

## Structural Analysis of Bimetallic Nanoparticles prepared in Sub- and Supercritical Fluids by means of EXAFS

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### Introduction

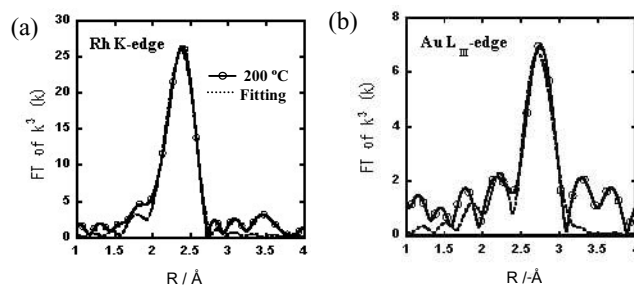
Small size particles of nanoscale have collected much attention from the view points of both science and industry due to their remarkable properties in catalytic, magnetic, and optical fields. Among various kinds of metals, gold (Au) is one of the most popular species under investigation. In this work, we will present the results of synthesizing small size of Au nanoparticles in the presence of Rh ions using a high-temperature and high-pressure reactor. Until now we have demonstrated that the thermal reduction of mixtures of noble metal ions such as platinum and rhodium ions under the high-temperature and high-pressure conditions produced fine nano-particles whose structure are different from those produced under the ambient condition[1,2]. Here we will demonstrate that this method produces a unique mixture of fine metal particles composed of gold and rhodium[3].

### Experimental

The colloidal dispersions of nanoparticles protected by PVP have been synthesized by flowing the solutions (1/1 volume mixture of water and ethanol) containing Au(III) ion or Au(III) and Rh(III) ions through the reactor at high-temperature and high-pressure in a few seconds (25MPa, 150–200 °C) by an HPLC pump. As sources of metal ions, sodium chloroauric acid(III) and rhodium chloride(III) were used. In the mixture solutions of ions, the mole fraction ratio of Au to Rh was 1. The total ionic concentration was 1.5 mM, and the concentration of PVP was 1.5 g dm<sup>-3</sup>. The obtained samples were condensed and then poured into cells for EXAFS measurements, and Au-L<sub>III</sub> and Rh-K edges' EXAFS spectra were collected at room temperature in a transmission mode at BL-10B and 9A.

### Results and Discussion

In the case of the solution containing Au ion only particles of nearly 50 nm were produced by our method according to the TEM observation. On the other hand, in the case of mixture solution of Au and Rh ions, two kinds of particles with obviously different sizes were produced. Relatively small particles (about 2.5 nm) are seen around larger particles (about 7.5 nm) gathering each other. Figure 1 shows the Fourier transforms of Rh K-edge and Au L<sub>III</sub>-edge of EXAFS spectra, respectively. Both absorption edges of the samples are almost successfully fitted to a single atomic species using the reference foils



**Figure 1.** Fourier transforms of EXAFS oscillations of nanoparticles produced by the reduction of both Au and Rh ionic solution with PVP at 25 MPa and 200 °C. The results of Rh K-edge and Au L<sub>III</sub> edge are shown in (a) and (b), respectively.

**Table 1.** Coordination numbers from EXAFS analysis of nanoparticles produced by the reduction of both Au and Rh ions in water and ethanol 1/1 mixture with PVP at 25 MPa and various temperatures.

Sample	Edge	Bond	Coordination Number	
			150 °C	200 °C
Au/Rh (1/1)	Au-L <sub>III</sub>	Au-Au	9.4 ± 2.9	8.9 ± 2.2
	Rh-K	Rh-Rh	6.6 ± 2.3	7.3 ± 2.5

while a little gap can be seen in the peak of 2.2 and 2.7 Å on Au L<sub>III</sub>-edge. This result indicates that the cluster unit of each nanoparticle is composed of almost single atomic species of Au or Rh, respectively. Table 1 shows the coordination number (C.N.) obtained from the fitting. From the average C.N., the particle sizes are around 1.0 nm for the Rh-K edge, while those from Au L<sub>III</sub>-edge around 2.0 nm, using the truncated octahedral structure model. Average size probed by EXAFS is known to be generally smaller than that of particles observed in the TEM image because it is attributed to the structure of a monocrystalline cluster unit which composes nanoparticles. From these results the smaller one is expected to be a Rh particle and the larger one to be an Au. Preliminary analysis of the bond-lengths using high resolution TEM images also supports this assignment. The detail analysis is now under way.

### References

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