

EXAFS characterization of hydride formation in nanocrystalline Pd

Kazuyuki HASEGAWA¹, Hirofumi KANOH*¹, Takehisa KONISHI¹
 Yoshiyuki HATTORI¹, Tomonori OHBA¹, Katsumi KANEKO¹
¹Chiba Univ., Chiba, 386-8522, Japan

Introduction

Metallic palladium is known to present a very high catalytic activity toward a wide range of applications. Recent interest in metallic Pd may be attributed both their catalytic activities and to the fact that they represented a novel storage medium for H₂ storage. However, metallic Pd particles are not stable in air and both their recovery and recycling for H₂ storage are often difficult. Recently we have reported that stable nanoporous metallic Ni colloids are produced by the thermal decomposition of Ni doped poly(vinyl alcohol) (PVA) films [1]. Subsequently, we also obtained the nanocrystalline Pd by the thermal decomposition of Pd doped PVA films. The nanocrystalline Pd can adsorb and desorb H₂ at ambient temperature and pressure. In this report, the structural changes of nanocrystalline Pd responsible for the H₂ adsorption were discussed, and the changes in the structural parameters of Pd nanocrystalline were calculated by EXAFS analysis.

Experimental

The PVA films, whose thickness about 1 mm, were soaked in the saturated Pd(NO₃)₂/1M HNO₃ solution. Then, the films were washed with distilled water and were dried at room temperature. The films were calcined at 793 K for 10 h under N₂ gas flow. The thermal decomposition of Pd doped PVA films gave the resulting nanocrystalline Pd. The XAFS measurements were performed on Pd K-edge at BL-10B and AR-NW10A beam lines with transmission mode. The program code FEFF8 was used to calculate the theoretical phase and amplitude for curve fitting.

Results and discussion

Figure 1 shows the radial distribution functions (RSFs) calculated from EXAFS signals for the Pd foil, nanocrystalline Pd (nano-Pd), and H₂ adsorbed nanocrystalline Pd (nano-Pd-H). Although the RSF for nano-Pd is almost the same as that of Pd foil, the intensity of the peaks in the nano-Pd is much smaller than that in the Pd foil, suggesting the decrease in the amplitude of EXAFS signals related to the particle size and structural disordering. The structural parameters are calculated from EXAFS data by curve fitting the first peak of the RSFs and results are shown in Table 1. The Debye-Waller factor (σ) of the nano-Pd was larger than that of the Pd foil, suggesting the degradation of the structures in Pd clusters. The drastic decrease in the coordination number (N) of the Pd particles was also observed, owing to the formation of the very small clusters.

The RSF data for nano-Pd-H showed that the changes in the Pd-Pd distance were readily apparent from a comparison of peak positions in the RSF. The Pd-Pd distance (R) for the nano-Pd is 2.74 Å which is the same as that of the Pd foil. However, the Pd-Pd distance increased by 3.3% to 2.83 Å for nano-Pd-H. The σ value for nano-Pd-H was $7.97 \times 10^{-3} \text{ \AA}^2$ which was larger than that of nano-Pd ($7.05 \times 10^{-3} \text{ \AA}^2$). The relatively larger σ value for nano-Pd-H is indicative that the structural disordering was induced by H₂ adsorption. These results suggest that H₂ molecules are adsorbed into nanocrystalline Pd and that hydrogen atoms occupy the octahedral interstices of the Pd fcc lattice.

Table 1: The structural parameters of Pd foil, nano-Pd, and nano-Pd-H calculated from EXAFS signals.

	N	R (Å)	σ ($\times 10^{-3} \text{ \AA}^2$)
Pd foil	11.2	2.74	6.34
nano-Pd	7.1	2.74	7.05
nano-Pd-H	8.2	2.83	7.97

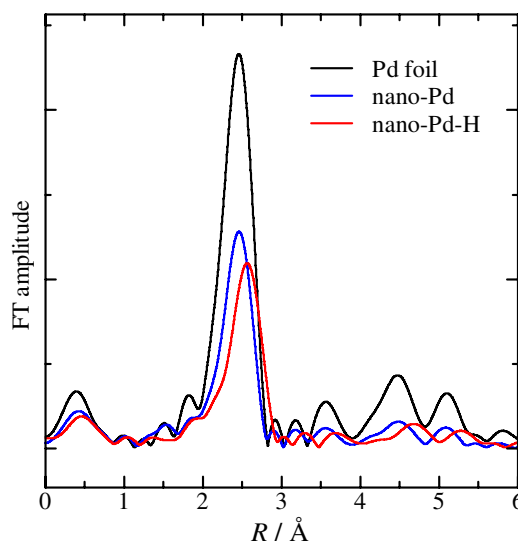


Figure 1 The RSFs of Pd foil, nano-Pd, and nano-Pd-H calculated from EXAFS signals.

References

[1] Y. Hattori et al., Adv. Mater. 15, 529 (2003).

* kanoh@pchem2.s.chiba-u.ac.jp