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EXAFS Analysis in Forming of Metal Colloids in Water-in-scCO$_2$ Microemulsions

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Introduction

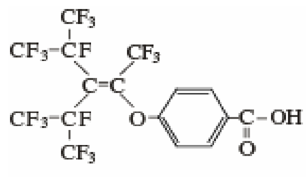
The environmentally benign, nontoxic, and nonflammable supercritical fluids such as water and carbon dioxide (sc-CO$_2$) are the two most abundant and inexpensive solvents. Water-in-scCO$_2$ dispersions in the form of microemulsions offer new possibilities in waste minimization for the replacement of organic solvents in separations, reactions, and materials formation processes [1]. In this study, we have tried to synthesize cupper nanoparticles (Cu nanoparticles) by the chemical reduction of Cu(ClO$_4$)$_2$ using reducing reagent such as NaBH$_4$ in the presence of fluorinated surfactants in water-in-scCO$_2$ microemulsions, and have investigated the average particle size of the Cu nanoparticles by means of EXAFS measurements.

Experimental

Cu nanoparticles were synthesized in a high-pressure SUS 316 cell (inner volume of 14.0 mL) equipped with four optical windows: two of them were CVD diamond windows for *in-situ* EXAFS measurements and the other two were quartz windows for the UV-Vis absorption measurements. Water-in-scCO$_2$ microemulsions containing Cu(ClO$_4$)$_2$ were prepared by adding sc-CO$_2$ into the cell which contained fluorinated surfactant PFNA aqueous solution (kindly provided by NEOS Co. Ltd.), Cu(ClO$_4$)$_2$·6H$_2$O (1.58×10^{-3} mol) and NaBH$_4$ aqueous solution. The water-to-surfactant molar ratios (w) were w=126. The cell was then kept at 35 °C and 25MPa for 120 min with continuous stirring to form a single-phase microemulsions. During the stirring, the reduction of Cu ions to form Cu(0) particles in the microemulsions occurred. The *in-situ* EXAFS measurements were performed at BL-9A and/or BL-9C in the irradiation with UV light from a 500W high-pressure Hg lamp. EXAFS spectra of Cu-K edge were collected in a transmission mode to estimate the coordination number of Cu nanoparticles in the water-in-scCO$_2$ microemulsions.

Results and Discussion

Figure 1 shows the μ(E) vs E for Cu^{2+} species in the water-in-scCO$_2$ microemulsions (water content in the system is 17.9 wt%) which are consisted of PFNA and Cu(ClO$_4$)$_2$·6H$_2$O aqueous solution with w=126 before photo-reduction. The dotted line (a) shows the background spectrum obtained from the high pressure cell with CVD diamond windows with sc-CO$_2$ at 35 °C and 25MPa. Diffraction spikes from CVD diamonds are not observed in this experiment, which is different from the case of single crystal diamonds (not shown in this report). The dashed line (b) shows the spectrum obtained from water/sc-CO$_2$/PFNA emulsions in the same cell equipped with the CVD diamond windows. The solid line (c) is obtained by the subtraction of spectrum (a) from spectrum (b). The present data were obtained from the measurement during the stirring of the emulsions, resulting in getting a worse S/N spectrum. It is expected that the data quality as for S/N will become better without the stirring of these emulsions. Based on these results, it is suggested that the size of water pool in water-in-scCO$_2$ microemulsions would be huge so that the EXAFS spectrum would be disturbed by the stirring. The reduction procedures with NaBH$_4$ and the detailed analysis are in progress.



PFNA M.W.=544

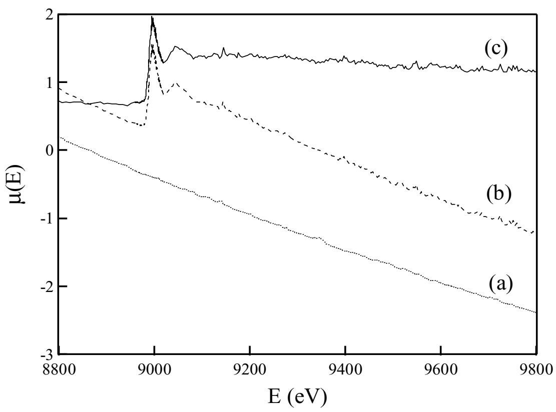


Fig. 1. X-ray absorption coefficient μ(E) at the Cu-K edge for (a) sc-CO2, (b) water/sc-CO$_2$/PFNA microemulsions, and (c) the subtracted one.

References

[1] J. M. DeSimone and W. Tumas, Green Chemistry using liquid and supercritical carbon dioxide, Oxford University Press, New York, 2003.

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