Hydrogen/deuterium absorption capacity of Pd nanomaterials and its relation with heat generated upon loading of hydrogen isotope gases

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Abstract: Using Sievert's method, hydrogen/deuterium absorption capacity was measured for Pd nanopowder and nanocomposites of nanoPd/γ Al_2O_3 and nanoPd/ZrO_2. For these materials, heat evolution upon loading of hydrogen isotope gases was also measured by a flow calorimeter. In order to identify the properties of metallic Pd nanoparticles, both measurements were conducted repeatedly three or four times without exposing the samples to air. It was found that both apparent absorption capacity and heat evolution depended strongly on the degree of oxidation of Pd. The amount of the oxidized Pd in each sample was estimated from the difference between the apparent and the true values of hydrogen/deuterium absorption capacity and used to evaluate the heat generated from chemical reactions. The hydrogen absorption capacity at 1MPa was found to be slightly smaller than that of Pd bulk for all the Pd nanomaterials studied. The heat evolution was composed of two stages, i.e., the first stage during pressurizing the samples from 0 to 1MPa and the second stage where the the sample was kept under a fixed pressure of 1MPa. The heat generated in the first stage was largely explained by taking into account two chemical reactions, i.e., the water formation reaction and the hydride/deuteride formation reaction. It was noted that in the second stage, where the heat generated from chemical reactions was hardly expected to occur, a small heat power was observed intermittently when the samples were loaded with deuterium gas.

Keywords: condensed matter nuclear reaction**,** Pd nanoparticles, hydrogen isotope gases, absorption capacity, heat evolution, gas loading

1. Introduction

Arata and Zhang have recently reported that by simply loading nanocomposites of Pd/ZrO_2 or Pd/Ni/ZrO_2 with deuterium gas, they have observed a heat generated from a deuteron-deuteron (D-D) nuclear fusion reaction [1]. The D-D nuclear fusion reaction has been suggested from the observation of a remarkable increase of ^{4}He in the gas sampled from the powder sample after the loading experiments [1]. It has been expected that nano-sized Pd particles absorb enough deuterium atoms to induce the nuclear fusion reaction. Actually, for the nanoPd/ZrO_2 system, a very high value of hydrogen absorption capacity has been reported [2].

Kitamura et al. have constructed a twin type flow calorimeter to evaluate qualitatively the heat generated by loading of Pd/ZrO_2 nanocomposite with hydrogen isotope gases, and have observed anomalously large energies of hydrogen isotope gas absorption as well as large D/Pd and H/Pd ratios of about 1.1 [3]. They have also observed a significant difference in the heat power between deuterium and hydrogen after the finish of deuteride or hydride formation reaction at the early stage of the gas loading.

In this study, the relationships between the size of Pd particles, the absorption capacity of hydrogen (/deuterium), and the heat generation upon loading of hydrogen isotope gases were investigated for nanomaterials of Pd ; nanopowder of Pd [4] and nanocomposites of Pd/γAl_2O_3 [4] and Pd/ZrO_2 [5]. The hydrogen/deuterium absorption capacity was measured with the Sievert's method [6]. The heat power generated upon pressurizing the materials with hydrogen isotope gases was measured with a flow calorimeter. In order to examine the influence of oxidized Pd on absorption capacity and heat evolution, both of these properties were measured three to four times repeatedly, without exposing the samples to air. Prior to each measurement, the samples were heat treated in vacuum in order to remove the absorbed molecules or to eliminate completely the hydrogen or deuterium absorbed in the preceding measurement.

2. Experimental

2. 1. Materials

The materials used in this study were: Pd nanopowder (^{TM}AY4030) obtained from Tanaka Kikinzoku Kogyo with average Pd particle size 10 ~ 20nm; Pd-γAl_2O_3 composites with Pd concentrations of 13 and 20wt% with average Pd particle size 2~5nm; 30wt%Pd/ZrO_2 composites obtained from Santoku Corporation with average Pd particle size ~10nm. Foils of Pd 0.1mm thick with purity 99.95% were used as a reference sample of Pd bulk.

2.2. Hydrogen storage capacity

A pressure-composition (PC) isotherm apparatus (Suzuki Shokan Co. Ltd) was used to measure hydrogen absorption capacity as a function of pressure up to about 1MPa at room temperature (300K). The purity of hydrogen and deuterium was 99.99999% and 99.995%, respectively.

2.3. Calorimetry

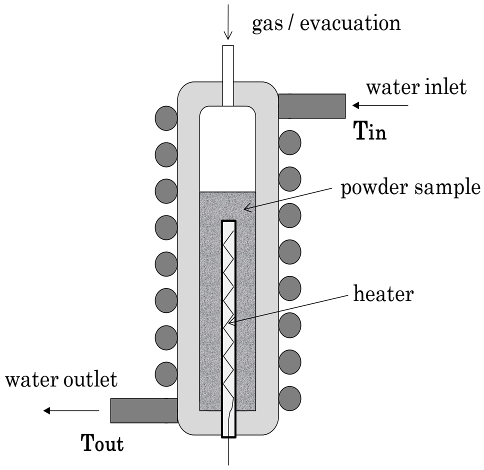

Figure 1. Schematics of the calorimeter [4].

The heat evolution associated with loading of hydrogen isotope gases was measured with a flow calorimeter [4]. Figure 1 shows the schematics. The difference in the temperature between the inlet (T_{in}) and outlet (T_{out}) of the cooling water was measured with thermocouples of alumel-chromel. The flow rate of water was measured using a Coriolis-force type flow meter. The temperature difference, $T_{out} - T_{in}$, and the flow rate of water were registered every 30 seconds and used to calculate the heat power. An electric heater was mounted at the center of the sample vessel and used to determine the recovery rate of heat, i.e. the ratio of the calculated heat power with the measured temperature difference and the flow rate of water to the heat power supplied by the electric heater. A value of 0.55 was used as the recovery rate [4], which was almost independent on the species of the used gas (H_2, D_2, He), the gas pressure in the range 0 ~1 MPa, and the electric heater power in the range of 1~5W. In order to suppress the fluctuation and the drift of the measured output power, the calorimeter system was thermally insulated from the ambient atmosphere using a thermal insulation material. The accuracy of the calorimeter was ± 50mW. The gases were supplied into the sample vessel through a needle valve and a mass flow controller. The flow rate of gas was about 20ml/min.

3. Results and discussion

3. 1. Hydrogen absorption capacity

As a reference for Pd bulk, PC isotherms were measured for a Pd foil sample of about 3g. The measurements were made three times repeatedly. Prior to each measurement, the sample was heat treated in vacuum for more than 2 hours at 523K and was subjected to the PC isotherm measurement without exposing the sample to the air. The results are shown in Figure 2.

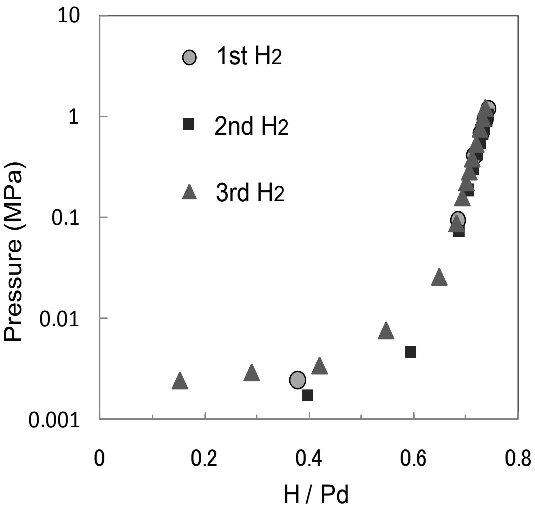

Figure 2. PC isotherms for the foil sample of Pd. The measurements were made 3 times repeatedly at 300K.

It is seen that the curves of the three times measurements are almost identical. The absorption capacity, H/Pd, at 1MPa is 0.74, which agrees well with the value for Pd bulk reported in the literature [7].

In Figure 3, the PC isotherms are shown for the nanocomposite sample of 20wt%Pd/γAl_2O_3. The measurements were made 3 times repeatedly with H_2. In this figure, it is remarkable that the H/Pd value at 1MPa for the measurement of the first time, i.e. 2.4, is much larger than the values for the measurements of the second (0.68) or the third (0.70) times. This difference between the first and second measurements is definitely attributed to oxidized Pd, i.e. PdO, which is often contained in nano-sized Pd materials [4].

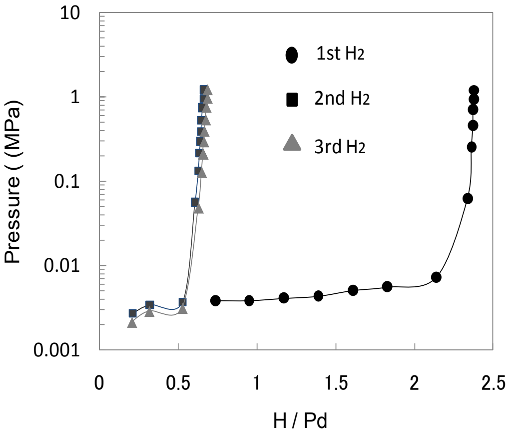

Figure 3. PC isotherms for 20wt%Pd-γAl_2O_3. The measurements were made 3 times repeatedly at 300K.

If the Pd particles are initially oxidized and reduce to metallic Pd during the first time measurement, then both of the following chemical reactions occur in the first time measurement :

$PdO + H_2 \rightarrow Pd + H_2O + \triangle H(water)$ (1)

$Pd + (x/2)H_2 \rightarrow PdH_x + \triangle H\ (hydride)$ (2)

The water formation reaction (1) gives an apparent H/Pd ratio of 2.0, and the hydride formation reaction (2) gives a true value of hydrogen absorption capacity x. The value of x is obtained from the experiment in the second or third time measurement and x is 0.68 ~ 0.70 for the sample of 20wt%Pd/γAl_2O_3 as seen in Fig.2.

If the Pd particles are initially 100% oxidized, an apparent H/Pd ratio of ~2.7 should be obtained in the first time measurement. If the Pd particles are partially oxidized, the degree of oxidation is obtained from the difference between the apparent and the true H/Pd values. The observed value of 2.4 for the sample of

Table 1. Variation of H/Pd or D/Pd at 1MPa with the order of measurement cycle for foil and nanomaterials of Pd at 300K.

Material	1st	2nd	3rd	4th
Pd foil	0.74 ± 0.02 (H_2)	0.74 ± 0.02 (H_2)	0.74 ± 0.02 (H_2)	
nanoPd (AY4030)	0.82 ± 0.02 (D_2)	0.69 ± 0.02 (D_2)	0.70 ± 0.02 (D_2)	0.71 ± 0.02 (H_2)
13wt%Pd/γAl_2O_3	2.7 ± 0.2 (D_2)	0.71 ± 0.02 (D_2)	0.72 ± 0.02 (D_2)	0.72 ± 0.02 (H_2)
20wt%Pd/γAl_2O_3	2.4 ± 0.2 (H_2)	0.68 ± 0.02 (H_2)	0.70 ± 0.02 (H_2)	
30wt%Pd/ZrO_2	2.6 ± 0.2 (H_2)	0.68 ± 0.02 (H_2)	0.70 ± 0.02 (H_2)	

20wt%Pd/γAl_2O_3 indicates that 85 at% of Pd in the as synthesized sample is in the chemical state of PdO [4]. Similarly, from the PC isotherm measurements, the degree of oxidation of Pd particles in the as-received or as-synthesized samples was estimated to be 6 at%, 100 at% and 95at% for Pd powder AY4030, 13wt%Pd/γAl_2O_3 and 30wt%Pd/ZrO_2, respectively.

It should be mentioned that in Fig.2, no difference in the H/Pd ratio at 1MPa is seen between the three measurements, indicating that the foil sample is 100% metallic in the as-received state.

The results of the repetitive measurements of hydrogen/deuterium absorption capacity for nanoPd materials are summarized in Table 1, including the results for the foil sample of Pd. It is seen that the H/Pd or D/Pd ratios of the metallic nanoPd materials are slightly smaller than the value of Pd bulk or the foil sample of Pd.

3. 2. X-ray diffraction

From the repeated measurements of hydrogen absorption capacity, it has been suggested that PdO reduces to metallic Pd during loading of hydrogen up to 1MPa at 300K. Figure 4 shows the X-ray diffraction patterns for the sample of 13wt%Pd/γAl_2O_3 before and after the four cyclic PC isotherms measurements [4]. As shown in Fig. 4, the sample before the measurements consists of γAl_2O_3 and PdO, while the sample after the measurements consists of γAl_2O_3 and metallic Pd.

It is considered that PdO reduces to metallic Pd during the first time loading of hydrogen, because the H/Pd values at and after the second time measurements do not change as shown in Fig.3. Therefore, PdO easily reduces to metallic Pd once it is exposed to hydrogen at room temperature.

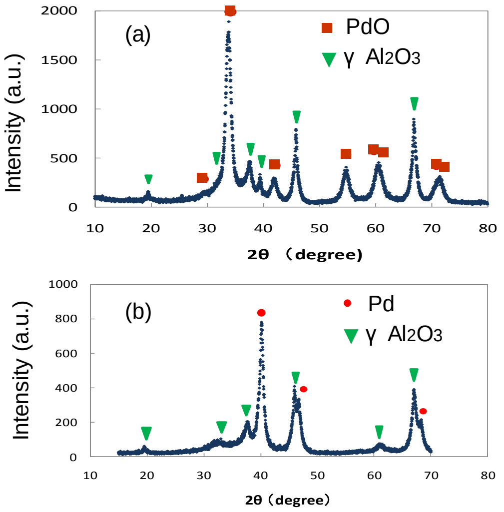

Figure 4. X-ray diffraction pattern for 13wt%Pd/γAl_2O_3: (a) before and (b) after repetitive PC isotherms measurements.

3.3. TEM observation

The repetitive measurements of PC isotherms also resulted in a morphological change of Pd particles, i.e., the size of the Pd nanoparticles became larger after the measurements. The change was most remarkable for Pd nanopowder AY4030. Figure 5 compares TEM images before and after the measurements or the four cycles of loading and deloading with deuterium or hydrogen (first three cycles wih D_2 and the fourth with H_2 [4]).

As seen from the TEM images in Fig.5, the average size of Pd particles is initially 10 ~ 20nm, but it is about 50nm after the four repetitive measurements.

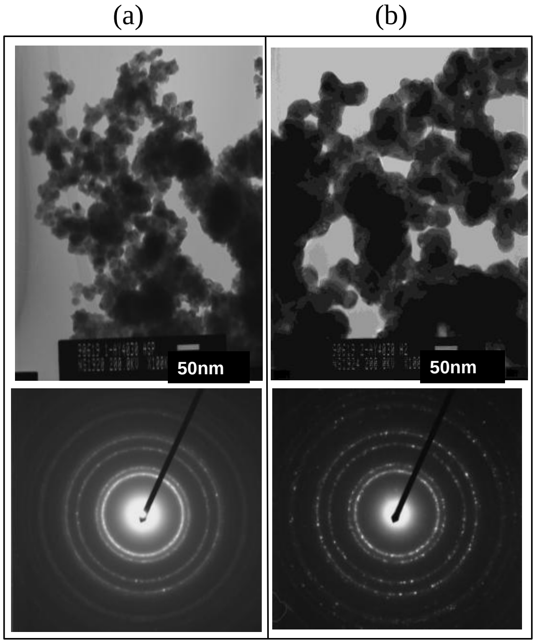

Figure 5. TEM image and electron diffraction rings for (a) before and (b) after four cycles of loading and deloading of deuterium/hydrogen.

The electron diffraction rings are spotted for the sample after the measurements as seen in Fig.5. This fact also indicates that the size of the crystalline grains becomes larger as a result of cycles of loading and deloading of hydrogen or deuterium. Similar increases in the size of Pd particles have also been observed for nanocomposite samples [4, 5]. The observed grain growth is considered to arise from the local temperature rise at the contact point of contacting Pd particles owing to the heat generated by the chemical reactions (1) and (2). However, the melting point of Pd, 1827K, seems to be too high to explain the grain growth by the rise of the local temperature. The degree of oxidation of AY4030 is only 6at% and the heat mainly comes from the hydride formation reaction (2) with much smaller heat of formation compared to the reaction (1). The reason for the grain growth is not yet fully clear.

It should be mentioned that the measured values of the hydrogen absorption capacity may be for Pd particles with sizes larger than their initial sizes.

3.4. Heat evolution with loading of hydrogen isotope gases

3.4.1. First stage

The composite sample 20wt%Pd/ γ Al_2O_3 of 42.5g (Pd : 8.5g) was mounted in the sample vessel of the calorimeter. The sample was first evacuated, heated up to 523K under vacuum and maintained at the temperature for about 2 hours, followed by cooling to room temperature. Then, deuterium gas was supplied to the sample at a flow rate of about 20ml/min. When the pressure reached a value of 1MPa, the gas supply was stopped and the sample was maintained under a fixed pressure of 1MPa. Figure 6(a) shows the thermal output power and gas pressure as a function of time for the first loading with D_2.

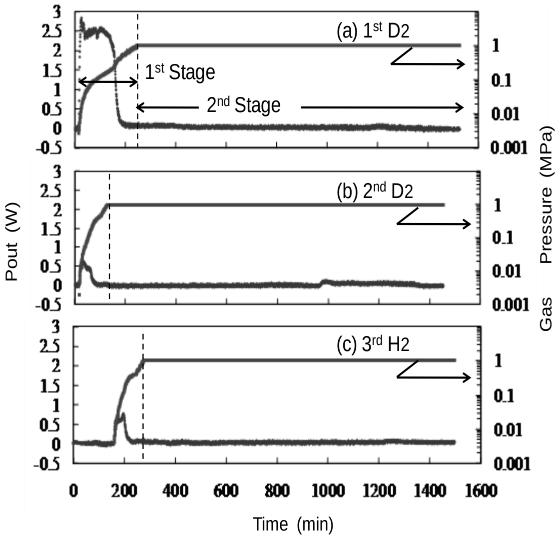

Figure 6. Heat power and gas pressure as a function of time for 20wt%Pd-γAl_2O_3; (a) the first cycle loading with D_2 , (b) the second cycle loading with D_2, (c) the third cycle loading with H_2 [4].

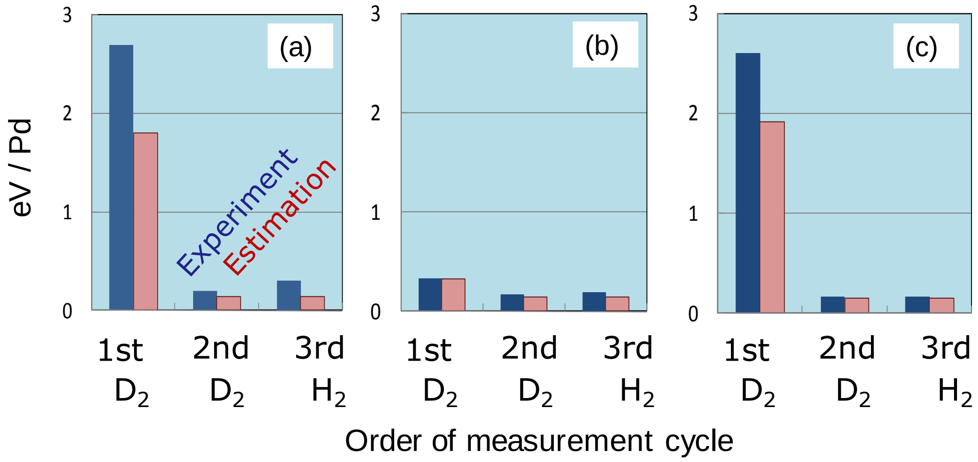

Figure 7. The variation of the heat generated in the first stage with the order of measurement cycle for (a) 20wt%Pd/ γ Al2O3, (b) Pd nanopowder AY4030, and (c) 30wt%Pd/ZrO2. The experimental values are compared to the estimated ones.

After the first measurement of heat evolution, the sample was again evacuated, heated up to 523K, maintained at this temperature for 2h in order to eliminate the absorbed deuterium completely. Then, the sample was subjected to the second loading with D_2 at room temperature (Fig.6 (b)). Similary, the third loading was conducted with H_2 (Fig.6 (c)). Here we define the first stage as the period where the pressure was raised from 0 to 1MPa, the second stage as the period where the sample was maintained under the fixed pressure of 1MPa. It is clearly seen in Fig.6 that the heat evolution in the first stage is remarkable in the first time measurement while it decreases greatly in the second or third time measurement. This behavior is quite similar to that of hydrogen absorption capacity, suggesting that the heat evolution in the first stage is related with the chemical reactions (1) and (2). In Figure 7, the variation of the heat generated in the first stage with the order of measurement cycle is shown. The experimental values are compared to the estimated ones. The estimation was made assuming that in the first time measurement, both of the reactions (1) and (2) contributed to the heat evolution while only the reaction (2) in the second and third time measurements. The values of ⊿H(water) = -178kJ/molPd [8] and ⊿H (hydride) = ⊿H(deuteride) = -40kJ/molH_2 [9] were used. The ratio of the oxidized Pd to the total Pd before the first time measurement was taken to be 85at% as determined above.

Similar results for Pd nanopowder AY4030 and nanocomposite of Pd/ZrO_2 are also shown in the figure for comparison. It is seen in Fig.7 that the heat generated in the first stage is largely explained by the chemical reactions (1) and (2). Therefore, in the first stage, it seems difficult to identify the heat evolution from nuclear origin, even if a small portion of the generated heat is nuclear.

3.4.2. Second stage

The chemical reactions associated with loading the Pd nanomaterials with hydrogen isotope gases up to 1MPa are considered to cease until the pressure reaches 1MPa. Therefore, in the second stage, where the gas pressure is fixed at 1MPa, no chemical reactions are expected to occur. In Figure 8, the same data as in Fig.6 are shown with the vertical axis magnified by ten times.

It is noted in Fig.8 that in the first and second loadings with D_2, an output power as small as 0.05~0.1W is observed for a period of about three and six hours, respectively. On the other hand, as seen in Fig.8 (c), no such anomalous heat evolution is observed

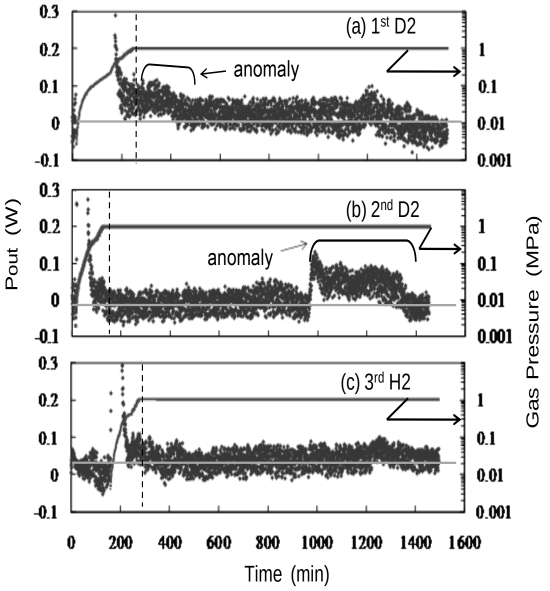

Figure 8. The same data as Fig.6 are shown with the vertical axis enlarged by 10-fold. The vertical dotted line indicates the boundary of the first stage and the second stage, and the horizontal gray lines the zero level of Pout [4].

in the third loading with H_2.

Similarly, the results for the Pd nanopowder sample of 26g and the Pd/ZrO_2 sample of 51.4g (Pd: 15.6g) are shown in Figure 9 and Figure 10, respectively. As indicated in the figures, similar evolutions of anomalous heat are also observed for these materials. All of these intermittent, anomalous heat evolutions are observed when the materials are loaded with deuterium. Therefore, it cannot be ruled out that these heat evolutions in the second stage are nuclear origin, as reported by Arata and Zhang and by Kitamura et al. However, in the present study the observed anomalous heat power is as small as 0.05~0.1W which is close to the detection limit of the calorimeter used here. In order to clarify the origin of the anomalous heat evolution in the second stage, it is required to enhance the anomalous heat power and/or to improve the accuracy of the calorimeter.

4. Conclusions

(1) Nanomaterials of Pd often contain PdO, which

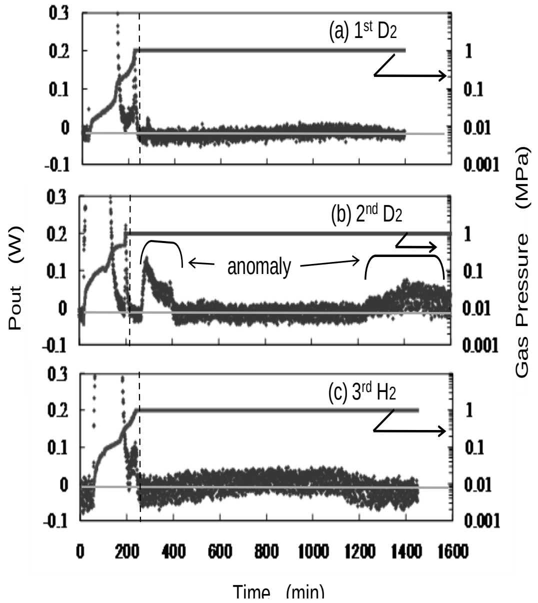

Figure 9. Heat power and gas pressure as a function of time for Pd nanopowder AY4030; (a) the first cycle loading with D_2, (b) the second cycle loading with D_2, and (c) the third cycle loading with H_2. The vertical dotted line indicates the boundary of the first stage and the second stage, and the horizontal gray lines the zero level of Pout [4].

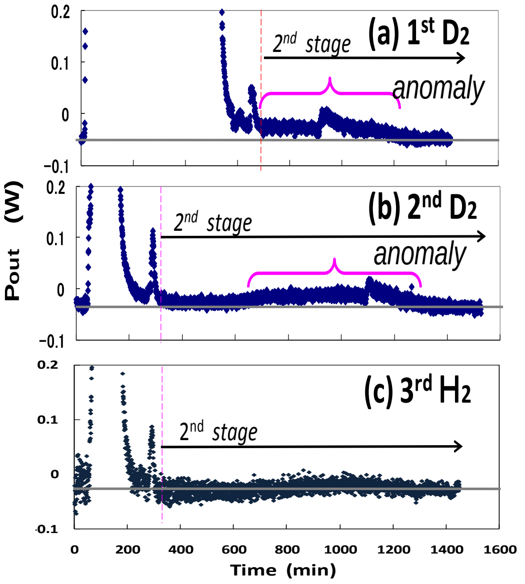

Figure 10. Heat power and gas pressure as a function of time for 30wt%Pd/ZrO_2 nanocomposite; (a) the first cycle loading with D_2, (b) the second cycle loading with D_2, and (c) the third cycle loading with H_2. The vertical dotted line indicates the boundary of the first stage and the second stage, and the horizontal gray lines the zero level of Pout [5].

strongly affects apparent absorption capacity and heat evolution upon loading of hydrogen isotope gases. The extent of oxidation can be estimated from the difference between the apparent and true values of absorption capacity for hydrogen/deuterium.

(2) PdO is reduced to metallic Pd when it is exposed to hydrogen. Therefore, hydrogen absorption capacity of metallic Pd particles is obtained by cyclic measurements of PC isotherms.

(3) The hydrogen absorption capacity H/Pd at 1MPa was 0.70 ∓ 0.02 for all the nanoPd materials studied here, which was slightly smaller than the value 0.74 of Pd bulk.

(4) The size of the Pd particles was found to be increased significantly after cyclic measurements of PC isotherms.

(5) Similar to the absorption capacity, the heat generated in the first stage was also affected strongly by the degree of oxidation of Pd particles. The experimental value of heat generated in the first stage was largely explained by the water formation reaction and the hydride formation reaction.

(6) When the Pd nanomaterials were loaded with deuterium, a heat power as small as 0.05 ~ 0.1W was observed intermittently in the second stage where chemical reactions were hardly expected to occur.

Acknowledgements

We thank N. Suzuki for TEM observations. We also thank A. Kitamura of Kobe University and A. Takahashi of Technova Inc. for discussions.

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