EXAFS Study on Au-Pd Nanoparticles Prepared by Sonochemical Technique

Hiroe Takatani [1] (13421), Mioko Nakanishi [1] (13422), Ryoichi Taniguchi [1] (13461), Fuminobu Hori [1] (13436), Yasuo Nishihata [2] (1166), Jun'ichiro Mizuki [2] (302) and Akihiro Iwase [1,*] (5905)

1) Research Institute for Advanced Science and Technology, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai, Osaka 599-8570, Japan
2) Synchrotron Radiation Research Center, Japan Atomic Energy Research Institute, 1-1-1, Koto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

Au-Pd nanoparticles were sonochemically prepared by the simultaneous reduction of the aqueous solution containing Au^{3+} and Pd^{2+} ions with sodium dodecyl sulfate (SDS) or polyethylene glycol monostearate (PEG-MS). In case of SDS, Au-Pd nanoparticles exhibited core-shell structure consisting of Au-core and Pd-shell and showed higher catalytic activity than Pd nanoparticles. On the other hand, PEG-MS generated the mixture of core-shell and random alloy structured Au-Pd nanoparticles, which had inferior catalytic activity to Au/Pd/SDS. It is important to examine the structure of Pd-shell that dominates the catalysis. However the characterization is difficult due to the thin shell and poor crystallization. In this study, the local structures are examined by transmission and fluorescence EXAFS for Pd K-edge at SPring-8 BL14B1 station.

The Pd K-edge FT-EXAFS spectra for Pd foil, Pd nanoparticles, Au/Pd/SDS and Au/Pd/PEG-MS are shown in Fig.1. Transmission and fluorescence methods show basically the same tendency. The interatomic distance, R, of Pd nanoparticles increased by about 2.5% against Pd foil. The EXAFS spectrum of Au/Pd/SDS was analyzed with three-component model, Pd-Pd bond at Pd-shell, and Pd-Pd and Pd-Au bonds at the Au-core/Pd-shell interface. The R (Pd-Pd) was larger than that of Pd nanoparticles, probably resulting of the effect of Au-core with the larger lattice constant and the nano-order spherical form. In contrast, the analysis for Au/Pd/PEG-MS shows that they have both sides of core-shell and Au-Pd alloy structure. Two-component fitting of Pd-Pd and Pd-Au bonds shows that the R (Pd-Pd) is larger than that of Pd foil and nanoparticles, and is smaller than that of Au/Pd/SDS. Based on these results, the measurements such as in-situ EXAFS of the hydrogenation catalysis are in progress to evaluate the relationship between the core-shell structure and the catalytic activity in more detail.

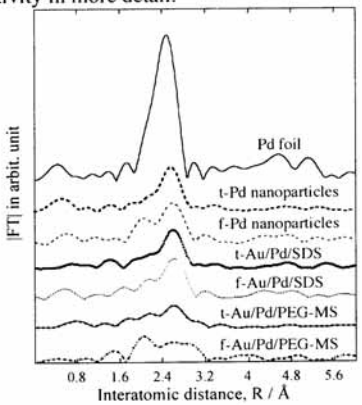

Fig. 1 Pd K-edge transmission (t-) and fluorescence (f-) FT-EXAFS spectra for several nanoparticles.

Changes in the structure of nanometer-sized silica particles at high pressures

Takashi UCHINO*[,a] (6864), Tomoko YAMADA[a] (13096), Atsuko ABOSHI[a] (13125), Yasuhiro INAMURA[b] (6622), and Yoshinori KATAYAMA[b] (1214)
[a] Department of Chemistry, Kobe University, Kobe, Hyogo 657-8501, Japan
[b] Spring-8, Japan Atomic Energy Research Institute, Sayo, Hyogo 679-5198, Japan

We have recently found that a densified transparent silica glass is prepared when the fumed silica (nanometer-sized amorphous silica powders) are compressed at ~8 GPa even at room temperatures [1]. As for normal bulk silica glass, permanent densification occurs only when the sample is pressed at pressures more than ~10 GPa. It is hence interesting to investigate why fumed silica shows such an elastic compression behavior at pressures lower than those observed for normal bulk silica glass. To clarify the point, in this work, we carried out *in situ* X-ray diffraction measurements on fumed silica with a cubic-anvil-type high-pressure apparatus installed at BL14B1.

We used a nonporous amorphous fumed silica (specific surface area = 390±40 m^2/g; particle size 7 nm) obtained from Sigma. The fumed silica sample is practically free of metal ions but has a number of surface OH groups. To remove these surface OH groups, the samples were preheated at 1000°C for 3 h. We measured energy dispersive X-ray diffraction spectra of fumed silica at 8 different scattering angles in the range $3^\circ<2\theta<16^\circ$ at pressures up to 7.4 GPa using white X-rays with energy of 20-170 keV. The diffraction data obtained at each 2θ were then combined and averaged to form a single structure factor $S(Q)$. Applied pressure was calibrated from the lattice constant of NaCl.

Figure 1 shows the X-ray structure factor of fumed silica as a function of applied pressure. At ambient conditions, our data are basically in agreement with those observed for normal silica glass. We found that the first sharp diffraction peak shifts from Q~1.52 to 1.93 $Å^{-1}$ with increasing pressures up to 7.4 GPa, whereas the peak at ~5.0 $Å^{-1}$ shifts to lower values of Q. Although similar changes in $S(Q)$ have been shown to occur in normal bulk silica glass under high pressures [2], we should note that the observed shifts are more obvious than those reported for normal bulk silica glass. Thus, the present results have shown that the structure of nanometer-sized silica particles is more vulnerable to change at elevated pressures as compared with that of normal bulk silica glass.

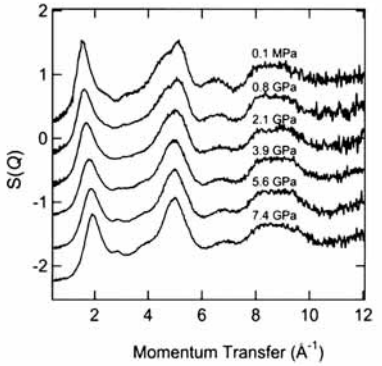

Fig. 1 Pressure dependence of $S(Q)$ measured for fumed silica between 0.1 MPa and 7.4 GPa.

References

[1] Uchino *et al.*, Phys. Rev. B **67**, 092202 (2003).
[2] Inamura *et al.*, SPring-8 User Exp. Rep. No. 10 (2002B) p. 44.