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Structural Analysis of Noble Metal Nanoparticles under Supercritical Conditions by means of EXAFS

Masafumi HARADA*[1], Yoshifumi KIMURA[2], and Daisuke ABE[3]
[1]Department of Textile and Apparel Science, Faculty of Human Life and Environment,
Nara Women's University, Nara 630-8506, Japan
[2]International Innovation Center, Kyoto University, Kyoto 606-8501, Japan
[3]Department of Chemistry, Graduate School of Science,
Kyoto University, Kyoto 606-8502, Japan

Introduction

The synthesis of nanometer scale metal-polymer composites is of crucial importance for realizing unique size-dependent optical, catalytic, magnetic, and electronic properties compared to their bulk counterparts, and can enhance a variety of technologies including coating, environmental, chemical processing, and sensing applications. The high-pressure and high-temperature systems to synthesize metal nanoparticles have been mainly limited the cases of metal oxide such as solvothermal reactions in supercritical water [1]. By using the high-temperature conditions of dense fluids which are not possible under ambient pressure, it may be possible to change the rate limiting process to create the nanoparticles, 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. The obtained rhodium colloidal dispersions in three different solvents have characteristic features.

Experimental

Rhodium colloidal dispersions were synthesized by passing solutions of mixture of $RhCl_3 \cdot 3H_2O$ and poly(N-vinyl-2-pyrrolidone)(PVP) through the high-temperature and high-pressure SUS cell. The preparation conditions of temperature and pressure were 343-573 K and 25 MPa, respectively. Three different solvents such as water, ethanol, and water/ethanol(1/1) were employed. The obtained samples were then poured into cells for EXAFS measurements, and Rh-K edge EXAFS spectra were collected at room temperature in a transmission mode at BL-10B to estimate the diameter of Rh particles.

Results and Discussion

Figure 1 shows the Rh-K edge EXAFS Fourier transforms for the obtained solutions of 1:1 mixture of 30 mM Rh/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 as the reactant solution, whose peak is assigned to the bond of Rh^+-Cl^-. With increasing the temperature up to 423 K, the peak due to the bond of Rh^+-Cl^- completely vanishes and another peak increases due to the bond of Rh-Rh. It is assured that no rhodium oxides are resident after the reduction at high-pressure and high-temperature (>423K). As shown in Table 1, the coordination numbers (C.N.) of Rh atom around the Rh atom is 10.5±0.8, which is almost constant above 473 K, and the particle diameter estimated from C.N. ranges between 3 and 4 nm.

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

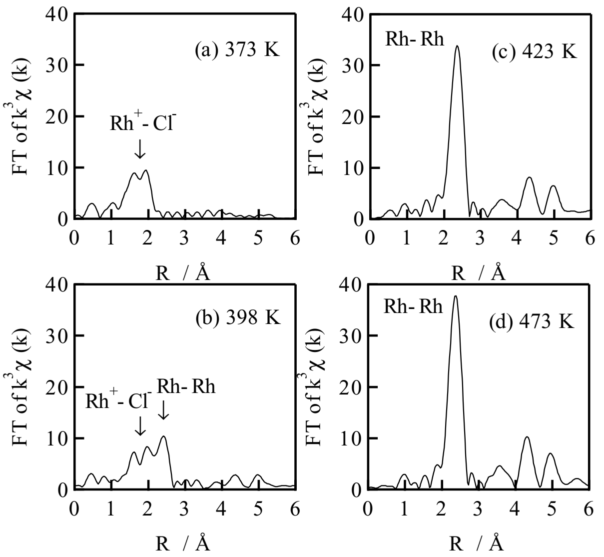

Fig. 1 Fourier transforms of Rh-K edge for Rh solutions created at different temperatures and at 25 MPa.

Table 1. Curve-fitting results of Rh colloidal dispersions

T (K)	Solvent	C. N.	Particle diameter(nm)
423	1: 1	8.9	2.0
473		10.5	3.6
533		10.0	3.0
473	H_2O	10.7	4.3
473	EtOH	8.3	1.6

References

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*harada@cc.nara-wu.ac.jp