Radiation-Induced Copper Particle Cluster Formation in Aqueous $CuCl_2$: An XAFS Study

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Introduction

Using x-ray synchrotron radiation as a structure probe in aqueous chemistry and geochemistry has become an important technique during the past decade. Although x-ray studies employing a third-generation synchrotron source have yielded important information in the above area and related fields, in the case of experiments involving aqueous solutions, there appear to be instances where the incident x-ray beam alters the chemical properties of the sample. This is due mainly to the effects of high-brilliance x-rays on water. Jonah[1] states that intense x-rays and gamma rays cause radiolysis of water in aqueous solutions, producing species such as H^+, H, OH, OH^- , and hydrated electrons, e_{aq}^-. These transient species may interact with themselves, water, solute components, or other free radicals that are generated by irradiation. This study focuses on the radiation-induced copper particle formation in a dilute aqueous solution of $CuCl_2$. The sample was irradiated by intense x-rays, which were used to simultaneously monitor the structural changes by means of x-ray absorption fine structure (XAFS) spectroscopy.

Methods and Materials

Cu K-edge XAFS scans were made at the PNC-CAT ID-20 undulator beamline. An aqueous solution of $CuCl_2$ (55ppm) was enclosed in a hydrothermal diamond anvil cell.[2] The sample chamber consists of cup-shaped cavity, 300 µm in diameter, in the center of the upper diamond anvil face and a 300-µm-diameter hole in a 50-µm-thick Re gasket. The solution was irradiated by an x-ray beam that traveled through the upper diamond in a direction parallel to the anvil face. The XAFS spectra were collected in the fluorescence mode, in the standard 90º orientation to the incident x-ray beam, using a 13-element Ge detector. The undulator gap voltage was maintained at 55 eV throughout the collection of data, giving a flux of approximately 5 x 10^{11} photons/s. Ten successive XAFS spectra were collected within about 6 h.

Results and Discussion

Figure 1 shows the Fourier transforms of $\chi(k)$ data of successive XAFS spectra (A to E), with A being the Fourier transform of the first XAFS spectrum, in comparison with the Fourier transform of the Cu foil c(k) data. A increase in the amplitude occurs with time of irradiation, especially in the first shell Fourier transform. The peaks in spectrum A show a noticeable shift toward lower R-values. The principal features of the Fourier transforms of spectra B to E shown in Fig. 1 resemble those of data measured from bulk copper, at least up to the third peak. However, when fitting was attempted with the bulk copper model, only spectra D and E were in close agreement. In contrast, fitting spectra A, B, and C required modifications in the standard model.

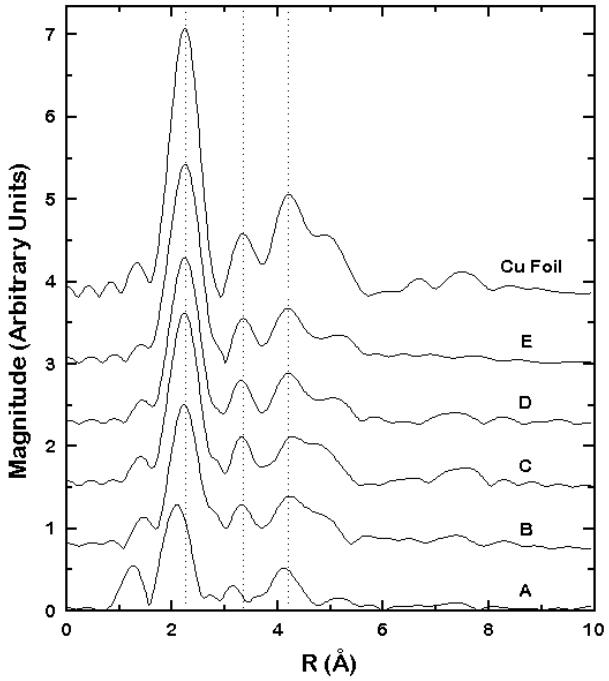

FIG.. 1

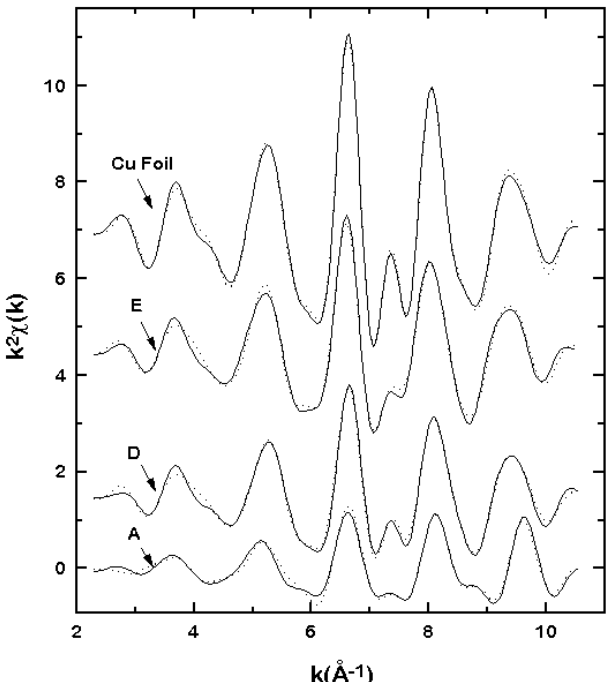

FIG.. 2

Spectrum A (multiple shell fit) was fit with a 19-atom face centered cubic (fcc) copper cluster whereas spectra B and C were fit with a mixture of a 19-atom fcc copper cluster and bulk copper models. Figure 2 shows the multiple shell fits (dashed lines) for the $k^2 \bullet \chi$ (k) data (solid lines) that was obtained by filtering the Fourier transform peaks in the range 1.5 to 4.7 Å for spectrum A and in the range 1.5 to 5.8 Å for spectra D and E. Analyses show that, initially, the clusters have a nearest neighbor distance of 2.48 ± 0.02 Å. This increases to 2.55 ± 0.01 Å with time, indicating that the clusters approach the lattice dimensions of bulk copper. Similarly, the Debye-Waller factor of the copper clusters is found to increase by 50 to 55% over the range of time of irradiation. The nearest neighbor coordination number is found to increase in a manner consistent with the decrease in the surface-to-volume ratio as the average cluster size approaches its bulk dimensions. The cluster size estimates made by using the observed bond distances yield an approximate size of 7 Å for the 19-atom fcc cluster. Results obtained from fitting spectra B and C suggest the existence of a mixture of clusters (5-10 Å across), leading up to bulk-like clusters with successive collection of the XAFS spectra. The copper ions in the solution are reduced to the metallic state by reacting with the hydrated electrons as a result of radiolysis of water by the incident x-ray beam. Under a reduced flux of approximately 5×10^{10} photons/s, a substantial decrease in the rate of reduction of copper ions was observed. These results suggest that low-brilliance x-rays may be more suitable for XAFS analysis of low-concentration Cu and other metal-bearing solutions.

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