Materials Science

12C/2003G088

XAFS study on sonochemically synthesized Au-Pd composite nanoparticles supported on γ-Fe_2O_3 nanoparticle

Hiroaki NITANI*[1], Takashi NAKAGAWA[1], Masato YUYA[1], Takahiro ONO[1], Shuichi EMURA[2], Satoshi SEINO[2], Kenji OKITSU[3], Yoshiteru MIZUKOSHI[4],Takao A. YAMAMOTO[1]
[1]Graduate School of Engineering, Osaka Univ., 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
[2]The Institute of Scientific and Industrial Research, Osaka Univ., Ibaraki, Osaka 567-0047, Japan
[3]Graduate School of Engineering, Osaka Pref. Univ., 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan
[4]Faculty of Engineering, Nagasaki Univ., 1-14 Bunkyo-machi, Nagasaki, Nagasaki 852-8521, Japan

Introduction

The nano-sized catalyst plays an important role in the fuel cell and many important processes such as those in the petrochemical industry because of its higher specific surface area, and therefore lower weight and cost. For developing more advanced catalytic material, a composite nanoparticle involving two or more material phases has been studied. Au-Pd bimetallic nanoparticle supported on γ-Fe_2O_3 nanoparticle is one of the most promising materials for new type of catalyst which has high catalytic activity and collectability by the use of magnet. We examined the substructure of the Au-Pd nanoparticles by the techniques of XAFS.

Experimental

An aqueous solution of 50 mL containing $HAuCl_4$, Na_2PdCl_4 (Au/Pd atomic ratio = 1:1) and commercial γ-Fe_2O_3 nanoparticle powder was prepared. The solution was irradiated at 20 °C for 1 hour by the ultrasonic wave of the frequency and power of 200 kHz and 200 W, respectively. The detailed explanation of the mechanism for the reduction of metal ions with the ultrasonic wave is described in the previous report [1]. Au-L_{III} XAFS measurements were performed. X-ray absorption spectra were obtained at the BL-12C beam line of KEK-PF. All the measurements were performed in air at room temperature in the transmission mode. Synchrotron radiation was monochromated by using an Si(111) crystal. Unwanted high harmonics were eliminated with a focusing Rh mirror. The intensities of incident and transmitted X-rays were measured with ionization chambers. The photon energy was calibrated with the first inflection point on the edge jumps of Au foil.

Results and Discussions

A typical XANES spectrum of the sample is shown in Fig. 1, together with those of reference materials, Au foil (metal) and Au_2O_3. It is clear that the spectrum features of the sample well agree with those of the metal reference. We conclude that Au exists in the metallic state in the sample. Figure 2 shows obtained RDF of the present sample, in which a split peak is noticed around 0.25 nm. Considering bond-lengths, this peak must reflect two bonds, Au-Au bond and Au-Pd bond. Then the theoretical fit was performed with the "FEFFIT" and "FEFF7" code assuming the single scattering path. The coordination numbers determined around Au atoms, $N_{Au\text{-}Au}$ = 10.2 and $N_{Au\text{-}Pd}$ = 1.4, significantly differ from each other. The interatomic distance between neighboring Au atoms, $R_{Au\text{-}Au}$ = 0.287 nm, well agrees with the Au-Au bond of bulk Au, 0.288 nm, whilst that from Au to Pd $R_{Au\text{-}Pd}$ = 0.281 nm differs from $R_{Au\text{-}Au}$. These results indicate that each Au atom is surrounded mainly by Au and a little by Pd. If the composite spherical nanoparticle of Au-Pd = 1:1 with 8.3-nm diameter (which determined from TEM observation) has a core-shell substructure, it is calculated to have an Au core with 6.6-nm diameter and a Pd shell with 0.86-nm thickness. Since the Au atoms at the core-shell interface are faced to coordinate not only to Au atoms but also to Pd atoms, the average coordination number, $N_{Au\text{-}Au}$, is smaller than the value, 12, in the fcc structure. Assuming the present size and composition of the present bimetallic nanoparticle, it was calculated as $N_{Au\text{-}Au}$ = 11.2, which reasonably agrees with $N_{Au\text{-}Au}$ = 10.2+2.6, determined by the present EXAFS analysis. The results of these structural analyses indicated that the nanoparticles supported on γ-Fe_2O_3 nanoparticles had a core-shell structure in which a thin Pd layer envelopes an Au particle.

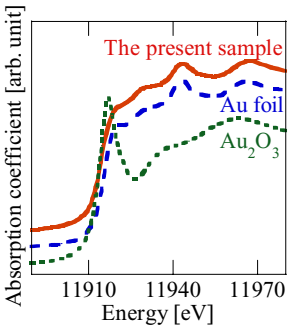

Fig. 1. Au-L_{III} edge XANES spectra of the sample and reference materials

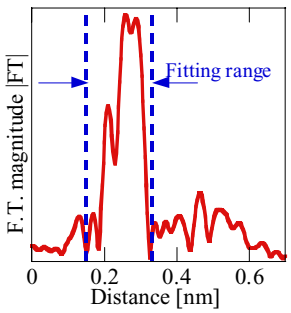

Fig. 2. RDF of the sample. The broken line shows the range of EXAFS fitting.

References

[1] Y. Mizukoshi et al., J. Phys. Chem. B 101, 7033 (1997).

* h-nitani@mit.eng.osaka-u.ac.jp