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Structural analysis of Noble metal nanoparticles under supercritical conditions by means of EXAFS

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Introduction

Small metal particles of nanoscale are interesting materials academically and industrially, and the synthesis methods have widely been researched in order to make size-controlled particles. Among various methods, chemical reduction of metal ions using a polymer as a protective reagent is one of the promising ways to prepare small metal particles [1]. Previous application of the high-pressure and high-temperature system to synthesize small metal particles have been mainly limited the cases of metal oxide such as solvothermal reactions in supercritical water [2]. By using the high-temperature conditions of dense fluids which is not possible under ambient pressure, it may be possible to change the rate limiting process to create the nano-particles, which offers another possibility to control the particle size. In this study, we present the results of the synthesis in three different solvent fluids (water, ethanol, and mixture of water and ethanol) at high temperatures and high pressures, and the resulted colloidal dispersions in three different solvents show characteristic features.

Experimental

Concentrated platinum colloidal dispersions ([Pt]=30mM) were prepared from heating of the mixture of $H_2PtCl_6 \cdot 6H_2O$ and poly(N-vinyl-2-pyrrolidone)(PVP) solutions. The preparation conditions of temperature and pressure were 373-573 K and 25 MPa, respectively. Dilute platinum colloidal dispersions ([Pt]=3mM) were also prepared by the same method. The reduced samples were then poured into cells for EXAFS measurements.

Pt-L_3 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 obtained solutions of 1:1 mixture of 30 mM Pt/H_2O and 30 g/dm^3 PVP/C_2H_5OH at various temperatures and at 25 MPa. The solution prepared at 373 K shows the same peak position and intensity as the reactant solution, whose peak is assigned to the bond of Pt^+-Cl^-. With increasing the temperature to 423 K, the peak due to the bond of Pt^+-Cl^- vanishes and another peak increases due to the Pt-Pt bond. It is assured that no platinum dioxides are resident after the reduction at high-pressure and high-temperature(>423K). The coordination numbers of Pt atom around the Pt atom is 9.2 0.3, which is almost constant above 473 K, as shown in Table 1.

On the other hand, it is notable that there is a large effect of the solvent on the productivity and dispersity of Pt nano-particles under high temperature in Table 1.

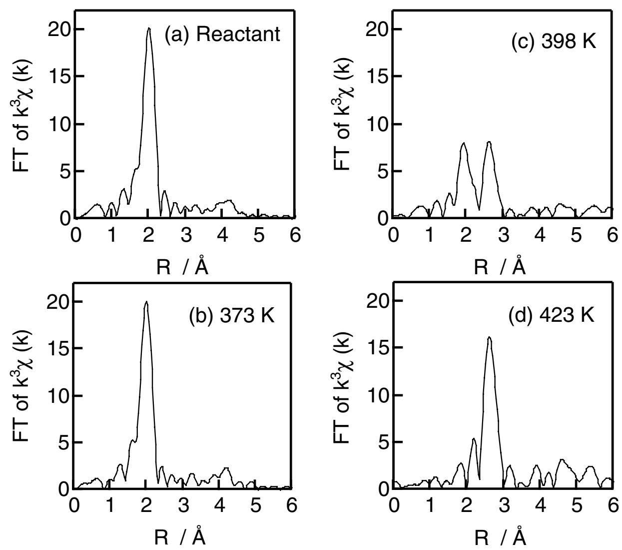

Fig.1 Fourier transforms of Pt-L_3 edge for Pt solutions created at different temperature and at 25 MPa.

Table 1. Curve-fitting results for Pt colloids

T (K)	Pt (mM)	PVP(g/dm^3)	Solvent	C. N.
423	30	30	1: 1	8.4
473				9.2
473	30	30	H_2O	8.0
473	7	3	EtOH	10.1

References

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