XAFS Study of the Binding Geometry of Oxometallate Anions to Self-Assembled Monolayers on Mesoporous Supports

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Introduction

The use of arsenic and chromium in an array of agricultural and industrial processes has resulted in groundwater contamination of many industrial sites.[1] This contamination has created the need for effective groundwater remediation strategies for the selective removal of the oxometallate anions (arsenate and chromate). Recently, the synthesis of self-assembled monolayers on mesoporous supports (SAMMS) lined with cationic metal complexes as a novel anion-binding material was reported.[2] To understand the interfacial chemistry of these cationic SAMMS, both to evaluate them as anion sorbent materials and to look at their long-term stability as potential waste forms, we must understand not only how well the anion is associated with the metal complex but also how well the metal complex remains anchored within the mesoporous support. Therefore, we have undertaken a detailed study of the local atomic environment around the metal complex (Cu) both before and after the oxometallate anions are bound to the SAMMS interface. The stereochemical insight to be gained is critical for the development of selective anion-specific sorbent materials.

Methods

All of the SAMMSs samples studied here consisted of Cu(II) ions bound to three ethylenediamine (EDA) ligands within the monolayer on the mesoporous silica. The first sample was unladed SAMMS, indicating that no anion had been introduced. The other SAMMS samples were all exposed initially to SO_4. Then one portion was exposed to AsO_4 and another to CrO_4. Therefore, the four samples are (1) unladen SAMMS, (2) SAMMS + SO_4, (3) SAMMS + SO_4/CrO_4, and (4) SAMMS + SO_4/AsO_4.

Fluorescence Cu, As, and Cr K-edge x-ray absorption fine-structure (XAFS) data were collected at MR-CAT3 at the APS. A double-crystal silicon [111] monochromator was used to select the incident x-ray energy. The undulator gap was tapered and scanned. Linearity tests[4] indicated less than 0.3% nonlinearity in the experimental setup for 50% attenuation of the incident x-ray intensity.

The analysis software is part of the UWXAFS package.[5] Standard procedures were used to subtract the background. All of the measurements were made at least twice, and the resulting $\chi(k)$ data were averaged (see Fig. 1a). The value for $S_0^2 = 0.82 \pm 0.10$ was determined from a Cu_2O standard, to reduce the number of parameters determined in the fit.

Results and Discussion

Fifteen models were tested in the fitting process of the SAMMS + SO_4 data. Figure1b shows the Fourier transform of the SAMMS + SO_4 data and the best-fit model. Our results support the conclusion that the tetrahedral oxometallate anions are bound directly to the metal center of Cu-EDA SAMMS through a direct Cu-O bond in a monodentate fashion. During the process of oxoanion binding, the Cu center undergoes a geometry change from octahedral to trigonal bipyramidal. This leaves the Cu coordination sphere filled with one chelating EDA ligand, two coordinated secondary amines, and the bound oxoanion. The loss of symmetry that accompanies this geometrical change alleviates any orbital degeneracy, thereby enhancing the stability of the interfacial complex. This enhanced stability, coupled with the lack of dissociation observed with the oxometallate anions, suggests that these laden SAMMS may very well have excellent long-term stability as waste forms.

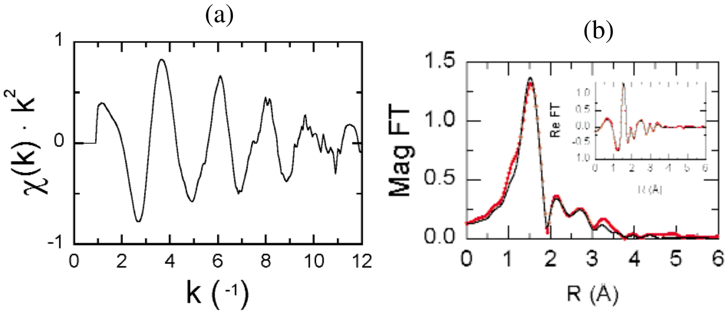

FIG. 1. Example of data taken on the SAMMS + SO_4 sample. a) Averaged $\chi(k)$ data. b) Fourier transform data (circles) and fit (line).

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References

[1] A. Davis, P. De Curnou, and L.E. Eary, Environ. Sci. Technol. **31**, 1975-1991 (1997).

[2] G.E. Fryxell, J. Liu, T.A. Houser, Z. Nie, K.F. Ferris, S. Mattigod, M. Gong, and R.T. Hallen, Chem. Mater. **34**, 2329-2345 (1999).

[3] C.U. Segre, N.E. Leyarovska, L.D. Chapman, W.M. Lavender, P.W. Plag, A.S. King, A.J. Kropf, B.A. Bunker, K.M. Kemner, P. Dutta, R.S. Druan, and J. Kaduk, Synchrotron Radiation Instrumentation: Eleventh U.S. Conference **CP521**, 419-422 (2000).

[4] K.M. Kemner, A.J. Kropf, and B.A. Bunker, Rev. Sci. Instrum. **65**, 3667-3669 (1994).

[5] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, and D. Haskel, Physica B **208/209**, 2995-3009 (1995).