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A Time Resolved XANES Study of an Organo-Clay Redox System

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Abstract: *In situ*, time-resolved X-ray absorption near edge structure (XANES) spectroscopic measurements of tetraphenylboron (TPB)-treated Fe-bearing clay minerals were conducted to investigate whether smectite structural Fe was reduced during surface-enhanced oxidative degradation of TPB. Reference samples were prepared by reducing varying amounts of structural Fe with Na-dithionite in an inert atmosphere. Analysis of the Fe K_{α} X-ray fluorescence near edge structure of reference and TPB-treated samples was accomplished by comparing the ratios of edge crest intensities at energies corresponding to oxidized and dithionite-reduced samples following intensity normalization and energy calibration. About 15% of nontronite structural Fe was reduced during the course of the reaction with TPB, whereas more than 50% of the structural Fe in montmorillonite was reduced. XANES spectroscopy provided additional spectroscopic evidence for differences in the reactivity of crystallographic sites of Fe within montmorillonites (both *cis* and *trans* Fe) and nontronites (predominantly *cis* Fe) and suggests that TPB reacted preferentially with *trans* Fe.

1. INTRODUCTION

Tetraphenylboron (TPB) is used to precipitate Cs^{+} from liquid high level radioactive wastes [1]. Upon sorption to Fe-bearing smectites (layered aluminosilicates), TPB undergoes degradation to form specific reaction products consistent with a surface-facilitated oxidation mechanism [1, 2]. The objectives of this study were to establish whether oxidative degradation of TPB at smectite surfaces is coupled to reduction of Fe(III) within the crystalline structure of minerals, and if so, to estimate the fraction of structural Fe(III) involved in the reaction.

2. MATERIALS AND METHODS

Two Fe-bearing montmorillonites, (SWy-2; API #25) and two nontronites (NG-1 and SWa-1) were selected to provide a range in total structural Fe(III) contents. Powdered clay samples (60 mg) were mixed for 2-5 minutes with 0.33 mL of 1M (1:1 ethanol: water) TPB. The pastes were then enclosed within mylar film with kapton tape for XANES analysis. The mixtures used insured that, if a redox couple existed, at least a 2: 1 excess of electrons from the degradation of TPB were available to react with structural Fe(III). The nontronites were diluted into Fe-free hectorite (HCa-1) to a total Fe content of 5% of the total mass prior to mixing with TPB to minimize self absorption effects. Reference samples were prepared by reducing the clays with Na-dithionite under inert atmospheric conditions after Stucki *et al.* [3]. Wet chemical determination of Fe(II) and total Fe on the reference samples was accomplished following Komadel and Stucki [4].

XANES experiments were conducted at the microprobe beamline (X-26A) at the National Synchrotron Light Source, Brookhaven National Laboratory under its normal configuration using a channel-cut Si(111) monochromator and focusing mirror [5]. This configuration provides an energy resolution for XANES measurements of about 1.5 eV. XANES (-80 to -40 eV at steps of 2 eV; -40 to +100 eV at 0.7 eV steps; +100 to +700 eV at 20 eV steps; all at 2 s/step) spectra were collected by measuring the Fe K_{α} fluorescence intensity as a function of incident beam energy (7.1 KeV) with an energy dispersive Si(Li) detector. Automated spectral collection allowed for approximately 60-min incremental measurements of the reaction of TPB with structural Fe(III) as well as periodic measurement of the SWa-1 reference spectrum.

Spectral processing was accomplished by (1) normalizing the energy of all spectra to the absorption energy at half maximum of the step height relative to the untreated nontronite SWa-1, (2) subtracting the baseline (defined as the slope of the linear fit from -80 to 25 eV below the absorption edge), and (3) normalizing to total Fe content at the absorption step height (defined by the absorbance of the continuum extrapolated from the linear fit of the absorption data from 100 to 600 eV above the absorption edge). The ratio of the normalized edge crest intensities (arrows in Figure 1) at +4.1 eV (the dithionite treated samples with the highest level of reduction) and at +8.85 eV (oxidized SWa-1) were used to estimate structural Fe reduction by TPB. A five point Savitzky-Golay smoothing function was applied to XANES spectra for presentation only.

3. RESULTS AND DISCUSSION

Time-resolved Fe K_{α} fluorescence XANES spectra collected as TPB reacted at the surfaces of smectites indicate that oxidation of TPB is coupled to the reduction of structural Fe(III) in all four Fe-bearing smectites (Figures 1-3). Earlier studies showed that oxidative degradation of TPB did not occur when sorbed to Fe-free hectorite [2]. Reduction of structural iron(III) by Na-dithionite resulted in expected and predictable changes in the XANES spectra of the montmorillonite (SWy-2) and nontronite (SWa-1). Surface-facilitated oxidation of TPB by Fe-bearing clays caused similar changes in the XANES spectra of the smectites. The spectral features included a decreased intensity at the edge crest near +8.85 eV (relative to the untreated nontronite SWa-1) with a

Figure 1: Time resolved Fe K_{α} fluorescence XANES spectra of the redox reaction of tetraphenylboron (TPB) with structural Fe(III) in montmorillonite SWy-2. Spectra were normalized as described in text. Arrows indicate the location of the edge crest at 4.1 and 8.85 eV observed for dithionite-reduced SWy-2 and nontronite SWa-1 and used to estimate the reduction levels achieved by TPB.

Figure 2: Edge crest intensity ratios (intensity at 4.1 eV ÷ intensity at 8.85 eV) as a function of Fe(II) content in smectites reduced tetraphenylboron (TPB). Lines represent polynomial fits of dithionite-reduced references (hollow markers) used to estimate the Fe(II) content of the TPB-reduced samples (solid markers). Numbers near solid markers indicate time of reaction with TPB (hours). Inset: expanded plot of the edge crest intensity ratio as a function of Fe(II) content for the dithionite-reduced nontronite SWa-1 indicating the presence of two distinct crystallographic sites of structural Fe.

concomitant intensity increase near 4.1 eV, and a consistent shift of the entire spectra toward lower energies with time of reaction, as shown for the montmorillonite SWy-2 (Figure 1).

Calculation of the ratio of the intensities at 4.1 and 8.85 eV against Fe(II) content in the dithionite-reduced reference series (Figure 2) provided an estimate of Fe reduction during reaction with TPB (Figure 3). Differences in the intensity ratio were less evident for the nontronite due to the greater initial total Fe content, and therefore a lower fraction of Fe(II) following the reaction (Figure 2). For the montmorillonites, maximum levels of reduction were achieved within 10-12 hours followed by some re-oxidation of structural Fe(II) (Figure 3). Greater than 50% of the structural Fe in montmorillonites appeared to be reduced during reaction with TPB, whereas only 10-15% of the structural Fe of nontronites was reduced. Interestingly, the total amount of Fe(III) reduced by TPB in both montmorillonites and nontronites was nearly the same (0.35-0.5 mmol g⁻¹).

Figure 3: The reduction of structural Fe(III) in smectites as a function of time of reaction with tetraphenylboron (TPB) as measured by time-resolved XANES spectroscopy.

Comparison of the XANES spectral parameters with Fe(II) reduction by both dithionite and TPB (Figure 2) revealed differences in the reactivity of crystallographic Fe for the two smectite types. Note that the shape of the intensity ratio plot with increased Fe(II) changed dramatically near 0.8 mmol g^{-1} Fe(II) (about 20% of total) for the dithionite-reduced nontronite (inset, Figure 2), indicating that two different reduction reactions may have occurred in nontronite. In contrast, the reaction of TPB at the surface of montmorillonite could be fit by a quadratic polynomial over the final Fe(II) contents achieved. Since the ratio of TPB to structural Fe(III) in this study was controlled at a level to ensure an excess of electrons upon formation of the redox couple, we propose that the differences observed are related to the crystallographic site of structural Fe(III) within the different smectite types.

Both montmorillonites and nontronites contain predominantly (> 99%) octahedral Fe, however the crystallographic site of octahedral Fe in montmorillonites is distributed at random in both *cis* (hydroxyls at adjacent apexes) and *trans* (structural hydroxyls at opposite apexes of octahedron) configuration, whereas for nontronites the crystallographic site of octahedral Fe is predominantly in *cis* configuration [6]. However, magnetic susceptibility measurements of the nontronite SWa-1 have indicated that as much as 20% of structural Fe could be in a *trans* configuration [7]. This finding is supported by the shape of the intensity ratio plot at higher levels of Fe(II) for the dithionite-reduced nontronite (inset, Figure 2) and by the reduction of about 50% of the structural Fe in montmorillonite (Figure 3). Thus, it is probable that the *trans* crystallographic site is the reactive Fe(III) fraction responsible for surface-facilitated oxidation of TPB in both montmorillonites and nontronites.

4. CONCLUSIONS

Time-resolved Fe K α XANES measurements demonstrated that oxidative degradation of TPB is coupled to the reduction of Fe(III) to Fe(II) within the crystalline structure of both nontronites (Fe-rich) and montmorillonites (Fe-poor). Analysis of the XANES spectral features indicate that TPB may react preferentially with octahedral Fe(III) in *trans* crystallographic sites in smectites.

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