Materials Science

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Photochemical Synthesis of Ag Particles in Tween20/Water/Ionic Liquid Microemulsions at High Pressure CO_2 System

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Introduction

Combinations of ILs with $scCO_2$ have been received increasing attention for separation, chemical reactions, and material synthesis. Typically, ILs can dissolve large amounts of CO_2, but ILs are usually insoluble in $scCO_2$ [1]. Recently the biphasic IL-$scCO_2$ systems have gained importance in separation and catalysis reactions [2, 3]. In this study we have performed the *in-situ* fluorescence EXAFS measurements to investigate the Ag particle formation in the biphasic system of water-in-ILs microemulsions under a high pressure CO_2.

Experimental

Colloidal dispersions of Ag particles were synthesized in a high-pressure SUS 316 cell (inner volume of ca. 10 mL) by the photoreduction of the Ag^+-containing water-in-[OMIm][BF_4] microemulsions in the presence of Tween20 under the high-pressure CO_2. The high-pressure cell has 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-irradiation from mercury lamp. Tween20/water/[OMIm][BF_4] microemulsions containing $AgClO_4$ were prepared by adding CO_2 into the cell which contained a mixture of $AgClO_4$ aqueous solution, Tween20, [OMIm][BF_4], and benzoin for photoreduction. The weight fraction of Tween20 was varied from 0.11 to 0.66, and the [OMIm][BF_4]-to-Tween20 molar ratio (R) and the water-to-Tween20 molar ratio (w) was changed accordingly as shown in Fig. 1. The concentration of [Ag^+] in the system was 4.4 mM. The cell was kept at 35°C and 25 MPa for 1 h with continuous stirring to form microemulsions. After stirring, the microemulsion was photo-irradiated for 5 h to investigate the reduction of Ag^+ and the formation of Ag particles.

The *in-situ* EXAFS measurements were carried out in a fluorescence mode at NW10A beam line in PF-AR. EXAFS spectra at Ag-K edge were collected by a 19-element Ge solid-state detector to evaluate the electronic state and the coordination number of Ag particles. Data analysis was performed by REX2000 (Rigaku Co.).

Results and Discussion

Fig. 1(a) shows the Fourier transforms of colloidal Ag particles at the high-pressure CO_2. In all three samples, the peak observed around 0.26 nm is assigned to an Ag-Ag metallic bond, which is observed in the case of Ag foil. Compared with the results of the colloidal Ag particles released to the ambient air after *in-situ* measurements, as shown in Fig. 1(b), the peak intensity obviously depends on the value of $W_{Tween20}$, and the difference between *in-situ* and *ex-situ* measurements are not noticeably observed. The detailed analysis is in progress.

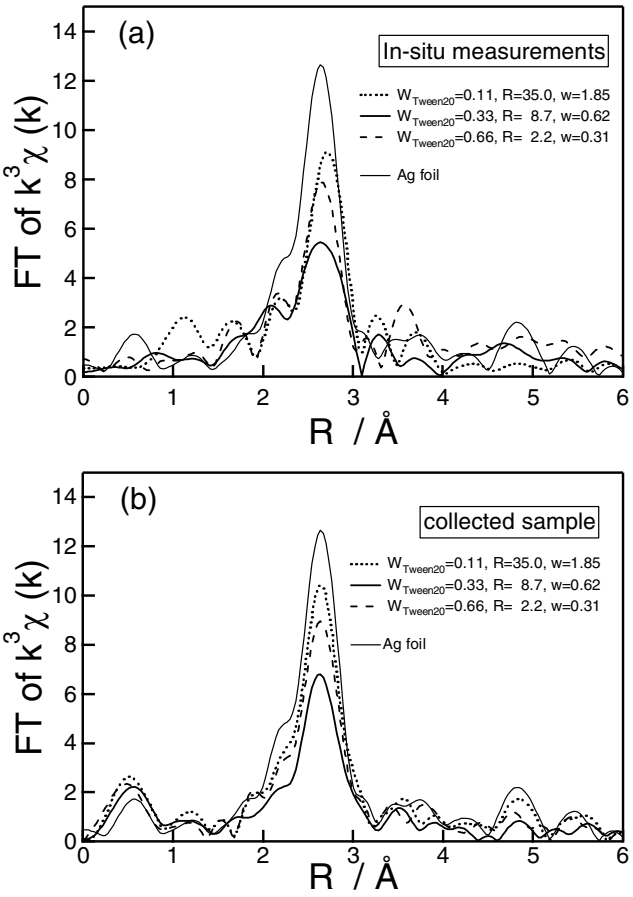

Fig. 1. Fourier transforms of the Ag-K edge EXAFS spectra for (a) in-situ and (b) ex-situ colloidal Ag particles at the different values of $W_{Tween20}$, in addition of Ag foil.

References

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