XAFS Study of the Catalytic Effects of Ag, Au, and Cu on the Reductive Dechlorination of Carbon Tetrachloride by Green Rust

E. J. O'Loughlin,[1] S. D. Kelly,[1] K. M. Kemner,[1] D. R. Burris[2]
[1] Environmental Research Division, Argonne National Laboratory, Argonne, IL, U.S.A.
[2] Air Force Research Laboratory, Tyndall AFB, FL, U.S.A.

Introduction

Recently, green rusts (GRs) have been shown to be capable of reducing a number of organic and inorganic contaminants including nitrate, chromate, selenate, and chlorinated hydrocarbons. Although the reductive transformation of many contaminants is thermodynamically favored in suboxic environments, these reactions are often kinetically constrained. Many studies have demonstrated the catalytic activity of aqueous metal complexes in the reduction of a range of contaminants, suggesting the potential for enhanced contaminant reduction by GR in the presence of select metals. This paper describes the use of x-ray absorption fine structure (XAFS) spectroscopy to gain insight into the catalytic effects of Ag, Au, and Cu on the reductive dehalogenation of carbon tetrachloride (CT) by GR.

Materials and Methods

Experiments examining the reduction of CT by GR alone and by AgGR, AuGR, and CuGR were performed as described by O'Loughlin and Burris.[1] For the XAFS studies of AgGR, AuGR, and CuGR, suspensions containing 2 g of GR$_{SO_4^{2-}}$ in 45 ml of water were spiked with 200 µmol of Ag(I), Au(III), or Cu(II), yielding molar Ag/Fe, Au/Fe, and Cu/Fe ratios of 0.01. After 48 h, the suspensions were centrifuged. The pellets were resuspended in distilled deionized water and centrifuged again. The GR was washed twice more in this manner. After the final washing, the GR pastes were mounted in holes machined in Plexiglas sample holders. All XAFS measurements were made at the MRCAT sector 10-ID[2] beamline at the Advanced Photon Source.

Data for x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra were collected at the Ag and Cu K edges and the Au L$_{III}$ edge. The incident x-ray intensity was measured with an ion chamber filled with N$_2$ gas, while the x-ray fluorescence intensity was measured with a Lytle detector in the Stern-Heald configuration[3] filled with free-flowing Ar at atmospheric pressure. Linearity tests[4] indicated less than 0.35% nonlinearity for a 50% decrease in incident x-ray intensity. The incident x-ray intensity varied by less than 15% throughout the energy range of the XAFS measurements. To reduce radiation-induced chemical effects, energy scans were collected at six different locations, with two to five one-minute measurements made at each location. No time dependent change in the XANES data was observed for any of the samples. The codes contained in the UWXAFS package[5] were used to analyze the XAFS data. Standard procedures were used to subtract the background.

Results and Discussion

Although CT is reduced by GR alone, the rate of CT reduction by GR is dramatically enhanced by the addition of Ag, Au, or Cu (Fig. 1). The XANES spectra of Ag, Au, and Cu in GR suspensions clearly indicate reduction to Ag(0), Au(0), and Cu(0) by GR (data not shown). The EXAFS data suggest long-range order in the reduced metal phases (as shown for Cu in Fig. 2), however it is not possible to determine if they have formed discrete particles or have plated on the iron oxide surface. The enhanced reduction of CT in Ag(0)GR, Au(0)GR, and Cu(0)GR systems may be analogous to the enhanced reduction of chlorinated hydrocarbons by bimetallic reductants (e.g., palladized Fe(0)). As either thin surface films or surface-associated particles, the coupled GR and reduced metals may form galvanic cells in which the GR serves as the anode and is oxidized, while CT is reduced at the metal surface. Additional experiments are needed to fully elucidate the mechanism(s) responsible for the observed catalytic effect.

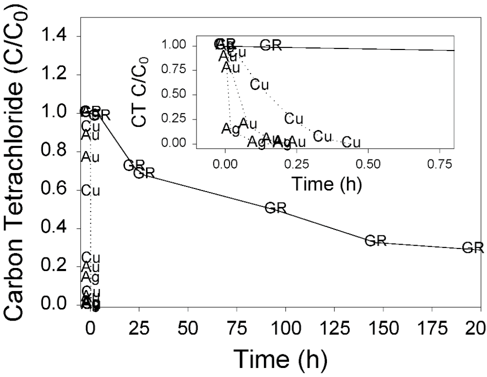

FIG. 1. Catalytic effect of Ag, Au, and Cu on CT reduction by GR. CT reduction by GR alone is indicated by the solid line.

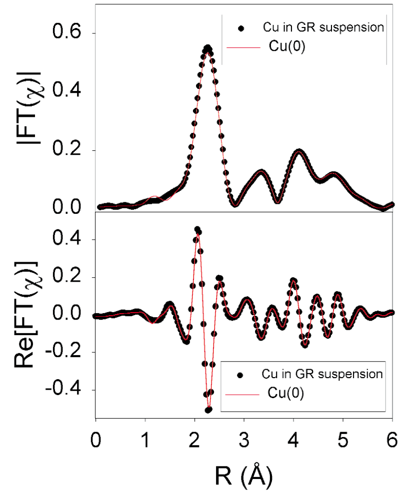

*FIG. 2. The magnitude |FT(χ)| and real part Re[FT(χ)] of the Fourier transform of χ(k)*k data for Cu in a green rust suspension and for Cu foil (Cu(0)).*

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References

[1] E.J. O'Loughlin and D.R. Burris, in “Reductive dehalogenation of carbon tetrachloride by Cu amended green rust,” 219th American Chemical Society National Meeting, San Francisco, CA, Division of Environmental Chemistry Preprints of Extended Abstracts 40(1), 62-63 (2000).

[2] 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. Duran, and J. Kaduk, in *Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference*; Vol. CP5321, eds. P.A. Pianetta, J.R. Arthur, and S. Brennan (American Institute of Physics, New York, 2000), p. 419-422.

[3] E.A. Stern and S.M. Heald, Rev. Sci. Instrum. **50**, 1579-1583 (1979).

[4] K.M. Kemner, 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**, 117-120 (1995).