

Journal of Alloys and Compounds 389 (2005) 234-242

Journal of ALLOYS AND COMPOUNDS

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# Hydrogen storage in spherical and platelet palladium nanoparticles

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Received 6 May 2004; accepted 8 June 2004

#### Abstract

The PdH<sub>x</sub> system is used to investigate possible benefits of hydrogen storage in nanoparticulate matter. Particles of different morphology (platelets/tabular or spherical) were synthesized with minimum dimension in the 4–10 nm range via reverse and bilayer-micellular techniques. High specific surface area (SSA ~ 40–80 m<sup>2</sup>/g) was obtained for all Pd samples studied. For most particles, it was found that the SSA can only be maintained if processing or H-adsorption temperatures did not exceed  $T \sim 50-100$  °C. The isothermal hydrogen uptake (to 10 bar) of the nanoparticles was measured gravimetrically at 50 °C and compared with that of bulk powders (~micron grain Pd). It was noticed that the nanoparticulate isotherm plateaus ( $\alpha + \beta$ -phases) were not as flat, or as wide, as in the bulk. Several samples were observed to store 10–20% more than the bulk at 10 bar, suggesting that surface and subsurface sites in nanoparticulate matter provide an additional and significant set of adsorption sites. In fact, using the width of the  $\alpha + \beta$  plateau as a measure of the normal bulk (octahedral, O) site concentration, we can estimate that many of the nanoparticulate samples studied exhibit a larger fraction of subsurface sites than bulk-like O-sites. Post-synthesis hydrazine washing has been observed to be a crucial factor in enhancing the hydrogen uptake performance of the nanomaterials studied—a marked improvement in the washed samples over the unwashed ones suggests a possible removal of some of the disadvantageous organics from the sample surfaces.

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Keywords: Palladium; Hydrogen storage; Micellular synthesis; Isotherms; Subsurface sites

# 1. Introduction

The Palladium–Hydrogen system is one of the most widely and thoroughly investigated bulk metal–hydrogen systems studied to date, mainly because of the availability of pure samples and the fact that no special surface treatments of the bulk samples are required [1,2]. Palladium belongs to the second transition metal series, with 10 electrons in the 4d electron shell and exhibits high magnetic susceptibility and high electronic specific heat, since its electronic density of states at the Fermi level is the highest of any pure metal. Experimental and theoretical investigations have proved that in transition metals like Pd, the electron accompanying the proton of the dissociated hydrogen atom enters the s- and d-bands of the host metal, changing the density of states at the Fermi surface and causing shifts of the energy bands [3]. These electronic reactions produce both short-range and long-range interactions between the electronic species. Besides bringing about changes in local and global electronic structure of the host metal, hydrogen also induces changes in the cohesive forces between atoms in the host matrix, as evidenced by several theoretical investigations [4,5]. Neutron diffraction studies in various metal-hydrogen systems have shown that hydrogen occupies interstitial sites in the metal lattice. This process causes the nearest-neighbor metal atoms to move farther apart from each other, causing an increase in the nearest-neighbor separation between atoms. In palladium, the lowest energy sites that are occupied by hydrogen are the interstitial sites with octahedral symmetry [6]. However, as all the octahedral interstitials are progressively filled by hydrogen, a 'spill-over' occurs as hydrogen occu-

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 $<sup>0925\</sup>text{-}8388/\$$  – see front matter M 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2004.06.105

pies the next higher energy tetrahedral interstitials, driven by a higher molecular gas fugacity, which is in turn governed by the higher gas pressure.

We report here, on the synthesis, characterization and hydrogen adsorption studies of nanoparticulates of palladium, prepared in spherical and platelet morphology. The results of our hydrogen adsorption studies are also compared with results on bulk Pd and nanocrystalline Pd. It should be emphasized that the investigations carried out here have been on weakly coupled nanoparticles of Pd, as contrasted with nanocrystalline materials that have been previously investigated [7,8,10–16].

# 1.1. Why can 'nano' be better for hydrogen storage?

Nanocrystalline materials have already been shown to have distinct differences in their hydrogen uptake characteristics when compared with their bulk counterparts. Rapid H-diffusion has been reported to take place along the grain boundaries in nanocrystalline materials, improving the kinetics for H-adsorption and desorption. Nanoparticulates (or loosely aggregated nanoparticles), on the other hand, can exhibit characteristic benefits of their own. First, small nanoparticles have been reported to exhibit dilated lattices that would result in larger interstitial volumes for hydrogen storage (and possibly, lower the H-binding energy). This could result in better storage characteristics. Second, nanoparticulates may offer a new set of surface and subsurface adsorption sites. Neutron scattering studies [17] have revealed that hydrogen occupies surface region sites in nanomaterials, in addition to the regular interstitial and grain boundary sites. Third, the characteristic hydrogen ion diffusion length is automatically reduced to the nanoparticle radius, or the minimum dimension for tabular particles. This would, of course, result in faster kinetics for hydrogen adsorption/desorption. Fourth, nanoparticulates are distinctly more resistant to hydrogen-induced morphological changes such as hydrogen-induced decrepitation, hydrogen-induced amorphization [18,19], etc. Fifth and finally, nanoparticle heterostructures can be designed to optimize hydrogen storage performance, i.e., core-shell structures and added hydrogenpermeable passivation coatings, etc. are possible.

Recent hydrogen adsorption studies on nanocrystalline palladium [7] have shown that the amount of hydrogen uptake in nanocrystalline PdH<sub>x</sub> is higher than that for the bulk material in the solid solution region of the isotherms (i.e., x < 0.1 for the  $\alpha$ -phase). However, in the hydride phase region ( $\beta$ -phase), the maximum hydrogen concentration was observed to be significantly lower than that observed in bulk materials. Mutschele and Kirchheim [8,9] proposed an explanation that the increase in the  $\alpha$ -phase H concentration [H]<sub> $\alpha$ </sub> was due to an increase in the hydrogen solubility at the grain boundaries and the decrease in the  $\beta$ -phase concentration [H]<sub> $\beta$ </sub> was attributed to the fact that the significant grain boundary regions do not transform to the  $\beta$ -phase. However, Eastman et al. [10] carried out in situ X-ray diffraction studies that showed that the entire nanocrystalline Pd sample is converted into the B-phase on hydriding. Small angle neutron scattering studies by Sanders et al. [11] have suggested that this behavior (increase in  $[H]_{\alpha}$  and decrease in  $[H]_{\beta}$ ) is attributed to the occupancy of hydrogen in the surface of the grains contacting the voids. In addition, a significant decrease in the 'miscibility gap' (width of the plateau region) of the isotherms has been explained based on hydrogen occupancy at the surface and subsurface sites [14,15]. This has also been verified through Monte-Carlo simulations of the pressure-composition isotherms of nanometer-sized palladium clusters on hydrogen loading [12]. Proton spin-lattice relaxation times  $T_1$  (determined though NMR measurements) and magnetic susceptibility  $\chi$  results in nanocrystalline Pd hydrides indicate an inhomogeneous distribution of hydrogen in the lattice with most of the hydrogen appearing to occupy the grain boundaries. The  $\alpha$ - $\beta$  phase mixture in the plateau region of the isotherm is reflected in the anomalous behavior of the proton spin-lattice relaxation time  $T_1$  [13]. From experimental volumetric pressure-composition studies on nanoscale clusters of Pd, Pundt et al. [14] and Sachs et al. [15] have postulated that the observed enhancement in hydrogen solubility in the solid solution region of the isotherms is due to the presence of additional subsurface sites for hydrogen occupancy. Similarly, recent work on nanocrystalline magnesium has shown that the kinetics of hydrogen uptake is significantly faster in nanocrystalline materials, when compared with the bulk [16].

# 2. Experimental details

All chemicals used in this study were reagent grade. Palladium nitrate hydrate (Aldrich Chemical Co.) was used as the palladium source. Igepal CO-520 (Rhodia Chemical), cyclohexane (Aldrich Chemical Co.), octylamine (OA) (99%, Aldrich Chemical Co.), amylamine (AA) (99% Aldrich Chemical Co.), ethanol (Pharmco), palladium (purity 99.9%+, 1–1.5  $\mu$  Aldrich Chemical Co.), and hydrazine hydrate (Aldrich Chemical Co.) were all used as received. De-ionized water was used for all synthesis.

# 2.1. Reverse micelle synthesis of spherical nanoparticles

Micelles were prepared using a procedure similar to that of Li et al. [20]. Poly(oxyethylene)nonylphenyl ether (Igepal CO-520) and cyclohexane are mixed, and the prescribed volume of 0.04 M aqueous Pd(NO<sub>3</sub>)<sub>2</sub> is added to form the reverse micelle phase. The particle size was controlled by varying the ratio R = [water]/[surfactant]. The solution was rapidly stirred and equilibrated for 1 h. Hydrazine hydrate was added to reduce the Pd<sup>2+</sup> to Pd metal, as the solution was stirred rapidly for 5 min. After 20 h of equilibration, a volume of ethanol, equal to the volume of cyclohexane was added to the solution to decompose the reverse micelle. The black product was allowed to settle and the clear solution was decanted and discarded. Ethanol and a small amount of hydrazine hydrate (to reduce any PdO that might be present) were again added to ensure that all Igepal CO-520 was removed. This wash process was repeated four times and the sample was allowed to dry in air.

# 2.2. Lamellar bilayer synthesis of platelets

Lamellar bilayers were prepared using a procedure similar to that of Yener et al. [21]. Octylamine, amylamine and 0.04 M aqueous  $Pd^{2+}$ , as the nitride, were used to form the lamellar bilayer phases. Surfactant octylamine and cosurfactant amylamine were added in a weight ratio of 25:1, respectively. It has been shown by Adair et al. [22] that bilayers based on octylamine resulted in inorganic (CdS or Ag) platelets with poorly defined edges. Anisotropically shaped clusters were also produced. To prevent the formation of an anisotropically shaped cluster, amylamine was added to increase the amount of hydrophobic functional groups and tail groups, thereby increasing the amphiphilicity [23] and increasing the thermodynamic phase stability.

To a solution of octylamine and amylamine, the prescribed volume of aqueous Pd<sup>2+</sup> was added. After mechanical agitation for 5 min, the solutions were allowed to equilibrate for 1 h. Hydrazine hydrate was then added and the solution agitated. After equilibrating for 20h in ethanol, a volume of ethanol equal to the volume of octylamine was added to decompose the bilayer. The resulting black powder was allowed to settle and the clear solution was decanted. Ethanol was again added to ensure that all organics were removed. This wash process was repeated four times and the sample was allowed to dry in air. Morphologies of the resultant particles are dependent on the ratio R = [water]/[surfactant]. Utilizing the phase diagram for octylamine and water [24], the synthesis conditions were chosen to produce the desired morphologies. In the lamellar bilayer phase region (at 25 °C, R < 10.7 but R > 3.5) platelets were produced, and their thickness and face size being determined by R. Regions outside of the lamellar phase region (at 25 °C, R < 16 but R > 10.7) gave samples of mixed morphologies, consisting of both platelets and spheres. Polarized light microscopy was used to verify that the birefringement bilayer phase was present when desired.

## 2.3. Other sample characterization

Powder X-ray patterns were obtained using a Sintage diffractometer using Cu K $\alpha$  radiation (of wavelength 1.5418 Å) and a Peltier-cooled detector. Samples were placed on quartz zero-background slides. Electron micrographs were obtained using a Phillips 420 transmission electron microscope (TEM) and a JOEL 2010F HRTEM. Energy-dispersive spectroscopy (EDS) was carried out using the Phillips TEM. Samples for TEM were dispersed in ethanol and deposited on Fomvar supported Cu grids. Platelet dimensions were determined by atomic force microscopy (AFM) (MultiMode, Digital instruments) using the tapping mode. Samples for AFM were prepared by placing a drop of sample dispersed in ethanol onto atomically flat, freshly cleaved mica. Specific surface area (SSA) measurements (N<sub>2</sub>-BET) were carried out using a Micromeritic Gemini. The fractions of PdO, organics, water, etc., on the nanoparticle surface were determined by thermogravimetric analysis (TGA) in flowing O<sub>2</sub> (TGA: TA Instruments SDT 2960).

## 2.4. Hydrogen uptake measurements

Isotherms of hydrogen uptake were measured gravimetrically on 40 mg samples using a high-pressure thermogravimetric analyzer (TGA Model #003 Hiden Inc.). Measurements were made primarily at 50 °C and in the pressure range 0-10 bar. The weight uptake data were corrected for buoyancy of the gas at all pressures. Ultra-high purity hydrogen gas (99.999% purity) was used for the uptake studies. Vacuum decontamination of the sample reactor and the adjoining pipe-work was carried out before and after each sample run to ensure that the system was free from traces of gaseous impurities. To ensure that the admitted hydrogen gas was free from oxygen and trace impurities, the hydrogen gas was passed through an oxygen/moisture trap (Megasorb Gas Purifier, Supelco Inc.), before being admitted into the sample reactor. The uptake isotherms for bulk palladium (purity 99.9%+, supplied by Aldrich) were verified using the instrument and the results were found to be in good agreement with reported results in literature [1].

#### 3. Results and discussion

#### 3.1. Material characterization

Following the synthesis and washing, all palladium nanoparticles were black, free-flowing powder. Powder Xray diffraction (XRD) showed a crystalline Pd phase for all morphologies (Fig. 1). XRD of the spherical particles synthesized by means of reverse micelle approach initially showed crystalline PdO as a minor constituent. However, upon washing with hydrazine hydrate, only pure crystalline Pd was ob-



Fig. 1. Powder X-ray diffraction of nano-Pd sample #2-65-10. The X-ray diffraction pattern of the sample matches that of standard Pd *h k l*'s are given.

Table 1 Selected data for nano-Pd samples studied for hydrogen uptake properties

Sample	R	Pd (%)	$d (\mathrm{nm})^{\mathrm{b}}$	$a  (nm)^c$	$t (\mathrm{nm})^{\mathrm{d}}$	η
Reverse micelle						
2-35 Spherical	2	95.34	4			1.05
2-71 Spherical	8	96.34	5			1.04
Bilayer						
2-65-7 Platelet	7	94.69		82	1.3	1.06
2-65-10 <sup>a</sup> Mixed	10	87.26		109	1.5	1.15
				327	2.8	
3-18 Platelet	8	96.80		70	2.0	1.03

R = [water]/[surfactant] and  $\eta = Pd$  weight correction factor determined by TGA and used in H-adsorption analysis.

<sup>a</sup> Mixture of both spherical and platelet morphology particles, with platelet particles having dimensions in the range ( $109 \text{ nm} \times 1.5 \text{ nm}$ ) to ( $327 \text{ nm} \times 2.8 \text{ nm}$ ).

<sup>b</sup> Diameter of spherical particle.

<sup>c</sup> Face size of platelet particle.

<sup>d</sup> Thickness of platelet particle.

served in the XRD. Particle sizes for spherical particles were determined from line broadening using Scherrer's equation (Table 1), and they were confirmed by TEM studies.

AFM, in the tapping mode, was used to obtain details on the platelet thickness and face size. The samples were dispersed in ethanol and a small drop placed on freshly cleaved mica. Two-dimensional images of the samples are shown in Fig. 2. Through an examination of the Z-axis profile (Z-scans in Fig. 2b), both the face size (*a*) and thickness (*t*) can be determined. The aspect ratio (A = a/t, where *a* is the particle diameter and *t* is the platelet thickness) in the range  $30 \le A \le 100$  was obtained with values of *t*,  $1 \le t \le 3$  nm (Table 1).

TEM images (Fig. 3) of the platelet faces were found to be in good agreement with the AFM results. Initially, all platelet samples on the Cu TEM grids were highly agglomerated and surrounded by organic byproducts. However, when the electron beam heated the particles, the residual organics apparently volatilized or reacted, breaking up the agglomerates and nicely dispersing the platelets in the field of view. EDX of individual platelets was conducted and re-confirmed the formation of nanoplatelet Pd (Fig. 4).

In some cases, TEM images of samples synthesized by the bilayer approach exhibited a mix of platelet and spherical morphologies; these are referred to here as the "hybrid" morphology. N<sub>2</sub>-BET experiments on the hybrid samples showed that they exhibit more tolerance to loss of BET surface area upon heating. Results of these observations will appear elsewhere [25]. Particle sizes of the spherical particles produced by reverse micelle were determined by HRTEM (Fig. 5). The mean particle size observed from TEM studies is consistent with results from XRD line broadening. Lattice fringes can be observed in some of the particles, consistent with their single crystal nature. From Fig. 5, it can also be observed that sintering between particles is minimal.



Fig. 2. Atomic force microscopy of sample #2-65-7 primarily containing Pd platelets. Part (a) shows a  $2 \mu m \times 2 \mu m$  area image taken in the tapping mode. In (b), we identify a smaller region of the image in (a) containing  $\sim$ 8 particles. The solid line in (b) is analyzed in (c) to determine the aspect ratio for a single platelet. The thickness (1 nm) and the diameter (80 nm) can be determined through examination of the Z-axis.



Fig. 3. TEM of platelet palladium particles (sample #3-18) synthesized by lamellar bilayer technique.

The N<sub>2</sub>-BET SSA versus temperature/time studies were done under vacuum (30 m Torr) to determine the characteristic sintering temperature for the Pd nanoparticles, as marked by a sudden loss in BET SSA. The nanoparticulate samples were successively heated from room temperature to 200 °C in 50 °C increments, and maintained at each temperature for the various times indicated. The samples were then cooled and SSA measurements were carried out. For spherical particles synthesized by the reverse micelle method, the SSA remains constant at a temperature of 50 °C for 32 h. Upon heating to 100 °C and holding for 15 min, the surface area dropped from 80 to  $10 \text{ m}^2$ /g. Bilayer-synthesized samples were found to be noticeably more robust against sintering, e.g., the SSA remains constant for 25 h at 150 °C, and then decreases less rapidly with time on increasing the sample temperature to 200 °C for 2 h. From these studies, we developed a protocol for activation in hydrogen in the high pressure TGA, i.e., all samples were heated only to 50 °C for 6 h in vacuum to remove residual organics, as the low temperature was required to retain the SSA (an exception



Fig. 4. Energy-dispersive X-ray spectroscopy of the nano-Pd platelet sample #3-18 shown in the inset. The elements Cu and C are both present in the carbon-coated copper grid.



Fig. 5. HRTEM of spherical particles synthesis by reverse micelle technique. Lattice fringes show that the particles are crystalline in nature. It can also be observed that sintering between particles is minimal.

was sample #NPd 3-18, which was heated to  $150 \degree C$  for 6 h).

Thermogravimetric analysis of our nanoparticulate samples in flowing  $O_2$  was carried out to determine the percentage of Pd in the sample (Fig. 6). The materials have large SSA and therefore, surface oxides and residual organics can be significant components of the sample mass not involved in hydrogen storage. Washing with hydrazine resulted in samples containing 90–96% Pd, the balance being surface contaminants. SSA values for these samples range from 50 to  $80 \text{ m}^2/\text{g}$ . The results of a typical TGA analysis in flowing  $O_2$  are presented in Fig. 6. The samples were heated slowly to



Fig. 6. TGA of platelet sample #3-33. Initial weight of sample was 9.7621 mg (A). The weight is observed to decrease slowly on heating to a temperature of  $\sim 200 \,^{\circ}$ C, above which the weight is observed to increase, probably due to the formation of PdO. At  $\sim 800 \,^{\circ}$ C, weight loss was again seen leaving pure Pd 9.219 mg (B) at 1000  $^{\circ}$ C. Sample is 94.4% Pd.

1000 °C in O<sub>2</sub> (7 °C/min). At 200 °C, all volatile organic byproducts were removed, and at ~300 °C the Pd is oxidized to PdO [26], increasing the mass, as shown in the figure. As the sample temperature reaches 850 °C, the PdO is spontaneously reduced to Pd. Above 850 °C, pyrolyzed carbons are removed as CO. We conclude that, at 1000 °C, the sample is primarily pure Pd. The TGA data proved to be a valuable tool to determine the weight fraction of Pd in these high SSA materials. The ratio between the initial and final weight of the sample in the TGA was used as a correction factor ( $\eta$ ) in hydrogen uptake studies to adjust the H-uptake data to the true Pd content (Table 1). The correction factor was typically ~1.03–1.06.

# 3.2. Hydrogen uptake studies

Since the Pd nanoparticles studied exhibit a loss in surface area on heat treatment above 100 °C (with the exception of some platelet and hybrid morphology Pd nanoparticulates), all hydrogen uptake isotherms were recorded at a temperature of 50 °C after outgassing in vacuum at 50 °C for 1–2 h. This degassing was done in situ in the TGA, followed by isothermal adsorption data collection.

#### 3.2.1. Nanoparticles with spherical morphology

Fig. 7A shows the pressure-composition isotherms of the spherical and the platelet samples with the pressure axis plotted on a logarithmic scale. Fig. 7B shows the low-pressure data in the pressure interval 0–800 mbar with the pressure axis on a linear scale. The hydrogen adsorption isotherms



Fig. 7. (A) Hydrogen uptake isotherms for the nanoparticle samples compared with that for bulk Pd sample in the pressure range 0-10 bar (pressure axis on log scale): (a) bulk Pd, (b) spherical nano-Pd 2-35-2 (4 nm), (c) spherical nano-Pd 2-71-8 (5 nm), (d) platelet nano-Pd 3-18 (70 nm × 2 nm), (e) platelet nano-Pd 2-65-7 (90 nm × 1.15 nm) and (f) hybrid nano-Pd 2-65-10 (109 nm × 1.5 nm). (B) Hydrogen uptake isotherms in the low-pressure region (0–800 mbar) with pressure axis on a linear scale for the nanoparticle samples compared with that for bulk Pd sample (a). The letters (a)–(f) identifying the samples have the same meanings as in (A).

recorded using our TGA show excellent reproducibility. The desorption isotherms for nano-Pd exhibited non-repeatable hysteresis effects that are not understood. This behavior was not observed for bulk Pd.

The hydrogen adsorption pressure-composition isotherms for our nano-Pd materials (Fig. 7) show the general features expected for bulk palladium [1]. That is, all the isotherms show three distinct regions, which in the bulk have been identified with the  $\alpha$ -phase (indicated by the dash-dotted line curve (a)—the solid solution phase), the  $(\alpha + \beta)$ -phase (indicated by the dashed curve (a)-the constant pressure twophase region) that marks the miscibility gap, and finally at the highest pressures, the  $\beta$ - or the hydride-phase, indicated by the dotted curve (a). In particular, the hydrogen adsorption isotherms for the nanoparticles with spherical morphology show the following distinct characteristics: (i) The hydrogen solubility in the  $\alpha$ -phase region (solid solution region) of the isotherms appears to be enhanced significantly when compared with that in bulk Pd [27]. (ii) The plateau region of the isotherm (the constant pressure two-phase field) acquires a positive slope and is considerably narrowed when compared

with that of bulk Pd. The total weight percent uptake at the highest pressure of 10 bar for the spherical nanopowders is less than that for the bulk Pd sample. However, the platelet morphology particles are observed to store more than the bulk (see the following). (iii) We note that the pressures  $P_{\alpha}$  and  $P_{\beta}$  in curve (a) marking respectively the roll-over and the upturn in the isotherm, appear to depend on the particle morphology (spherical or platelet).

As mentioned earlier, the experimental findings of large hydrogen solubility in the solid solution region of nanoscale clusters of Pd [14,15] have been attributed to hydrogen occupancy in subsurface sites in addition to the occupancy in interior octahedral sites in the lattice. The considerable increase in surface area of these materials can open up a large fraction of surface region sites for hydrogen occupancy. For estimates of the fraction of these sites in our samples, see Table 2. These sites supplement the regularly available octahedral sites within the bulk (bulk sites). Besides theoretical modeling studies, experimental investigations by various groups [28-32] employing thermal desorption spectroscopy (TDS) and electron energy loss spectroscopy (EELS) techniques have yielded strong evidence in support of the existence of surface and subsurface sites, with binding energies lower than those for the octahedral interstitial sites. These investigations also indicate that hydrogen has a greater tendency to enter and leave subsurface sites at lower temperatures than surface sites. These results imply that subsurface sites play a more important role in hydriding-dehydriding than surface sites. Previous reports have shown that subsurface sites have distinctly lower energies than the regular bulk sites and hence, offer a distinct potential energy minimum for hydrogen occupancy.

Srivastava and Balasubramaniam [33] have conducted modeling of hydrogen solubility and metal-hydrogen interactions in Pd clusters using statistical thermodynamics and a two-site model of hydrogen occupancy. They neglect the interactions between the hydrogen atoms in the metal. Their calculations have demonstrated the feasibility of Fermi-Dirac statistics in modeling metal-hydrogen interactions and they have shown that the subsurface site energies are lower than the regular (interior) octahedral site energies. Furthermore, they have found that the subsurface sites are preferentially occupied by hydrogen in clusters when compared with the situation in bulk Pd.

In our work, we investigate the hydrogen storage properties of spherical and platelet Pd nanoparticles. Therefore, the conclusions from the reported work on clusters [14,15,33] on preferential occupancy of subsurface sites in nanosized Pd clusters might be expected to apply to our larger nanoparticles. In fact, we also conclude that the enhanced hydrogen solubility in the  $\alpha$ -phase of the isotherms for our nanoparticles is due to preferential occupancy of hydrogen in the subsurface sites.

In bulk Pd, a transition from the  $\alpha$ -phase (solid solution region) to the two-phase plateau field occurs after hydrogen occupies all the available potential energy minima sites

Table 2 Estimates of the fraction of subsurface sites available in the nano-Pd samples

Pd nanoparticle studied	Estimated fraction of bulk-like sites $[x_2 - x_1]_{nano}/[x_2 - x_1]_{bulk}$ (%)	Estimated fraction of subsurface sites (%)
Spherical nano-Pd (2-35-2) (~4 nm)	31	69
Spherical nano-Pd (2-71-8) (~5 nm)	32	68
Platelet nano-Pd (3-18) ( $\sim$ 70 nm $\times$ 2 nm)	55	45
Platelet nano-Pd (2-65-7) ( $\sim$ 82 nm $\times$ 13 nm)	60	40
Hybrid nano-Pd (2-65-10) (~109 nm × 1.5 nm)	51	49

(bulk octahedral sites) to form a solid solution with the metal. Since the site energy of the subsurface sites available in Pd nanoparticles is clearly less than that of the bulk sites, it can be assumed that hydrogen occupying the subsurface sites does not result in the formation of a hydride phase. Furthermore, the upper boundaries of the plateau regions in the uptake isotherms for the Pd nanoparticle and the bulk are located at similar pressures, indicating that the energies of the bulk-like interior sites in all the nanoparticles are of comparable magnitude. Based on the above assumptions, a naive calculation of the fraction of the subsurface sites available for hydrogen occupancy can be carried out from the knowledge of hydrogen concentrations that define the boundaries of the plateau region (two-phase field), as suggested by Sachs et al. [15] for Pd clusters.

If we denote the hydrogen concentration x in PdH<sub>x</sub> at the beginning of the plateau region as  $x_1$  (the highest concentration at which the  $\alpha$  (solid solution)-phase alone is present), and the hydrogen concentration at the end of the plateau region as  $x_2$  (the lowest hydrogen concentration at which the ( $\alpha + \beta$ )-phase is present), the fraction of the number of subsurface sites  $N_{\text{subsurface}}$  to the total number of sites  $N_{\text{total}}$ , available in the nanoparticles can be approximated by the relation:

$$\frac{N_{\text{subsurface}}}{N_{\text{total}}} = 1 - \frac{[x_2 - x_1]_{\text{nano}}}{[x_2 - x_1]_{\text{bulk}}}$$
(1)

We use Eq. (1) as a relationship to quantify the changes in the plateau (two-phase field) brought about by the nanoparticle morphology. From (1), for the spherical nanoparticles, it is seen that the fraction of subsurface sites is quite high  $(\sim 70\%)$ . The fact that the subsurface sites outnumber the bulk-like sites and that the subsurface sites have significantly lower site energies when compared with the bulk sites is consistent with the pronounced increase in the  $\alpha$ -phase hydrogen concentrations in the nanoparticles studied. As such, it is probable that the onset of the two-phase field (nucleation of the hydride- or  $\beta$ -phase) proceeds mostly through the occupancy of a relatively smaller number of interior bulk-like sites in the case of the particles. This explains the narrowing of the miscibility gap (length of the plateau). The filling of the core bulk sites then occurs once all the subsurface sites have been saturated. The above arguments also support the observation that the values of  $x_{2(nano)}$  shift towards lower values in the spherical particles, as compared with the situation in bulk Pd.

The positive slope of the nanoparticle isotherm may indicate a distribution in binding energies of the core sites (the lower energy sites being filled up at lower pressure). From pressure-composition isotherm measurements and lattice gas model calculations carried out on Ti–H and Ti<sub>94</sub>Al<sub>6</sub>–H systems, Naito et al. [34] have explained the occurrence of sloping plateaus on the basis of a distribution in the binding energy of the sites occupied by hydrogen atoms in metals. Measurements carried out by Sachs et al. [15] on free clusters of Pd with a narrow size distribution also show a significant positive slope, although they do not associate this with the width of the cluster size distribution.

#### 3.2.2. Particles with platelet and hybrid morphology

The isotherms for samples with platelet morphology (Fig. 7) exhibit different behavior when compared with the spherical particles. One platelet sample  $[70 \text{ nm} \times 2 \text{ nm}]$ (#NPd 3-18)] shows a behavior similar to that of the spherical nanoparticles. However, another platelet sample  $[82 \text{ nm} \times 1.5 \text{ nm} \text{ (sample #NPd 2-65-7)}]$  shows an upshift of the entire (narrow) miscibility gap to higher concentrations (x). This behavior is also seen in hybrid sample #NPd2-65-10 (material comprising of both spherical and platelet nanoparticles). The significant shift in the value of  $x_{1(nano)}$ that is observed (Fig. 7(A)) in hybrid morphology samples can be attributed to the quenching of the surface sites by residual organics in the sample. However, further work would be needed to substantiate this argument. Changes in particle morphology could result in changes in the fraction of energetically favorable subsurface sites as well as the hydrogen solubility in these sites due to changes in chemical potential. Post-synthesis heat treatments of the platelet and hybrid morphology samples revealed a  $\sim 10\%$  increase in surface area with increasing temperature (not found in spherical morphology samples), even when heated from room temperature to 50 °C. Of course, an increase in surface area is expected to bring about an increase in the fractional population of surface and subsurface sites. Based on the above arguments, we propose that the significant increase in hydrogen solubility in the  $\alpha$ -phase and the significant upshift in the narrowed plateau region and  $x_{2(nano)}$  in platelet Pd are probably due to the combined effects of changes in the particle morphology as well as surface area of the particles. Similar effects have been reported from isotherm measurements on 5 nm clusters of Pd by Sachs et al. [15].

# 4. Summary and conclusions

Crystalline palladium nanoparticles have been synthesized with spherical platelet and mixed sphere platelet hybrid morphology. The nanoparticles have been characterized for their structure through powder X-ray diffraction, for their surface area behavior with temperature through BET surface area measurements, and for their morphology through TEM and AFM techniques. The increase in uptake of hydrogen by the Pd nanoparticles in the solid solution region of the isotherms and the decrease in the width of the miscibility gap, relative to bulk Pd, are attributed to the preferential occupancy of hydrogen in surface and subsurface sites at lower pressures. The positive slope of the plateau in the isotherms has been identified with a distribution of site energies, in the case of the Pd nanoparticles.

# Acknowledgements

The authors would like to acknowledge Honda R&D, Japan, for supporting this program of research. They gratefully thank J. Fujiwara, H. Goto and T. Furuta for many stimulating discussions during the course of this work.

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