Materials Science

15A/2003G232

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

Masafumi HARADA*[1], Kenji SAIJO[2], Yoshifumi KIMURA[3], and Takeji HASHIMOTO[2]
[1]Department of Textile and Apparel Science, Faculty of Human Life and Environment, Nara Women's University, Nara 630-8506, Japan
[2]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan
[3]International Innovation Center, Kyoto University, Kyoto 606-8501, Japan

Introduction

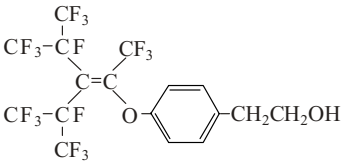
The use of compressed carbon dioxide as a reaction medium, either as a liquid or a supercritical fluid (sc-CO_2), offers the opportunity not only to replace conventional hazardous organic solvents but also to optimize and control the effect of solvent on chemical synthesis [1]. In this work, we have synthesized silver nanoparticles (Ag nanoparticles) by the photo-reduction of $AgClO_4$ in the presence of fluorinated surfactants in water-in-scCO$_2$ microemulsions [2, 3], and have investigated the average size of the Ag nanoparticles and their aggregates in the microemulsions during the photo-reduction by means of small angle X-ray scattering (SAXS) measurements.

Experimental

Ag nanoparticles 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 irradiation of UV light from a 500W high-pressure Hg lamp. Water-in-scCO$_2$ microemulsions containing $AgClO_4$ were prepared by adding sc-CO_2 into the cell which contained a mixture of a fluorinated surfactant FAR-2 ethanol solution (kindly provided by NEOS Co. Ltd.) and $AgClO_4$ (4.3×10^{-4} mol) aqueous solution. The water-to-surfactant molar ratios (w) were w=317 and 3.17 in the case of FAR-2. The cell was then kept at 35 °C and 25MPa for 60 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).

Results and Discussion

Figure 1 shows SAXS profiles (log I(q) vs. q) of water-in-scCO$_2$ microemulsions (water content in the system is 0.285 wt%) prepared from FAR-2 with (a) w=317 and (b) w=3.17 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, a decrease in intensity was observed after more than 1 hour reduction, as not shown in this report, which suggests that the formation of aggregates (or precipitates) of Ag particles might occur. Moreover, the larger ratio w does not remarkably give rise to the increase of scattering intensity in the small q range. Thus it is suggested that the size of water pool in water-in-scCO$_2$ microemulsions would depend on the sort of surfactant used, and does not so much change in the formation process of Ag particles during the photo-reduction. The detailed analysis is in progress.



FAR-2 M.W. = 568

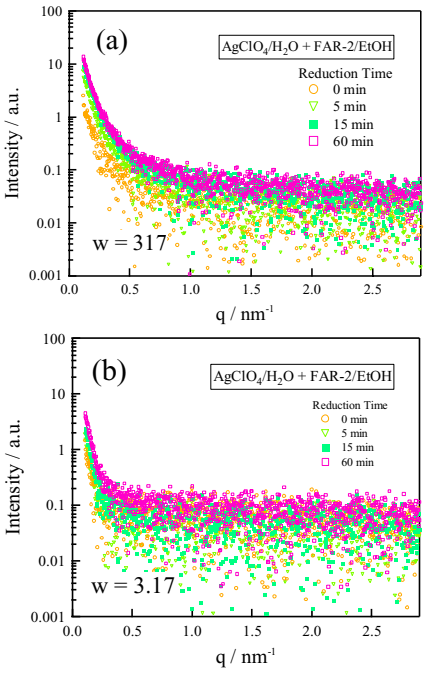


Fig. 1. SAXS profiles obtained from water/sc-CO_2/FAR-2 emulsions, (a) w=317 and (b) w=3.17.

References

[1] J. M. DeSimone and W. Tumas, Green Chemistry using liquid and supercritical carbon dioxide, Oxford University Press, New York, 2003.
[2] M. Ji et al., *J. Am. Chem. Soc.* **121**, 2631 (1999).
[3] N. Kometani et al., *Chem. Lett.* 682 (2000).
* harada@cc.nara-wu.ac.jp