

## In-situ observation of formation of Ag particles in water-in-scCO<sub>2</sub> emulsions

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### Introduction

Water-in-scCO<sub>2</sub> microemulsions have been used as "microreactors" for the synthesis of various metal particles [1-3]. Although many researches have been performed focusing on the synthesis of metal particles in water-in-scCO<sub>2</sub> microemulsions, there are a few reports that described the reduction process of metal ions and the formation of metal particles under high pressures. In this study we have synthesized Ag particles by the photoreduction and by the chemical reduction using hydrazine (H<sub>2</sub>NNH<sub>2</sub>) in the presence of AOT in water-in-scCO<sub>2</sub> emulsions and have investigated the average size of Ag particles by *in-situ* EXAFS measurements.

### Experimental

Ag particles 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 irradiation of Hg lamp. Water-in-scCO<sub>2</sub> emulsions containing AgClO<sub>4</sub> were prepared by adding CO<sub>2</sub> into the cell which contained a mixture of AgClO<sub>4</sub> 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. Metal concentration [Ag<sup>+</sup>] was fixed to 134 mM. The water-to-surfactant molar ratio (w) and water content was 1.37 and 2.32 wt% for photoreduction, and 2.74 and 4.64 wt% for chemical reduction, respectively. The cell was kept at 35°C and 25 MPa for at least 5 hours 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<sup>+</sup> ions and the formation of metallic Ag particles.

The *in-situ* EXAFS measurements were carried out at NW10A beam line in PF-AR. EXAFS spectra at Ag-K edge were collected to evaluate the electronic state and the coordination number of Ag particles. Data analysis was performed by REX2000 ver. 2.0.7 (Rigaku Co.).

### Results and Discussion

Fig. 1(a) shows the EXAFS oscillations of Ag solutions prepared by photo-irradiation. They do not remarkably change after the photo-irradiation. The spectrum before photo-irradiation is the same as that for an aqueous AgClO<sub>4</sub> solution (not shown in this manuscript). This behavior suggests that the reduction of Ag<sup>+</sup> is not

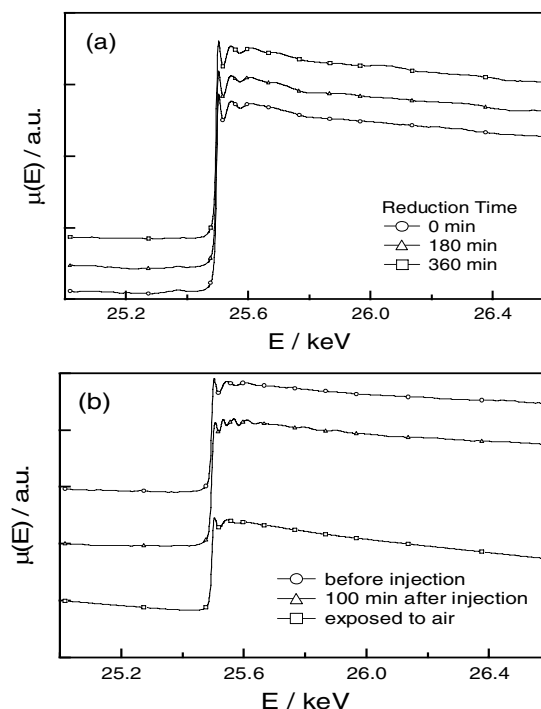


Fig. 1. X-ray absorption coefficient  $\mu(E)$  at the Ag-K edge for the Ag solutions prepared by (a) photoreduction with UV-irradiation and (b) chemical reduction with hydrazine.

completed after irradiation time of 360 min and a large amount of unreduced Ag<sup>+</sup> ions remains so that the spectral change is not enough to be detected. On the other hand, as shown in Fig. 1(b), EXAFS oscillations apparently change after the hydrazine injection. The spectrum for 100 min after injection possesses oscillations of metallic Ag foil, while the spectrum before injection looks like a spectrum of aqueous AgClO<sub>4</sub> solution. This confirms the creation of Ag-Ag bond and the subsequent formation of Ag particles. However, once the Ag particles under high pressure was subject to release under the ambient condition and exposed to air, the samples was transformed to the oxidized state and its spectrum changes from metallic-like to oxide-like characteristic of AgClO<sub>4</sub> compound.

### References

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