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Structural Change in Forming of Metal Particles in Water-in-scCO$_2$ Emulsions

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Introduction

Water-in-scCO$_2$ microemulsions have been used to synthesize various metal particles such as cadmium sulfide and silver (Ag) particles [1-3]. Although many researches have been performed focusing on the synthesis of metal particles in water-in-scCO$_2$ microemulsions, there are a few reports that described the formation process of metal particles under high-pressure conditions. In this study we have synthesized Ag particles by the photoreduction of silver perchlorate ($AgClO_4$) and by the chemical reduction using hydrazine (H_2NNH_2) as a reducing reagent in the presence of AOT in water-in-scCO$_2$ emulsions. We have also investigated the size of water droplets containing aggregates of Ag particles in the emulsions by *in-situ* SAXS measurements.

Experimental

Ag particles were synthesized in a high-pressure SUS 316 cell (inner volume of 13.5 mL) equipped with four optical windows: two of them were diamond windows for *in-situ* SAXS measurements and the other two were quartz windows for the UV irradiation of mercury lamp. Water-in-scCO$_2$ emulsions containing $AgClO_4$ were prepared by adding CO_2 into the cell which contained a mixture of $AgClO_4$ aqueous solution, AOT, F-pentanol, ethanol, and benzoin for photoreduction. In the case of the chemical reduction, hydrazine was introduced into the cell instead of benzoin. The water-to-surfactant molar ratios (w) and metal concentration [Ag^+] was fixed to 0.57 and 16.6 mM, respectively, and water content was 0.289 wt% for photoreduction and 0.868 wt% for chemical reduction. The cell was kept at 35°C and 25MPa for 3 h with continuous stirring to form emulsions. After stirring, the emulsion was photo-irradiated or chemically-reduced by the hydrazine for the designated time to investigate the reduction of Ag^+ and the formation of Ag particles. The *in-situ* SAXS measurements were performed at BL-15A. The scattering data was collected by a position sensitive proportional counter (PSPC).

Results and Discussion

Fig. 1(a) shows the SAXS profiles of water-in-scCO$_2$ emulsions before and after reduction for the designated time. Here q is the magnitude of the scattering vector, defined as $q = (4\pi/\lambda)\sin(\theta/2)$ where θ is the scattering angle and λ is the wavelength of X-ray. The intensity at a small q range ($q < 0.8$ nm^{-1}) slightly increases with the increase of reduction time. The intensity of irradiated samples for longer time is stronger than that of irradiated for shorter time. From their Guinier plots, the radii of water droplets in the emulsions slightly are found to decrease from 26.0 to 24.4 nm. The size of water droplet does not so much change during the Ag particle formation. As shown in Fig. 1(b), in the case of chemical reduction, the intensity at an overall q range measured tends to increase in a little amount when the reduction proceeds in time. Their Guinier plots indicate that the radii of water droplets slightly decrease from 26.2 to 25.0 nm, as the similar tendencies are seen in photoreduction.

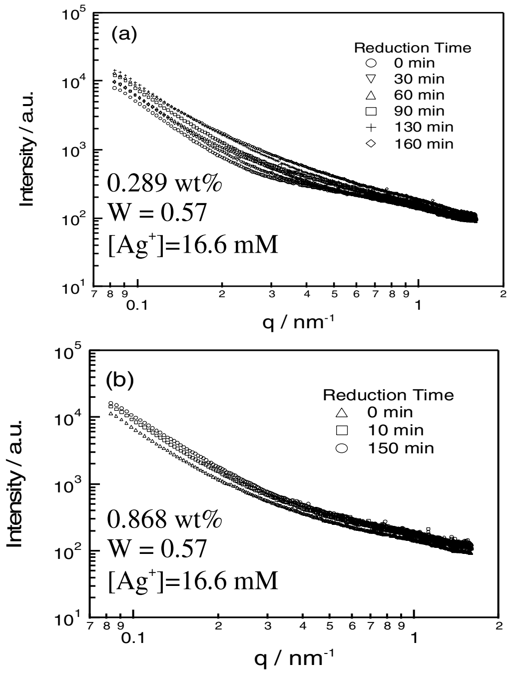

Fig. 1. SAXS profiles of the Ag colloidal solutions prepared by (a) photoreduction and (b) hydrazine reduction in the presence of AOT in water-in-scCO$_2$ emulsions.

References

[1] M. Ji et al., *J. Am. Chem. Soc.* **121**, 2631 (1999).
[2] H. Ohde et al., *Chem. Mater.* **13**, 4130 (2001).
[3] J. Liu et al., *Chem. Eur. J.* **11**, 1854 (2005).

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