Hydrogen absorption behavior of Pd nanoparticles

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Abstract

We report the hydrogen absorption behavior of the Pd nanoparticles (Pd NPs) with the clean surfaces i.e. without the any surfactants or contaminations. The Pd NPs with the clean surface have been fabricated by the gas evaporation method using He gas. The hydrogen absorption property has been investigated by the noble technique. The P-C isotherms of the hydrogen absorption of the Pd NPs have been obtained using the QCM without the exposure to the air. The equilibrium pressure of the Pd NPs for the hydrogen absorption is ambiguous in comparison with that of the Pd bulk due to the large specific surface area of the Pd NPs. The hydrogen absorption amount of the Pd NPs is much smaller than that of the Pd bulk. This decrease of the hydrogen absorption amount can be attributed to the lattice expansion in the Pd NPs. We describe the brief future plan using Pd L₃-edge NEXAFS in the last section of this article.

1. Introduction

Palladium (Pd) has been most well-known hydrogen storage material more than a century. Remarkable points of hydrogen absorption property of Pd are the temperature and the stability of the repetition for the hydrogen absorption reaction. Most of metals require high temperature for the hydrogenation reaction more than 300 °C. On the other hand, Pd can absorb and desorb the hydrogen (H₂) less than the room temperature. The H₂ molecule dissociates into H atoms on the Pd surface. After the dissociation on the surface, the H atom can go thorough into octahedral interstitial site of the Pd bulk via the subsurface sites [1-6]. The Pd also shows good stability for the both hydrogen absorption and desorption reactions which means well repeatability of the reaction and resistance to the surface oxidation. These properties make the Pd is the ideal material for the investigation of the fundamentals of the hydrogenation reaction. Many researchers have studied the morphology, thermodynamics and kinetics of the H-Pd system using the low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS), electron energy loss spectroscopy (EELS), nuclear reaction analysis (NRA) and so on [1-6].

Nanoparticles (NPs) also capture many scientific attentions in recent years. The NPs exhibit anomalous features by the reduction of the size which leads the significant increase of the active surface sites and the lattice strain in the NPs [7,8]. The other favorable aspects are the kinetics and thermodynamics of the absorption/desorption of H₂. The short diffusion length of H atom improves the kinetics of the hydrogen absorption and desorption reactions. Furthermore, in the case of Mg, the desorption energy for MgH₂ cluster decreases with the reduction of the size of the cluster [9,10].

In spite of the many efforts for the understanding of the hydrogen absorption and desorption reactions of the NPs, the surface agents complicate the further investigations. The Pd NPs can be oxidized easily in even if under the ambient condition [11], whereas the Pd bulk has the good resistance against the air oxidation. The surfactants or polymers protect the surface of the Pd NPs in the previous studies [12-14]. These compounds inhibit the surface oxidation and also the surface reaction with H_2 .

In this study, we have investigated the H_2 absorption property of the Pd NPs without the air oxidation and the any surface agents. We show the difference of the hydrogen absorption behavior between bulk and NPs. The repeatability of the hydrogen absorption reveals the irreversibility of the hydrogenation reaction in the Pd NPs. The Pd NPs have been fabricated by the gas evaporation method using Helium (He) gas [11]. The clean surface of the Pd NPs can be established by the aggregation of the Pd atoms in the He gas. However, the amount of the Pd NPs is limited less than 100 µg. This limitation of the amount causes the difficulty in the measurements of the hydrogen absorption property of the Pd NPs. In

order to obtain the hydrogen absorption property of the Pd NPs, we have used the quartz crystal microbalance (QCM). The QCM has high sensitivity for the mass change on the surface of the quartz crystal less than 1 ng. Moreover, the QCM sensor head can be connected directly into the vacuum chamber, which enables us to obtain the hydrogen absorption property of the Pd NPs without the exposure of the samples to the ambient air.

2. Experimental

The Pd NPs were fabricated by the gas evaporation method using 50 Torr of the He gas (99.99995%). The Pd wire (99.95%) was used as the evaporation source. The Pd NPs were deposited on the quartz crystal. The diameters of the Pd NPs were evaluated by the transmission electron microscopy (TEM). Figure 1 shows the bright field image of the Pd NPs obtained by JEM-2500SE (200 kV, JEOL Co., Ltd.). The average diameters of the Pd NPs were evaluated to be 4.1 nm. The selected area electron diffraction (SAED) patterns indicate the fcc lattice of the Pd NPs. The ring patterns of the SAED for the both Pd NPs samples are smeared out because of the nano-sized effect.

The characterization of the H₂ absorption property of the Pd NPs was carried out by the acquisition of the pressure-composition isotherm (P-C isotherm) with the QCM. The QCM can detect the mass change by the frequency shift of the quartz crystal. The frequency changes not only mass loading but also the gas pressure, viscosity and roughness of the surface [15-18]. The frequency shift of the quartz crystal in the gas atmosphere (Δf) is expressed by

$\Delta f = \Delta f_{\rm m} + \Delta f_{\rm p} + \Delta f_{\eta} + \Delta f_{\rm r} + \Delta f_{\rm T}$

where $\Delta f_{\rm m}$ is the frequency shift by the mass loading, $\Delta f_{\rm p}$ is the frequency shift by the pressure of the gas, Δf_{η} is the frequency shift by the viscosity of the gas, $\Delta f_{\rm r}$ is the frequency



Fig. 1 TEM bright field image of the Pd NPs and the size ditribution. SAED of the Pd NPs is shown in the inset figure.

shift by the entrapped gas in the roughness on the surface and Δf_T is the frequency shift by the change of the temperature.

In order to estimate the mass change of the Pd NPs by the absorption of H₂, we have to except any other frequency shifts caused by the H₂ gas atmosphere. The Δf_p and Δf_η can be excluded by the subtraction of the frequency shift of the reference QCM from that of the QCM loaded with Pd NPs [17,18]. However, the Δf_r can not be excluded in this way due to the difference of the roughness between the two QCMs. Kulchytskyy *et al.* have suggested that the Δf_r can be excluded by the substitute frequency shift during the exposure to the He gas [18]. The density and viscosity of the He gas are quite similar with those of the H₂ gas. In this study, we have excluded the frequency shift due to the gas by the subtraction of the frequency shifts of the both reference QCM and substitute shift during the exposure to the He gas. The Pd NPs were deposited on the quartz crystal (6 MHz) coated with Au and the amount of the Pd NPs was 50 µg.

3. Results and Discussion

3.1 Hydrogen absorption properties of the Pd NPs

Figure 2 shows the P-C isotherms for the 1st hydrogen absorption of the Pd NPs at 303 K. The P-C isotherm of the Pd black in Ref. 14 is also shown for the comparison between bulk and NPs. The difference between bulk and NPs is seen in the shape of the P-C isotherms. The P-C isotherm of the Pd bulk shows the clear plateau region at ~20 Torr which is correspond to the pressure of the miscibility state of the Pd, whereas the clear plateau region can not be seen in the P-C isotherm of the Pd NPs. Instead of the bulk like



Fig. 2 P-C isotherms for the hydrogenation of the Pd NPs at 303 K. The P-C isotherm of the Pd black (Pd bulk) is shown as the reference [14].

plateau region, the isotherm of the Pd NPs shows the plateau-like region which has a slope and a narrow width.

This difference of the shape of the P-C isotherms between bulk and NPs can be attributed to the effect of the increase of the specific surface area. The hydrogen concentration in the low pressure is typically associated to the solution of the H atoms into the bulk (α -phase). In the case of the NPs, the adsorption of H atoms on the surface appears in the low pressure region. The higher hydrogen concentration for the Pd NPs in the α -phase represents higher adsorption amount on the Pd NPs surface compared with the bulk.

3.2 Repeatability of the hydrogen absorption of the Pd NPs

In addition to the comparison of the P-C isotherms between bulk and NPs, Figure 2 also shows the P-C isotherms of the 2nd hydrogen absorption of the Pd NPs at 303 K, which reveals the repeatability of the hydrogen absorption of the Pd NPs. The Pd NPs have been exposed to the only pure H₂ gas or vacuum after the fabrication, namely they have not been exposed to any gasses except for the H₂ gas. The hydrogen solubilities in the both α - and β -phases of the Pd NPs are reduced by the repeat of the hydrogen absorption, in spite of the Pd bulk shows the stable hydrogen absorption up to H/Pd=0.6 after the some hydrogen absorptions [13, 14]. The P-C isotherms of the Pd NPs shows the significant decrease of the hydrogen solubility in the α -phase after the 1st hydrogen absorption due to the strong binding for H atoms on the Pd surfaces and subsurfaces [1-6].

Furthermore, the shape of the P-C isotherm has dramatically changed by the repeat of the hydrogen absorption. The isotherm of the 2nd hydrogen absorption of the Pd NPs shows the bulk-like plateau region in contrast to the 1st hydrogen absorption of the Pd NPs. This result supports the former discussion i.e. the ambiguous plateau of the 1st hydrogen absorption of the Pd NPs is caused by the hydrogen adsorption on the surface and subsurface of the Pd NPs. The bulk-like plateau of the 2nd hydrogen absorption is caused by the stabilization of the hydrogen atoms at the bulk site in the crystal structure of the Pd NPs. This result indicates that the hydrogen concentration in the bulk site of Pd NPs (\sim 0.2) is extremely poor in comparison with that of the bulk (\sim 0.6).

The decrease of the hydrogen concentration can be attributed to the lattice strain in the Pd NPs [12-14,20,21]. The lattice expansion causes the increase of the site energy for H in the octahedral sites in Pd lattice [20, 21]. The higher pressure of the plateau region is obtained by the higher site energy. The increase of the pressure of the plateau results the decrease of the hydrogen concentration at 760 Torr, which implies that the concentration of H in the smaller NPs reaches to that for the bulk state by the high pressure of H₂. In this

study, the lattice expansion with the reduction of the size of the Pd NPs has been observed by SAED ring patterns in Figure 1. The lattice spacing for (111) of the Pd NPs (4.1 nm) expands by 0.02 Å compared with that of the Pd NPs (5.6 nm) [8]. This lattice expansion causes the decrease of the hydrogen concentration of the Pd NPs.

3.3 Future plan using NEXAFS analysis

For the further improvement of this study, the site-selective analysis of the hydrogen absorption is required. The conventional P-C isotherm analysis gives us the only the pressure position of the plateau and the concentration of the hydrogen. We can estimate the contributions of the adsorption or absorption sites to the P-C isotherm, however, we can not identify precisely the contribution of the each site. Our idea is acquisition of the P-C isotherm using NEXAFS analysis. Kubota *et al.* have reported the difference of the NEXAFS structure between the hydrogen absorbed and adsorbed Pd/SiO₂ samples [22]. We can distinguish the each contribution to the P-C isotherm by the measurements of the partial hydrogen pressure dependence of the Pd L_3 -edge NEXAFS. In this section, we report briefly the attempt of the acquisition of the P-C isotherm of the Pd thin film by the NEXAFS analysis as the first step of this challenge. Figure 3 shows the hydrogen pressure



Fig. 3 The partial H_2 gas pressure (P_{H^2}) dependence of the Pd L₃-edge NEXAFS for the Pd thin film. All spectra were normalized with the respect to the height of the edge jumps.



Fig. 4 Pd L_3 -edge NEXAFS spectra of the Pd thin films before, during and after hydrogenation reactions. The residual spectrum was obtained by the subtraction of the NEXAFS spectrum of the Pd thin film before hydrogenation from that of after hydrogenation.

dependence of the Pd L₃-edge NEXAFS spectra for the Pd thin film at the room temperature. The Pd thin film was deposited on the Au coated quartz crystal by the DC magnetron sputtering using Argon gas. The thickness of the Pd thin film was 65 nm. The NEXAFS spectrum of the Pd thin film before hydrogenation was obtained under 760 Torr of the He gas flow. The partial pressure of the H₂ gas was controlled by the mixture fraction of the dilute hydrogen gas (4 wt% in He) with the pure He gas. The NEXAFS spectrum changes gradually with the increase of the partial H₂ gas pressure. The new peak structure appears at 3181 eV under the dilute hydrogen gas atmosphere (P_{H2} =58.5 Torr) which is correspond to Pd-H antibonding state [22]. After substitution of the dilute hydrogen gas to the pure He gas, the peak at 3181 eV is disappeared and the shape of the NEXAFS changes back into the one before hydrogenation, however, not completely as shown in Figure 4. The main peak of the NEXAFS after hydrogenation locates at higher energy side compared with that of the NEXAFS before hydrogenation which implies the existence of the another chemical state in the Pd thin film after hydrogenation. In order to emphasize this chemical state, the NEXAFS of the Pd thin film before hydrogenation was subtracted from the one after hydrogenation not to vanish the intensity of NEXAFS spectrum less than zero. The residual spectrum corresponds to the chemical state of the hydrogen adsorbed Pd surface or subsurface. The fraction of the residual spectrum is quite low less than 10% due to the low specific surface area of the Pd thin film.

Figure 5 shows the comparison of the P-C isotherms obtained by XAFS and QCM for the Pd thin film. The NEXAFS spectra in Figure 3 were fitted with the linear combination fitting (LCF) of the NEXAFS of the Pd thin film before hydrogenation, fully hydrogenated and hydrogen adsorbed Pd. The partial H_2 gas pressure was plotted in Figure 5 as the



Fig. 5 P-C isotherms (PCI) for the hydrogenation of the Pd film obtained by NEXAFS and QCM.

function of the weight of the NEXAFS for the fully hydrogenated Pd thin film (PdHx). The zero point of the weight of the component of PdHx were adjusted with the intersections of the two extrapolations of α -phase and plateau region. In a similar way, the 1 of the weight of the PdHx were adjusted with the intersections of the two extrapolations of plateau region and β -phase. We have successfully obtained good correspondence of the P-C isotherm obtained by the NEXAFS with the one obtained by QCM.

4. Conclusions

We have investigated the hydrogen absorption property of the Pd NPs without the any surface contaminations. The reduction of the crystal size of the Pd causes the ambiguous equilibrium pressure of the miscible state because of the high specific surface area of the NPs. The surface and subsurface of the Pd NPs are saturated with H atoms by the 1st hydrogen adsorption. This stable adsorption of H atoms decreases of the concentration of H in the α -phase. The hydrogen concentration at the bulk site of the Pd NPs dramatically decreases in comparison with the Pd bulk due to the expansion of the lattice spacing and the consequent increase of the energy of the octahedral site in the Pd lattice. We have also shown the correspondence of the P-C isotherms obtained NEXAFS and QCM. We will identify precisely the contribution of the hydrogen absorption and adsorption in the P-C isotherm for the hydrogenation of the Pd NPs.

Acknowledgement

The authors are grateful for the financial support of the Grant-in-Aid for Scientific Research (B) (No. 26289255), the Grant-in-Aid for Research Activity start-up (No. 26889034) from the Japan Society for the Promotion of Science (JSPS) and the Nitto Foundation.

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