In Situ Observation of Hydrogen Absorption in Palladium Nanoparticles

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Introduction

High capacity of hydrogen absorption in palladium has been reported more than a hundred years before [1]. Much interest has focused on the hydrogen positions in face-centered cubic (fcc) lattice Pd as well as the amount to be absorbed in the metal. According to neutron diffraction data, hydrogen atoms occupy the octahedral interstices of the lattice Pd leading to the rock salt structure (β phase). The phase transition from the solid solution (α phase) of Pd and hydrogen to β phase takes place with accompanying apparent pressure hysteresis. Nanometer-sized particles show interesting chemical and physical properties which are different from bulk properties in many materials. Also for the nanoparticles of palladium there are drastic changes of the miscible gap in the hydrogen pressure-composition (PC) isothermal [2]. Therefore, Pd nanoparticles (NPs) are expected to show amazing hydrogen absorption properties. However, local structures of Pd nanoparticles on the hydrogen absorption/desorption process are not fully investigated. In this study, we have adopted Pd L_3-edge X-ray absorption fine structure showing the excitation of electrons from the $2p$ to the $4d$ band. Moreover, *in situ* observations of the electronic structure around Pd in nanoparticles have been performed in Pd-H system.

Methods

Nanoparticle (NP) samples were synthesized by chemical reduction method. Sodium tetrachloropalladate solution (Na_2PdCl_4) was added to L-ascorbic acid and Poly[N-vinily-2-pyrrolidone] solution. From transmission electron microscope observations of the synthesized samples, it was found that shapes of Pd nanoparticles were cube 10 nm on a side.

The Pd L_3-edge (3.1 keV) XANES were performed at BL06 of Kyushu synchrotron light research center (SAGA-LS) in Japan, using a double crystal monochromator with Si(111) crystals. The Pd NPs and the bulk Pd as a standard were mounted in a custom-designed *in situ* reaction cell. The spectra were recorded at 100 ˚C in fluorescence mode with using silicon drift detector. The hydrogen pressure could be controlled from in vacuum to 100 kPa. Experimental XANES results were analyzed by FEFF 9.0 calculations performed with the clusters of more than 100 atoms.

Results and Discussion

Pd L_3-edge XANES spectra of the bulk Pd dynamically changed as function of hydrogen pressure. In the process of increasing hydrogen pressure, the absorption edge is shifted to higher energy and a new feature (at 3180 eV) is appeared at 40 kPa. These behaviors show the change of Pd electronic structure due to hydrogen absorption. On the other hand, in the process of pressure down, the absorption edge shift goes back at the original energy positon and the new peak is disappeared at 20 kPa. The pressure is lower than that in the hydrogen pressure up process. The hysteresis behavior is in good agreement with previous results such as the PCT measurement and lattice parameter change observed by X-ray diffraction and neutron diffraction. In the case of Pd NPs, the Pd L_3-edge XANES spectra show similar hysteresis but transition pressures are different from those of bulk Pd.

Conclusions

We investigated the local structure in Pd nanoparticles with a focus on the hydrogen absorption by Pd L_3-edge XAFS. Depending on the pressure of hydrogen, the changes in the experimental spectra were observed and the behaviors were clearly different from those of the bulk Pd.

References

[1] T. Graham, Phil. Trans. R. Soc. Lond. 156, 399, (1866)
[2] M. Yamauchi, R. Ikeda, H. Kitagawa and M. Takata, J. Phys. Chem. C, 112, 3294, (2008)