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Structural Change of Emulsions in Forming of Metal Colloids in Water-in-scCO₂ Microemulsions

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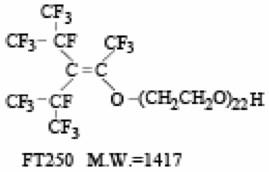
Introduction

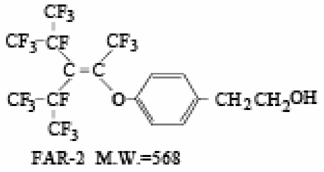
Supercritical carbon dioxide (sc-CO_2) has received much attention as a promising environmental benign alternative to toxic organic solvents because it is inexpensive, nontoxic and nonflammable, offering advantages over conventional oil-based microemulsions. It also has moderate critical temperature and pressure (31.1 °C and 7.38 MPa). Recently, Johnston et al. [1] have demonstrated the formation of water-in-scCO_2 microemulsion by using a perfluorinated surfactant PFPE. On the other hand, water-in-scCO_2 microemulsions with nanometer-sized water pools have provided various utilities serving as effective reaction vessels for inorganic, organic, and enzymatic reactions. However, only a few research groups [2, 3] have reported the photochemical formation of metal nanoparticles in water-in-scCO_2 microemulsions. In this work, we have synthesized silver (Ag) nanoparticles in water-in-scCO_2 microemulsions by photo-reduction, and have investigated the average size of the Ag particles and their aggregates in the microemulsions during the photo-reduction by means of small angle X-ray scattering (SAXS) measurements.

Experimental

Ag particles were synthesized in a high-pressure SUS 316 cell (inner volume of 13.5 mL) equipped with both two diamond windows for *in-situ* SAXS measurements and two quartz windows for the irradiation of UV light from a 500W high-pressure Hg lamp. Water-in-scCO_2 microemulsions containing $AgClO_4$ were prepared by adding a fluorinated surfactant FT250 (70 mM) or FAR-2 (176 mM) (kindly provided by NEOS Co. Ltd.) ethanol solution to the cell, following the addition of $AgClO_4$ (4.3×10^{-4} mol) aqueous solution of the same volume. The water-to-surfactant molar ratios (w) were w=4.1 and 1.4, respectively. The cell was then loaded with CO_2 at 35 °C and 25MPa for 20 min with continuous stirring to form a single-phase microemulsions. After stirring, the microemulsions were irradiated with UV light at designated time to perform the reduction of Ag ions to form Ag(0) particles in the microemulsions. The in-situ measurements were performed at BL-15A. The scattering data was collected by the position sensitive proportional counter (PSPC).



FT250 M.W.=1417



FAR-2 M.W.=568

Results and Discussion

Figure 1 shows SAXS profiles (log I(q) vs. q) of water-in-scCO_2 microemulsions prepared from (a) FT250 and (b) FAR-2 before and after photo-reduction, respectively. 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 ($q < 0.5$ nm^{-1}) depends on the surfactant employed, and tends to slightly increase with the reduction time increasing. However, the decrease in intensity appears after more than 1 hour reduction, as shown in 1(b), which suggests that the formation of aggregates (or precipitates) of Ag particles might occur. Thus it is suggested that the size of water pool in water-in-scCO_2 microemulsions would depend on the functional group of molecule of surfactant used, and does not change remarkably in the formation process of Ag particles during the photo-reduction. The detailed analysis is in progress.

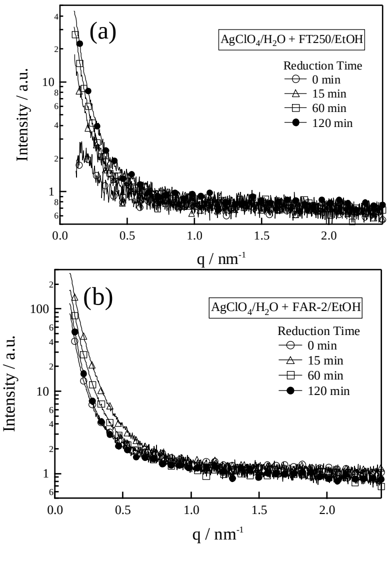


Fig. 1. SAXS profiles obtained from (a) FT250 and (b) FAR-2.

References

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