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EXAFS Studies of the Formation Mechanisms of Metal Clusters in Micelles of Surfactants

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Introduction

Colloidal dispersions of platinum and gold clusters are very active catalysts for hydrogenation or oxidation. The control of size and dispersity of metal clusters in colloidal dispersions is very important for improving the catalytic properties. Platinum and gold colloids are prepared by photo-reduction of $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$, respectively, in the presence of stabilizer such as polymers and surfactants [1]. The concentrated platinum and gold colloids are prepared in water/ethanol(1/1) solution dissolving water-soluble polymers [2], while the dilute platinum and gold colloids are prepared in aqueous surfactant solution with photo-activator. The aim of this study is the determination of the particle formation mechanisms in micelles of various surfactants as well as the change of average particle size in solution at the photo-reduction process.

Experimental

Concentrated platinum and gold colloids (9.65mM) were prepared from $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ by irradiation of 500W super-high-pressure mercury lamp in water/ethanol(1/1 v/v) solution dissolving poly(N-vinyl-2-pyrrolidone)(PVP). Dilute platinum and gold colloids (0.66mM) were also prepared by the same method in 100mM aqueous solution of surfactants (SDS: Sodium Dodecyl Sulfate, DTAC: Dodecyltrimethylammonium Chloride, PEG: Polyethylene Glycol Lauryl Ether) with benzoin, respectively. The reduced samples prepared in quartz cell at the designated duration of reduction were then poured into cells for EXAFS measurements.

Pt-L_3 and Au-L_3 edge EXAFS spectra were collected at the BL-10B and/or BL-12C. The EXAFS measurements of the concentrated colloids were carried out at room temperature in a transmission mode at BL-10B, while the measurements of the dilute colloids were performed in a fluorescence mode using a Lytle type detector at BL-12C.

Results and Discussion

Figure 1 shows the Pt-L_3 edge EXAFS Fourier transforms for the concentrated Pt colloids stabilized by PVP before photo-reduction, and after several minute's photo-reduction. For Pt ion solution (before reduction), the peak observed at 0.20 nm (phase shift uncorrected) is assigned to Pt-Cl bond with bond distance 0.232 nm. Increase of the reduction time causes decrease in intensity of the peak around 0.20 nm, and a new peak is simultaneously observed around 0.26 nm with the course of reduction time. These results indicate that disappearance of the Pt-Cl bond and development of the Pt-Pt bond concurrently occurred in PVP solution, and formation of Pt^0 particles with Pt-Pt bond of 0.276 nm.

On the other hand, the curve-fitting analysis of photo-reduced dilute Au colloids stabilized by SDS, DTAC, and PEG was conducted with the model parameters extracted from the reference compounds of Au foil and $HAuCl_4 \cdot 4H_2O$ solid powder. As for any surfactants, the Au-Au bond distance values for Au colloids coincided with the value of 0.287 nm for Au foil, but the coordination numbers (C.N.) were in the range of 6.0 – 8.1, that were apparently smaller than that (C.N. = 12) of Au foil. Thus, the Au colloids are strongly stabilized in micelles of surfactants in solution and become very stable, because the concentration (100mM) of surfactants (SDS, DTAC, and PEG) is significantly higher than their critical micelle concentration (cmc).

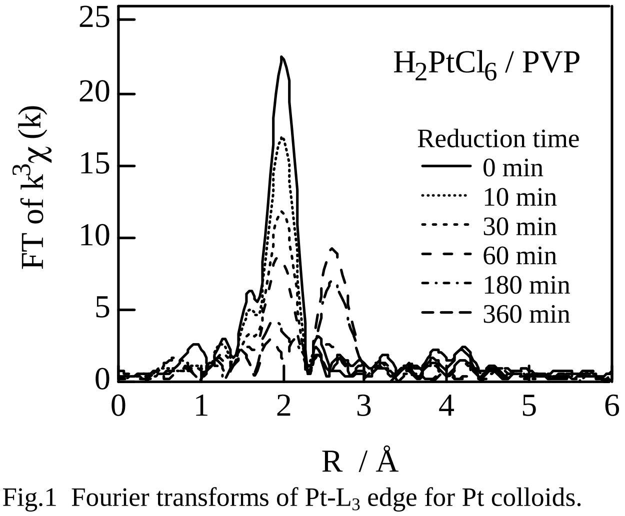

Fig.1 Fourier transforms of Pt-L_3 edge for Pt colloids.

References

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