

Research Article

# Isotope Effect for Heat Generation upon Pressurizing Nano-Pd/Silica Systems with Hydrogen Isotope Gases

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## Abstract

The isotope effect for heat generation upon pressurization with hydrogen isotope gases was clearly observed in a reproducible manner for nano-Pd/silica systems. For Pd/zeolite, the isotope effect decreased with increasing cycle of pressurization and almost disappeared at several cycles, whereas the effect was observed up to 15 cycles or more for Pd/FSM. Pd particles with sizes less than 2 nm are suggested to be essential for the isotope effect to be clearly observable.

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*Keywords:* Heat, Isotope effect, Nano-palladium, Porous silica

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## 1. Introduction

Arata and Zhang have reported that the heat arising from nuclear fusion reaction in solid is observed simply by pressurizing a nano-Pd/ZrO<sub>2</sub> system with deuterium gas [1]. Nano-sized Pd particles have been expected to absorb sufficient deuterium to induce low energy nuclear phenomena. Actually, a high value of hydrogen absorption capacity has been reported for the nano-Pd/ZrO<sub>2</sub> system [2].

Similar experiments with that by Arata and Zhang have been performed in several laboratories [3–6]. Kitamura et al. have constructed a twin type flow calorimeter and have measured quantitatively the heat generated upon pressurizing a nano-Pd/ZrO<sub>2</sub> system synthesized by Santoku Corporation [5]. They have observed a remarkable difference in the heat evolution between deuterium and hydrogen, i.e., a clear isotope effect for heat, which seems to support strongly the claim by Arata and Zhang. They have also reported a D/Pd or H/Pd ratio of 1.1, which far exceeds the literature value of 0.7 for Pd bulk [5].

Using a flow calorimeter, we have measured the heat generation for nano-Pd powder obtained from Tanaka Kikinzoku Kogyo, nano-Pd / $\gamma$ -Al<sub>2</sub>O<sub>3</sub> synthesized by us [6] and nano-Pd/ZrO<sub>2</sub> [7] obtained from Santoku Corporation. However, we have not observed any clear isotope effect for the heat with pressurization. Using Sievert's method, we have also measured hydrogen absorption capacity of these nano-Pd systems and have obtained values of H/Pd not exceeding that

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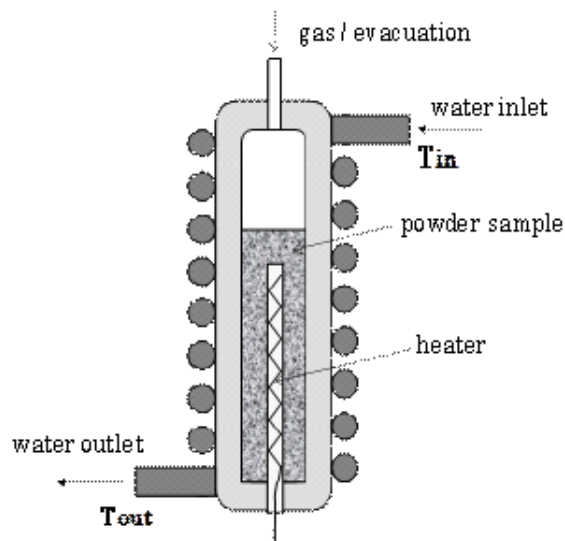


Figure 1. Schematic of the calorimeter.

of Pd bulk. Since nano-Pd particles are easy to coalesce and grow once they are exposed to hydrogen environment, it is not easy to pressurize nano-Pd systems keeping the initial size of the Pd particles. In this context, it should be mentioned that the nano-Pd/ZrO<sub>2</sub> powder used by Arata and Zhang may be different from the powders of Santoku Corporation, because the nano-Pd particles in Arata's sample seem to be embedded in ZrO<sub>2</sub> matrix, thus may be difficult to grow upon exposure to hydrogen. The growth of nano-Pd particles may be considerably suppressed if the particles are inside the pores of porous matrices. Kidwell et al. have used zeolite and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as porous matrices and observed a large, reproducible isotope effect for the heat using the porous matrices dispersed with small concentrations of Pd [8].

In this study, as the porous matrices we have used two silica's: zeolite and FSM (Folded Sheet Mesoporous silica) [9] with pores of about 1 nm and 1.5–2 nm, respectively. A clear isotope effect for heat with pressurization has been observed for both Pd/zeolite and Pd/FSM systems in a reproducible manner.

## 2. Experimental

### 2.1. Materials

The samples used in this study were 5.0 wt% Pd/ zeolite and 9.85 wt% Pd/FSM. Zeolite powder of Y-type (Faujasite) was obtained from Toso Corporation. The composition was SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (mol/mol) = 5.5, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> (mol/mol) = 1.0, and the size of the pore ~1.1 nm. The zeolite powder was dispersed with 5.0 wt% Pd by wet method using palladium nitrate.

Powder samples of FSM (3D-hexagonal type, P6<sub>3</sub>/mmc, pore size; 1.5–2 nm) synthesized in our laboratory were dispersed with 9.85 wt% Pd by wet method using palladium chloride.

## 2.2. Calorimetry

The heat generation with loading of hydrogen isotope gases was measured with a flow calorimeter. Figure 1 shows the schematic of the calorimeter.

The volume of the sample vessel was about 50 cm<sup>3</sup>. 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 recorded every 1–10 s 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 0.68 was used as the recovery rate, which was almost independent of the species of the gases (H<sub>2</sub>, D<sub>2</sub>, and He) used, of the gas pressure in the range 0–1 MPa, and of the electric heater power in the range of 1–5 W. In order to suppress the fluctuation and the drift of the measured output power, the calorimeter system was installed in a room of constant temperature. The accuracy of the calorimeter was  $\pm 50$  mW [6]. The gases were supplied into the sample vessel through a mass flow controller. The flow rate of the gas was about 20 ml/min.

## 3. Results

### 3.1. Heat measurement for 5 wt% Pd/zeolite

An as-synthesized 5 wt% Pd/zeolite sample of 30.7 g (Pd: 1.5 g) was loaded in the sample vessel of the calorimeter. The sample was first evacuated for two days at room temperature and heated up to 623 K in vacuum and maintained at the temperature for about 3 h, followed by natural cooling to room temperature. Then, deuterium gas was firstly supplied to the sample up to 1 MPa at room temperature (300K) and at a flow rate of 20 ml/min with a mass flow controller. When the pressure reached 1 MPa, the gas supply was stopped and the sample was maintained under the fixed pressure of 1 MPa for a period of about 1 h. Here, we define the first stage as the period where the pressure is raised from 0 to 1 MPa, the second stage as the period where the sample is maintained under the constant pressure of 1 MPa. The measurements of the heat power upon pressurizing with deuterium or hydrogen gases were repeated 16 times for the same sample without exposing the sample to air. Prior to each cycle of pressurization, the sample was always heat treated in vacuum at 623K for 3 h. The procedure of the heat measurements is shown in Fig. 2.

In Fig. 3, as a typical example, the heat power as a function of time is shown for the fourth cycle pressurization with deuterium gas. It is seen in Fig. 3 that the heat power rapidly increases as the supply of the gas is started, reaches a broad peak value, and then rapidly decreases followed by a small, nearly constant value. In the second stage, where the gas pressure is kept at 1 MPa, any heat power exceeding the detection limit is not observed.

From the variation of the gas pressure with time, the behavior of heat power is suggested to correlate with the palladium–hydrogen phase diagram;  $\alpha$ -phase, coexisting phase of  $\alpha$ - and  $\beta$ -phases, and  $\beta$ -phase, as shown in Fig. 3. This finding seems to indicate that the behavior of the heat power is dominantly caused by the metallic Pd particles at and after the second cycle.

The heat generated during pressurization is obtained by integrating the heat power in the first stage. Figure 4 shows the heat generated upon pressurizing the 5 wt% Pd /zeolite sample with hydrogen isotope gases up to 1 MPa as a function of pressurization cycle. In Fig. 4, the first cycle measurement was done with D<sub>2</sub>, the second cycle was done again with D<sub>2</sub>, the third cycle with H<sub>2</sub>, and so forth.

It is seen in Fig. 4 that the heat generated in the first cycle is remarkably large. This is due to the fact that in the as-synthesized state, the nano-Pd particles are in the form of PdO. When the oxidized Pd particles are exposed to hydrogen isotope gases, they are reduced to metallic Pd. This chemical reaction produces a large amount of heat. After the first cycle, it is expected that Pd particles are in metallic state and the heat obtained at and after the second cycle

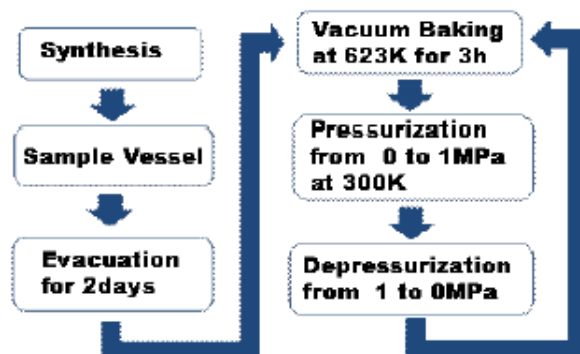


Figure 2. Procedure of the heat measurement.

pressurization is the heat for zeolite dispersed with *metallic* Pd.

It is noted in Fig. 4 that the heat generated with D<sub>2</sub> is clearly larger than the heat with H<sub>2</sub>. This difference, i.e., the isotope effect for heat with pressurization is observed up to several cycles in a reproducible manner. However, the difference decreases with increasing cycle and no isotope effect is seen at increased number of cycles above around 7–10.

Figure 5 compares the TEM images for the sample before and after the 16-cycle's measurement. In the as-synthesized state, Pd particles exist inside the pores, although Pd particles are also seen on the surface of zeolite grains (Fig. 5(a)). As seen in Fig. 5(b), almost all the Pd particles seem to precipitate on the surface of the zeolite grains after the 16-cycle's heat measurement. The size of the precipitated Pd particles is about 10nm or more, which is much larger than the size

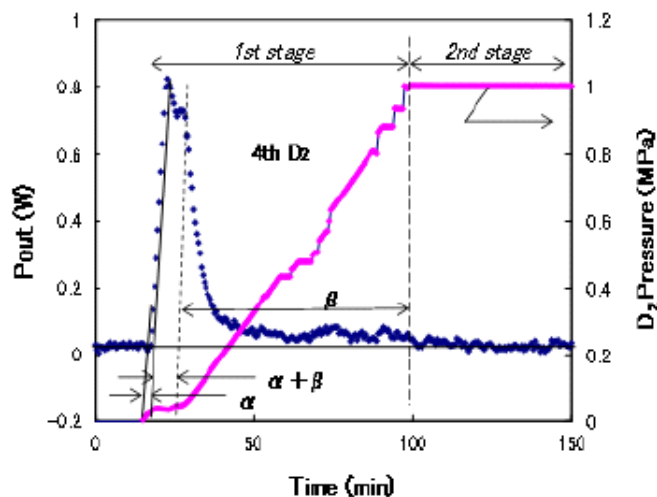
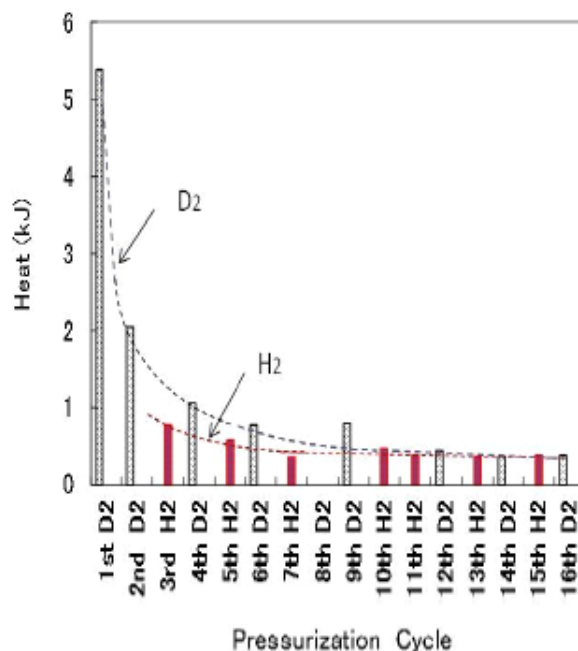


Figure 3. Heat power and gas pressure as a function of time for the fourth cycle pressurization with D<sub>2</sub> for 5 wt% Pd/zeolite.



**Figure 4.** Heat as a function of pressurization cycle for 5 wt% Pd/zeolite.

of the pore of the zeolite  $\sim 1.1$  nm.

### 3.2. Heat Measurement for Pd/FSM

Similar measurements were also performed for 9.85 wt% Pd/FSM. The measurements were repeated up to 15 cycles, following the same procedure shown in Fig. 2.

In Fig. 6, the heat generated with pressurization up to 1 MPa is plotted against pressurization cycle. The data of the first cycle is omitted in the figure, because the first cycle includes the heat of reduction for PdO. Prior to each measurement, the sample was always heat-treated in vacuum at 623 K for 3 h without exposing the sample to air.

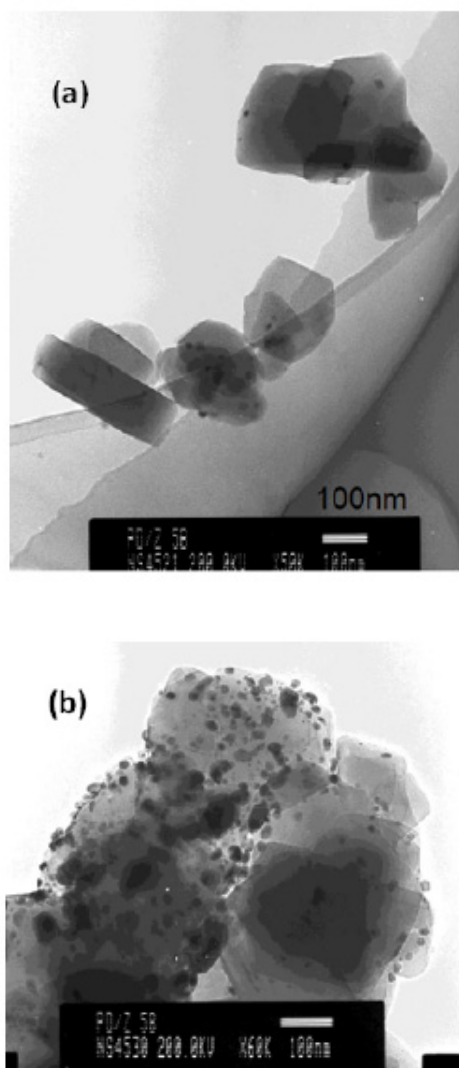
It is seen in Fig. 6 that the heats with D<sub>2</sub> are clearly larger than those with H<sub>2</sub>. Furthermore, the difference does not seem to become smaller with increasing cycle of measurement. The heat averaged over the cycles of D<sub>2</sub> pressurization is larger than the heat averaged over the cycles of H<sub>2</sub> by 29%.

Figure 7 compares the TEM images for the sample before and after the 15-cycle's measurement for heat with pressurization. In the as-synthesized state, Pd particles exist inside the pores of FSM. Some Pd particles with the size of several nm are also seen on the surface of the grains. As seen in Fig. 7(b), it is noted that Pd particles still stay inside the pores of FSM even after the 15-cycle's measurement. This is in contrast with the results for the 5 wt% Pd/zeolite sample.

#### 4. Discussion

In Fig. 4, the isotope effect for heat is seen only up to several cycles of pressurization for the 5 wt% Pd/zeolite sample. At higher cycles, the heat with D<sub>2</sub> is almost equal to the heat with H<sub>2</sub>, i.e., no isotope effect is observed.

First, we consider the heat generation at the increased number of pressurization. As the possible mechanisms at the



**Figure 5.** TEM images for 5 wt% Pd/zeolite: (a) as-synthesized and (b) after the 16 cycle's measurement of heat generation with pressurization. Dark spots are Pd particles.

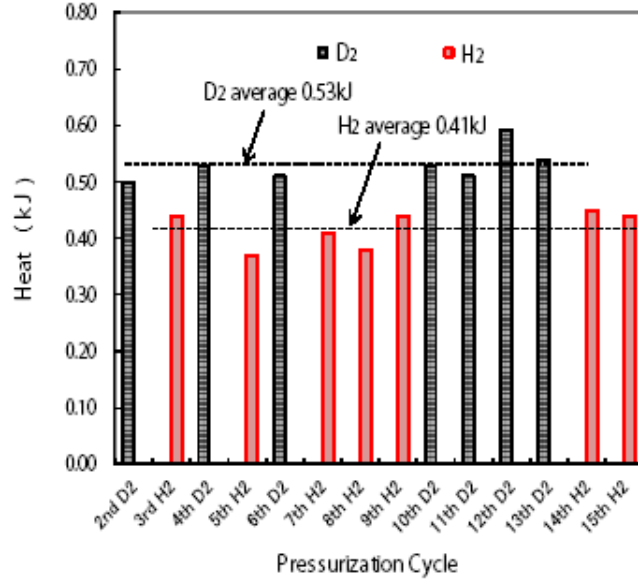


Figure 6. Heat as a function of pressurization cycle for 9.85 wt% Pd/FSM.

higher cycles, the followings are considered.

$$Q_{out}^{hi-cycl} = Q_{abs} + Q_{ads} + Q_{mech} \tag{1}$$

Here,  $Q_{abs}$  is the heat of hydrogen absorption for Pd, i.e.,



$Q_{ads}$  is the heat of hydrogen adsorption of zeolite matrix,  $Q_{mech}$  the mechanical work with pressurization by hydrogen/deuterium. It is known  $Q_{abs} = 40$  kJ/mol  $H_2$  [10]. In the present study, we experimentally obtained  $Q_{ads}$  for pure zeolite using the calorimeter. We obtained  $Q_{ads}(H_2) = 2.7$  kJ/mol, and  $Q_{ads}(D_2) = 2.9$  kJ/mol. The mechanical work was also measured to be  $1.15$  J/cm<sup>3</sup> using the blank sample vessel. Using these values, Eq. (1) was estimated and compared in Table 1 to the experimental value averaged over higher cycles from 11<sup>th</sup> to 16<sup>th</sup>. The calculated value agrees to the experimental one, suggesting that Eq. (1) is good for zeolite at higher cycles, where almost no isotope effect is observed.

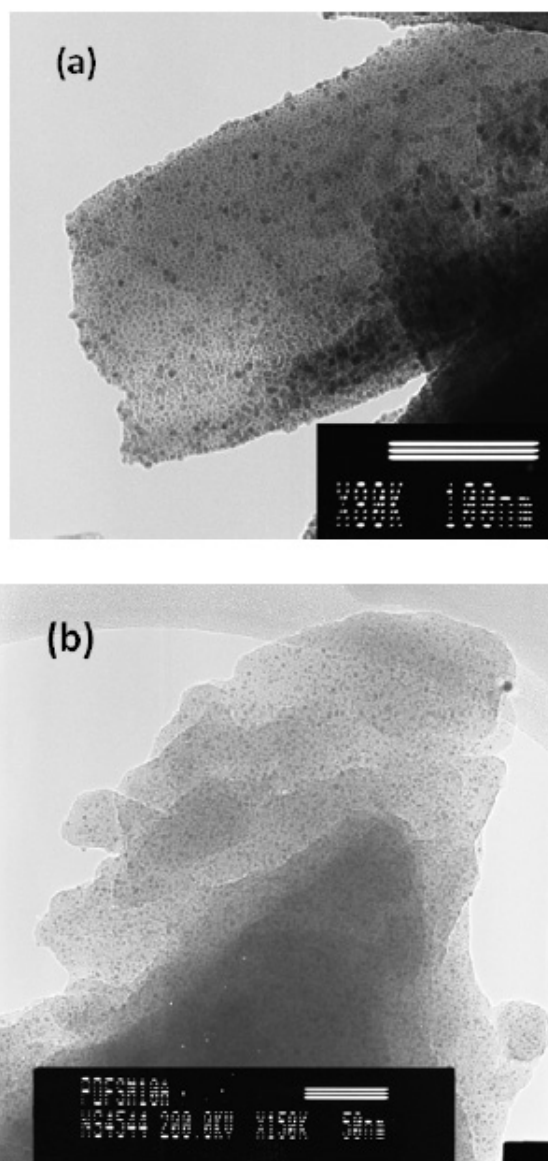
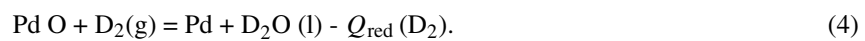
Next, we consider the heat at the first cycle where Pd is assumed to be in the state of PdO. We can assume that

$$Q_{out}^{1st} = Q_{abs} + Q_{ads} + Q_{mech} + Q_{red} + Q_{liq-sol}. \tag{3}$$

Table 1. Estimated and experimental heats at high cycles for 5 wt% Pd/zeolite sample (J).

	$Q_{mech}$	$Q_{ads}$	$Q_{abs}$	$Q_{out}^{hi-cycl}$
Estimation	44	130	198	372
Experiment				375

Here,  $Q_{\text{red}}$  is the heat of reduction for PdO, i.e.



**Figure 7.** TEM images for 9.85 wt% Pd/FSM: (a) as-synthesized and (b) after the 15 cycle's measurement of heat generation. *Dark spots are Pd particles.*



**Table 2.** Estimated and experimental heats at the first cycle for 5wt% Pd/zeolite sample (J).

	$Q_{\text{mech}}$	$Q_{\text{ads}}$	$Q_{\text{abs}}$	$Q_{\text{red}}$	$Q_{\text{liq-sol}}$	$Q_{\text{out}}^{\text{1st}}$
Estimation	44	130	198	2520	707	3600
Experiment						5380

Here,  $Q_{\text{red}}(\text{D}_2) = 178 \text{ kJ/mol Pd}$  [11]. The water produced by the reducing reaction is thought to be absorbed inside the pore of zeolite and becomes solid water. We assume  $Q_{\text{liq-sol}} = 40 \text{ kJ/mol D}_2\text{O}$ .

Table 2 compares the estimated value with the experimental one for  $Q_{\text{out}}^{\text{1st}}$ .

It is seen that the experimental value is considerably larger than the estimation. This fact suggests that there is an unknown source of heat to be taken into account. The unknown heat,  $Q_{\text{unknown}}$ , is 1780 J, which is about 33% of the experimental value.

In the second cycle, we assume that Pd particles exist in metallic state. Therefore, we assume

$$Q_{\text{out}}^{\text{2nd}} = Q_{\text{abs}} + Q_{\text{ads}} + Q_{\text{mech}} + Q_{\text{unknown}}. \quad (5)$$

If we further assume  $Q_{\text{unknown}}^{\text{2nd}} = Q_{\text{unknown}}^{\text{1st}}$ , we can estimate the value of  $Q_{\text{out}}^{\text{2nd}}$ , which is compared to experiment in Table 3.

The estimated value agrees approximately with the experimental one, although the estimation is a little larger than the experiment.

From these estimations, it is suggested that  $Q_{\text{unknown}}$  appears in the early cycles of pressurization in the case of 5 wt% Pd/zeolite. Figure 4 suggests that  $Q_{\text{unknown}}$  must become smaller with increasing cycle and disappears at higher cycles. The isotope effect observed at early cycles arises mainly from  $Q_{\text{unknown}}$ .

A possible candidate of  $Q_{\text{unknown}}$  is the D–H exchange reaction which has been discussed by Kidwell et al. [8] and Dmitriyeva et al. [12] in explaining the anomalous heat observed for low concentration Pd in oxide matrices including zeolite [8]. They estimated the heat due to D–H exchange reaction using gas analysis data and found that in some matrices the likely source of the anomalous heat is D–H exchange with the water present in the matrix [8,12]. In other matrices, however, no simple explanation of the excess heat could be made [8]. In the present study, the amount of water included in the matrix is negligible because the sample was always baked at 623 K in vacuum. However, silica's contain surface silanols and D/H exchange reaction of the silanols may generate a significant amount of heat and hence an isotope effect for heat generation. Therefore, it is required to estimate quantitatively the contribution from D–H exchange reaction of the silanols.

Isotope effect for heat with pressurization has also been clearly observed for 9.85 wt% Pd/FSM. It was noted for this sample that the difference in the heat between deuterium and hydrogen did not decrease with an increase of cycle up to at least 15 cycles, whereas the difference disappeared at several cycles for 5 wt% Pd/ zeolite.

The origin of these apparently different behaviors of the isotope effect seems to be correlated with the size of the Pd particles, i.e., the isotope effect is negligible if the size of the Pd particle is larger than about 10 nm. For the 5 wt% Pd/zeolite sample, a significant amount of Pd initially existed inside the pore of zeolite with a size of  $< \sim 1.1 \text{ nm}$  and

**Table 3.** Estimated and experimental heats at the second cycle for 5 wt% Pd/zeolite sample (J).

	$Q_{\text{mech}}$	$Q_{\text{ads}}$	$Q_{\text{abs}}$	$Q_{\text{unknown}}$	$Q_{\text{out}}^{\text{2nd}}$
Estimation	44	130	198	1780	2150
Experiment					2050

precipitated onto the surface of zeolite grain with increasing cycle of pressurization, resulting in the growth of Pd up to sizes of more than 10 nm. In the 9.85 wt% Pd/FSM sample, on the contrary, the Pd particles inside the pores of FSM kept staying there even after the 15-cycle's measurement, suggesting the size of Pd particles was mostly less than the size of the pore, i.e. 2 nm. These facts suggest that nano-sized Pd particles mainly cause the isotope effect for heat generation upon pressurization. The size of the Pd particles favorable to a clear observation of the isotope effect is less than about 2 nm.

Thus, it has been demonstrated that isotope effect for heat generation upon pressuring nano-Pd systems is strongly dependent on the size of Pd particles, which is easy to increase upon exposure to hydrogen. To suppress the growth of Pd particles, incorporation of Pd particles into the pores of porous materials is effective, although the stability of Pd particles is dependent on the size of the pores of the porous material. Therefore, to clarify the origin of the observed isotope effect for heat generation in nano-Pd systems, the influence of the Pd particle size on the isotope effect should be properly explained.

## 5. Conclusions

Differences in the heat generation upon pressurization with H<sub>2</sub> and D<sub>2</sub>, i.e., the isotope effect, were clearly observed for both Pd/zeolite and Pd/FSM systems in a reproducible manner. For Pd/zeolite, the difference decreased with increasing cycle of pressurization and almost disappeared at higher cycles, whereas it was almost constant for Pd/FSM. It was indicated that when exposed to hydrogen, the nano-Pd particles in the pores of zeolite migrated onto the surface of zeolite grain, whereas nano-Pd particles inside the pores of FSM kept staying there. It is suggested that the existence of Pd particles with sizes of less than 2nm is essential for the isotope effect to be clearly observable.

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