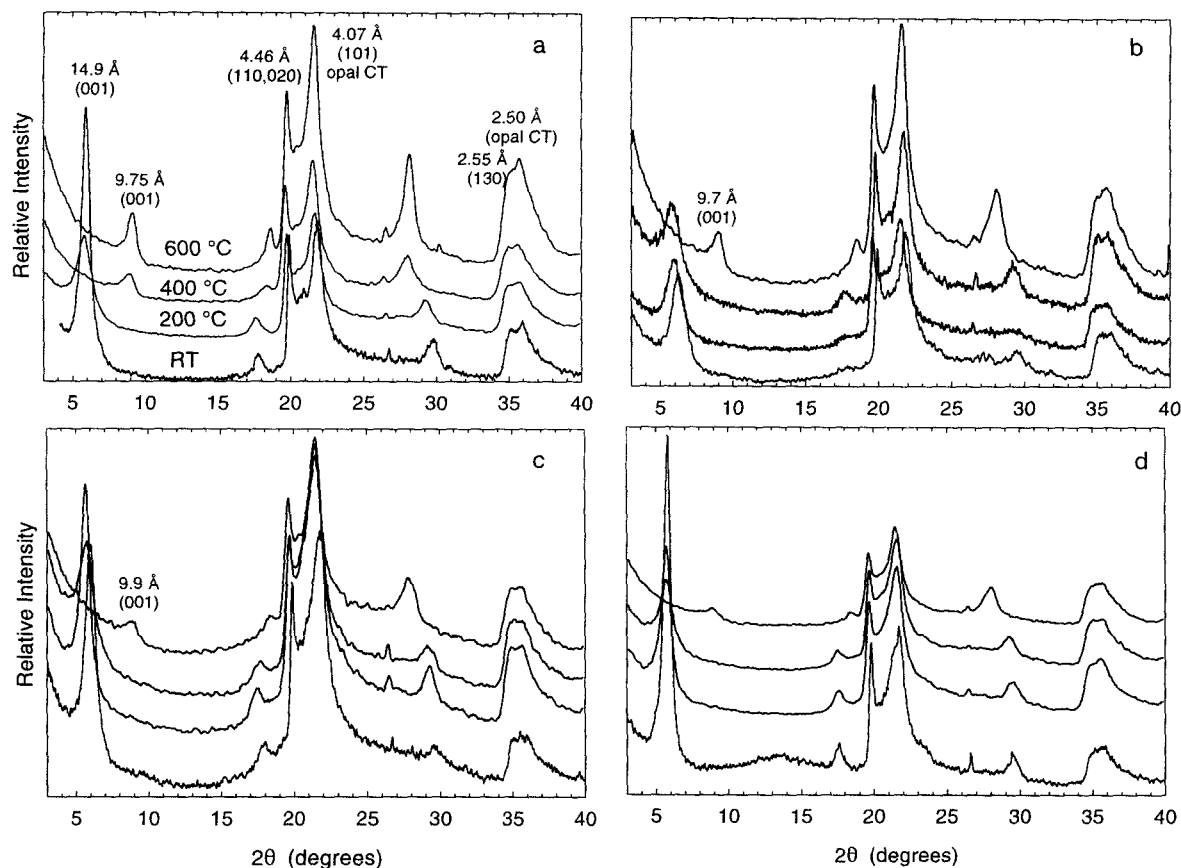| Clay sample	N_2 BET surface area (m^2/g)	wt. % silane determined by TGA	BET constant (c value)
unmodified clay	74	—	84
Cu(II)-clay	75, 71, 71	—	67, 90, 59
Ni(II)-clay	76	—	47
Pb(II)-clay	72, 116	—	97, 73
$C_{18}H_{37}SiCl_3$-met-Cu-clay	4, 4, 5		11, 20, 8
$C_{18}H_{37}SiCl_3$-Cu-clay	17		16
$C_{18}H_{37}SiCl_3$-hex	12	10.7	
$C_{18}H_{37}SiCl_3$-met	8	24.8	
$C_{18}H_{37}Si(OMe)_3$-hex	19	14.8	
$C_{18}H_{37}SiCl_3$-Ni-clay	15		18
$C_{18}H_{37}SiCl_3$-Pb-clay	15, 20		22, 15

Figure 2. X-ray powder diffraction patterns of (a) unmodified montmorillonite and clays modified with silanes: (b) $C_{18}H_{37}SiCl_3$-hex, (c) $C_{18}H_{37}SiCl_3$-met, and (d) $C_{18}H_{37}Si(OMe)_3$-hex at room temperature (RT) and progressively heated in N_2 at 200, 400, and 600°C in each case, as shown explicitly in (a).

may be adsorbed. Another possibility, however, is the evolution of HCl gas when using $C_{18}H_{37}SiCl_3$. The effect of this acidic medium on the clay surface may contribute to the formation of more hydroxyl groups as octahedral cations are leached from the structure, thereby producing two additional Si-OH groups (Rausell-Colom and Serratosa, 1987).

In the hexane-clay system, where the only H_2O present is in the clay interlayer, the organosilanes mainly undergo direct condensation reactions with the clay surface–OH groups. When the pure clay was pre-treated with water vapor before reacting with $CH_3(CH_2)_{17}SiCl_3$ in hexane, the percentage of silane coated increased significantly, from 10.7 to 20.6%. This verifies the effect of H_2O content on the amount of organic species coated on the clay surfaces.

Powder X-ray diffraction

XRD data were used to determine (1) whether the clay structure is altered by the organic modification processes, (2) the surface thermal stability of the coating, and (3) where (outer surface, interlayer, or both)

the organic species are located. Figure 2 displays XRD patterns of each untreated and modified clay (note trace for the unheated samples). The patterns are typical for smectite clays; see Figure 2 for peak assignments. Note that the clay also contains quartz and opal CT (a semi-amorphous form of cristobalite; peaks at 4.07 and 2.50 Å). Because the (*hk*) peaks remained nearly unchanged upon organic-loading, there was no structural damage induced by the coating process. There was also no change in *d* value after organic modification. The *d* value of 14.9 Å, which includes the thickness of the 2:1 layer at 9.6 Å plus the interlayer region, remains the same (at room temperature) in each case. This suggests that the organosilanes are fixed solely on the outer surfaces of the clay because inclusion of the long hydrocarbon chains, or hydrolyzed gelslugs, would increase the *d* values.

Thermal stability of the organic-modified clays was evaluated by heating to 200, 400, and 600°C under flowing N_2 for 2 h. Resulting XRD patterns are given in Figure 2. After heating to 200°C, no changes in *d* value were observed, although the (001) reflec-
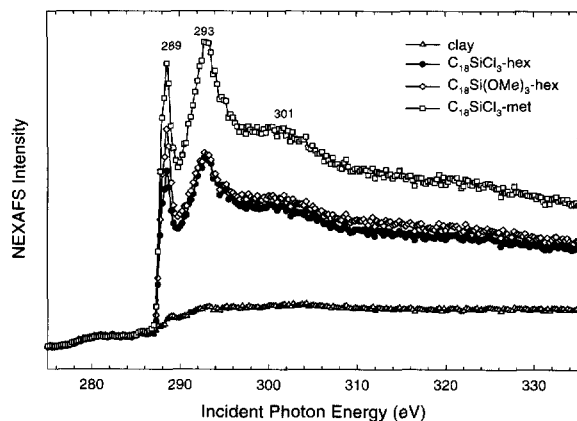
Figure 3. Carbon K-edge NEXAFS spectra of pure and modified montmorillonites.

Figure 4. Oxygen K-edge NEXAFS spectra of pure and modified montmorillonites.

tion peak of the unmodified clay broadened. Based on the TGA results (above), the removal of surface and some interlayer H_2O occurred at this stage. After heating to 400°C, the d values of the organic-modified clays remained unchanged at ~15 Å whereas it decreased, in both intensity and magnitude, for the unmodified clay. This collapse in spacing between 200–400°C for a smectite is related to loss of interlayer H_2O. In contrast, the organic-modified clays apparently formed coatings around the clay particles and restricted the removal of interlayer H_2O. The TGA data (Figure 1) show organic decomposition and subsequent weight loss at 500–550°C, at 600°C the d value for each sample collapsed to ~10 Å. The silane coatings have therefore acted to significantly delay the temperature of interlayer dehydration (by ≤200°C), even in the cases of just 10 wt. % organic coverage.

Near-edge X-ray absorption fine structure

Figures 3 and 4 show electron yield NEXAFS spectra of the carbon and oxygen K-edges of unmodified and silane-coated clays, respectively. The carbon K-edge NEXAFS spectra (Figure 3) display the typical saturated hydrocarbon chain resonances arising from transitions to C-H and C-C antibonding molecular orbitals at 288.6 and 293 eV, respectively (Stöhr, 1992). The weaker resonance at higher energy (~301 eV) is also attributed to transitions to C-C antibonding orbitals of long-chain alkane hydrocarbon molecules (Chen et al., 1994). Although the peak positions of these resonances remain constant among the three organoclays, the intensities vary and decrease in the order: $C_{18}H_{37}SiCl_3$-met ≫ $C_{18}H_{37}Si(OMe)_3$-hex > $C_{18}H_{37}SiCl_3$-hex. Because these silanes, octadecyltrichlorosilane and octadecyltrimethoxysilane, possess hydrocarbon chains of the same length, the NEXAFS intensities of the resonances related to the C-H and C-C orbitals should be proportional to the amount of silanes coated
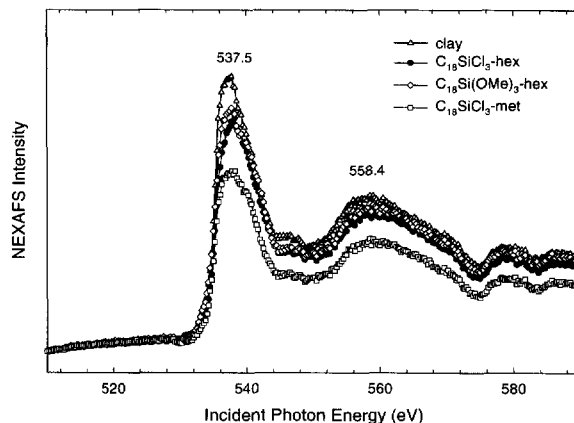
on the clay particles, excluding any –OMe groups that may remain on the $C_{18}H_{37}Si(OMe)_3$ clays. Apparently, the former occurs here because the NEXAFS intensities are in good agreement with the TGA results. As expected, no carbon K-edge NEXAFS resonances were observed for the unmodified clay.

Figure 4 shows the oxygen K-edge NEXAFS spectra. Two resonances at 537.5 and 558.4 eV are assigned to a one-electron transition from the O 1s orbital to the hybridized molecular orbitals of O 2p and Si 3p states (Stöhr, 1992). For unmodified clay and the $C_{18}H_{37}SiCl_3$-clay system, the only oxygen atoms present to produce NEXAFS signals are related to clay-surface oxygens that are part of the tetrahedral sheets. For the $C_{18}H_{37}Si(OMe)_3$-clay system, oxygen atoms can also arise from the methoxyl groups of the silane. The oxygen signal for the unmodified clay is more intense than for any of the modified clays. This result is expected because there is no silane coverage to "hide" the oxygen atoms. The $C_{18}H_{37}SiCl_3$-met clay displays the lowest oxygen K-edge NEXAFS intensity (highest coverage), which is consistent with the highest intensity in the carbon K-edge NEXAFS spectra and also the high wt. % in TGA. If coverage were complete, however, oxygen NEXAFS signals would be expected to be very weak, at least weaker than is observed. The additional benefit of the NEXAFS data over TGA or other methods is that, because this electron-yield detection method is sensitive to only the few top-most layers of the sample, organic coverage can be determined unequivocally to be on the outside of the clay surfaces rather than solely (if at all) in the interlayer.

Surface-area measurements

Nitrogen BET surface areas were measured for all samples. A value of 80 m^2/g was found for the unmodified clay, which is consistent with Carrado et al. (1990). Note, however, that the BET surface area de-

termined for montmorillonite represents interactions with only the outer particle surfaces because the interlayer of smectite minerals is inaccessible to nitrogen molecules (Rutherford *et al.,* 1997). A considerable reduction in surface area was observed upon organic modification (Table 1) which suggests that the organic silanes have effectively coated the outer surface of the clay particles to nitrogen adsorption. Because this organic "cage" is thermally stable, the application of these organic-modified clays for effective storage of certain species, such as hazardous metal ions, may be considered. Our preliminary studies have focused on the encapsulation of transition metals such as Cu^{2+}, Ni^{2+}, and Pb^{2+}. These are introduced to the interlayer by standard cation-exchange techniques and then the sample is treated with a hydrophobic coating of organosilane. Long hydrocarbon chains on the silane will coat the surfaces to a greater degree than short-chained silanes. We are testing these samples for leaching performance and will report the results elsewhere. In fact, Giaquinta *et al.* (1997) have tested this method to encapsulate uranium in different oxidation states for environmental remediation purposes. This encapsulating methodology is similar to the self-assembled monolayer technique that has been developed for formation of well-ordered monolayers on a variety of functional surfaces, such as silicon dioxide (Wasserman *et al.,* 1989; Maoz and Sagiv, 1987), gold (Nuzzo *et al.,* 1987; Porter *et al.,* 1987), alumina (Allara and Nuzzo, 1985; Ogawa *et al.,* 1985), and mica (Kessel and Granick, 1991).

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