Hydrogen Storage Property of the Pd Nanoparticle with Clean Surfaces Studied by QCM*

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The hydrogen absorption behavior of the Pd NPs has been investigated by the noble techniques. The Pd NPs with the clean surface have been fabricated by the gas evaporation method. The P-C isotherm of the hydrogen absorption of the Pd NPs has been obtained using the QCM without the exposure to the air. The P-C isotherms have shown the clear size dependent absorption behavior for the Pd NPs. Further absorption and desorption cycles decrease the solubility of H significantly in the Pd NPs. [DOI: 10.1380/ejsnt.2015.343]

Keywords: Palladium; Nano-particles; Hydrogen storage material; Quartz crystal microbalance (QCM); Gas evaporation method

I. INTRODUCTION

Palladium (Pd) is attractive material for many scientific fields such as catalytic chemistry and surface science because of the high surface activity. Especially, Pd plays an important role in the hydrogen energy technology. Pd can absorb and desorb the hydrogen (H_2) reversibly at the room temperature, although the other metals require high temperature for the hydrogenation reaction. The H_2 molecule dissociates into H atoms on the Pd surface. The H atoms are bound strongly at the hollow sites of the Pd surface even if at the room temperature [1-6]. After the adsorption on the surface, the H atom can penetrate into octahedral interstitial site of the Pd bulk via the subsurface sites. The Pd is the ideal material for the investigation of the fundamentals of the hydrogenation because of the high reactivity and the resistance against the oxidation. Many researchers have studied the morphology, thermodynamics and kinetics of the H-Pd system for more than three decades by 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 attract many scientific attentions in recent years. The NPs exhibit anomalous features

as the results of the reduction of the size which leads the significant increase of the active surface sites (edge, corner, ...) and the lattice strain in the NPs [7,8]. The other favorable aspects can be found out in the kinetics and thermodynamics of the absorption/desorption of H_2 . The short diffusion length of H atom improves the kinetics of the hydrogenation of the NPs. Furthermore, in the case of Mg, the desorption energy for MgH_2 cluster decreases with the reduction of the size of the cluster [9,10].

In spite of the many efforts for the understanding of the hydro-/dehydrogenation reactions of the NPs, the surface contaminations complicate the further investigations. The Pd NPs can be oxidized in even if under the ambient condition [11], whereas the Pd bulk possesses the good resistance against the oxidation. The surfactants or polymers protect the surface of the Pd NPs in the previous works [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 surface oxidation, the any surfactants and the polymers. We have focused on the size dependence and the repeatability of the hydrogen absorption. 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 obtained by the aggregation of the Pd atoms under the He gas atmosphere. However, the mass of the Pd NPs is limited less than 100 μg . This limitation of the mass of the sample causes the difficulty in the characterization of the Pd NPs. In order to obtain the H_2 absorption property of the Pd NPs, we

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FIG. 1. The schematic view of the formation of the Pd NPs by the gas evaporation method.

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 fabrication chamber of the Pd NPs, which enables us to observe the H_2 absorption property of the Pd NPs without the exposure of the samples to the air.

II. EXPERIMENTAL

The Pd NPs were fabricated by the gas evaporation method using 6.7 kPa of the He gas. The Figure 1 shows the schematic view of the formation of the Pd NPs. The Pd twisted pair wire (purity: 99.95%, diameter of the single wire: 0.3 mm ϕ) was used as the evaporation source. The size of the Pd NPs was controlled by the electrical power at the Pd source, i.e. the larger Pd NPs were able to be obtained with the high amount of the evaporated Pd atoms. The Pd NPs were deposited on the quartz crystal or the Nickel (Ni) polycrystalline substrate for the surface chemical analysis by the X-ray photoelectron spectroscopy (XPS).

The diameters of the Pd NPs were evaluated by the transmission electron microscopy (TEM) observation. Figure 2 shows the bright field image of the two types of the Pd NPs obtained by JEM-2500SE (200 kV, JEOL Co., Ltd.). The average diameters of the Pd NPs were 4.1 nm and 5.6 nm, respectively. 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 XPS measurement of the as-fabricated Pd NPs was carried out after the evacuation of the He gas to $\sim 7 \times 10^{-5}$ Pa. The Pd NPs on the Ni substrate were transported to the XPS analysis chamber via the vacuum path. The Mg K α X-ray was used as the excitation source. The kinetic energy of the photoelectron was measured by the concentric hemispherical analyzer (CHA, Phoibos-100, SPECS GmbH) with channeltron detectors (5 ch). The base pres-

FIG. 2. TEM bright field images, SAED patterns and the size distributions of (A) the Pd NPs (4.1 nm) and (B) the Pd NPs (5.6 nm). The average diameters and the standard deviations are also shown.

sure of the XPS analysis chamber was 7×10^{-8} Pa.

The characterization of the H_2 absorption property of the Pd NPs was established 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. 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

$$\Delta f = \Delta f_m + \Delta f_p + \Delta f_\eta + \Delta f_r + \Delta f_T \quad (1)$$

where Δf_m is the frequency shift by the mass loading, Δf_p is the frequency shift by the pressure of the gas, Δf_η is the frequency shift by the viscosity of the gas, Δf_r is the frequency 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 H_2 , we have to except any other frequency shifts caused by the H_2 gas atmosphere. The Δf_p and Δf_η can be excluded by the subtraction of the frequency shift of the reference QCM (shown in Fig. 1) 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. Kulchyt-sky 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 H_2 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 QCM sensor heads were set into the fabrication chamber of NPs as shown in Fig. 1. The Pd NPs were deposited on the quartz crystal (6 MHz) coated with Au and the amount of the Pd NPs was more than 30 μ g.

FIG. 3. Pd3d XPS spectrum of the Pd NPs (5.6 nm) and Pd bulk.

FIG. 4. The P-C isotherms for the hydrogen absorption of the Pd NPs at 303 K.

III. RESULTS AND DISCUSSIONS

A. Surface chemical analysis by XPS

Figure 3 shows the Pd3d XPS spectra of the Pd NPs (5.6 nm) and the Pd bulk. The spectrum of the Pd bulk was obtained using the Pd sheet (purity: 99.95%) cleaned by Ar^+ ion sputtering. The spectrum of the Pd NPs represents clearly the metallic state without any other chemical states such as the oxide. This result means that the surface of the Pd NPs can not be oxidized in the high vacuum. The slight chemical shift toward the lower binding energy side can be attributed to the extra atomic relaxation which is so-called “final state effect” [19].

B. The size dependence of the hydrogen absorption property of the Pd NPs

Figure 4 shows the P-C isotherms for the 1st H_2 exposure to the Pd NPs at 303 K. The size dependence of the H_2 absorption property can be seen clearly in the concentration of H. The reduction of the size of the Pd NPs causes the decrease of the hydrogen concentration at 760 Torr. The hydrogen concentration of the Pd NPs (5.6 nm) reaches to that of the Pd bulk ($\text{H}/\text{Pd}=0.7$). On the other hand, the P-C isotherm of the Pd NPs (4.1 nm) shows the hydrogen concentration less than 0.4.

The size dependence is also seen in the shape of the P-C isotherms. The P-C isotherm of the Pd NPs (5.6 nm)

shows the plateau region at ~ 15 Torr which is correspond to the pressure of the miscibility state of the Pd bulk, whereas the clear plateau region can not be seen in the P-C isotherm of the Pd NPs (4.1 nm). Instead of the bulk like plateau region, the isotherm of the Pd NPs (4.1 nm) shows the plateau-like region which has a slope and a narrow width.

These size dependencies 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 H_2 . Furthermore, the broadening of the site energy distribution is caused by the lattice strain. The slope of the plateau-like region in the P-C isotherm of the smaller Pd NPs is associated to the broad site energy distribution in the Pd lattice. 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 2. 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 size dependence in the P-C isotherm of the Pd NPs.

In addition to the lattice strain, the effect of the increase of the specific surface area can be seen in Figure 4. The increase of the hydrogen concentration in the low pressure is 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 smaller Pd NPs in the α -phase represents higher adsorption amount on the Pd NPs surface compared with the larger one.

C. The repeatability of the hydrogen absorption of the Pd NPs

Figure 5 shows the P-C isotherms of the repetitive hydrogen exposure to the Pd NPs at 303 K. The Pd NPs have been exposed to the only H_2 gas or vacuum after the fabrication, namely they have not been exposed to any gasses except for the pure H_2 . The hydrogen solubilities in the both α - and β -phases (hydride state) 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 $\text{H}/\text{Pd}=0.7$ after the some hydrogen absorptions as shown in Refs. 13 and 14. The P-C isotherms of the Pd NPs (4.1 nm) 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]. The isotherm of the 2nd hydrogen absorption of the Pd NPs (4.1 nm) shows the bulk-like plateau region at ~ 15 Torr. The decrease of the hydrogen solubility in the α -phase is also shown in the P-C isotherm of the Pd NPs (5.6 nm). The amount of the loss of the solubility in the α -phase after the 1st hydrogen absorption is less than that of the smaller Pd NPs because of the difference of the specific surface area. On

FIG. 5. The P-C isotherms for the repetitive hydrogen absorption of (a) the Pd NPs (4.1 nm) and (b) the Pd NPs (5.6 nm) at 303 K.

the contrary, the solubility in the β -phase decreases remarkably by the hydrogen absorption. This result means that the history of the hydrogen absorption remains in the Pd NPs and decreases the solubility in β -phase. We speculate that the lattice spacing has been expanded by the repeat of the hydrogen absorption [13,14,20-22]. The lattice expansion leads the increase of the interstitial site energy for the occupancy of the H atoms and the decrease of the solubility in the β -phase.

IV. CONCLUSIONS

In conclusion, we have investigated the hydrogen absorption property of the Pd NPs without the any surface contaminations. Especially, we have focused on the size dependence and the repeatability of the hydrogen absorption of the Pd NPs. The reduction of the size of the Pd NPs leads the increase of the equilibrium pressure of

the miscible state because of the expansion of the lattice spacing and the consequent increase of the energy of the octahedral site in the Pd lattice. The surface and sub-surface 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. It is speculated in this study that the repetitive hydrogen absorption causes the decrease of the solubility of the β -phase due to the increase of the interstitial site energy.

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