

Supporting Information for

New Insights on the Formation Process and Thermodynamics of the

α -phase PdH(D)_x through Direct Enthalpy Measurement of H(D)

Dissolution

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Characterization of the sample

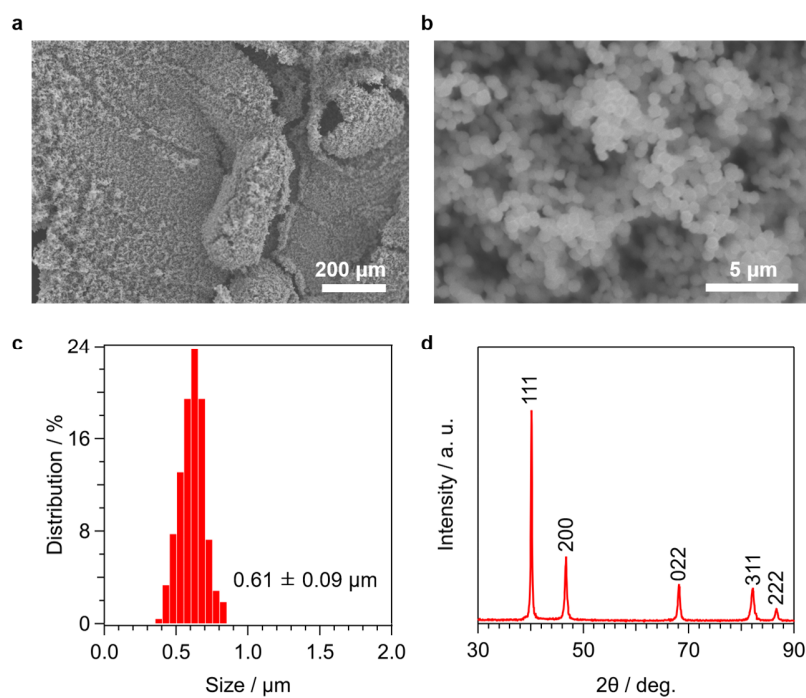


Figure S1. (a), (b) SEM images of Pd microparticles. (c) Size distribution of Pd microparticles obtained from the image in (b). (d) PXRD pattern of the sample.

Calculation of the H(D) absorption amount

Figure S2 shows the schematic picture of the gas line equipped with the calorimeter.^{1,2} The gas line can be divided into three regions, with the volume 1V , 2V , and 3V for *Regions 1*, *2*, and *3*, respectively. Only *Region 3* was kept in an adiabatic condition, and *Regions 1* and *2* were at room temperature. At the n th step of the measurement of the α phase, we first closed the valves V_2 – V_6 and NV_1 (V_1 was always open), and then introduced H_2 or D_2 gas into *Region 1* up to the pressure $^1P_n^i$. After opening V_3 , H_2 or D_2 gas was slowly introduced into the sample cell by controlling V_2 and NV_1 so as to maintain the adiabatic condition. After opening V_2 and NV_1 fully, we maintained the adiabatic condition until equilibrium was achieved.

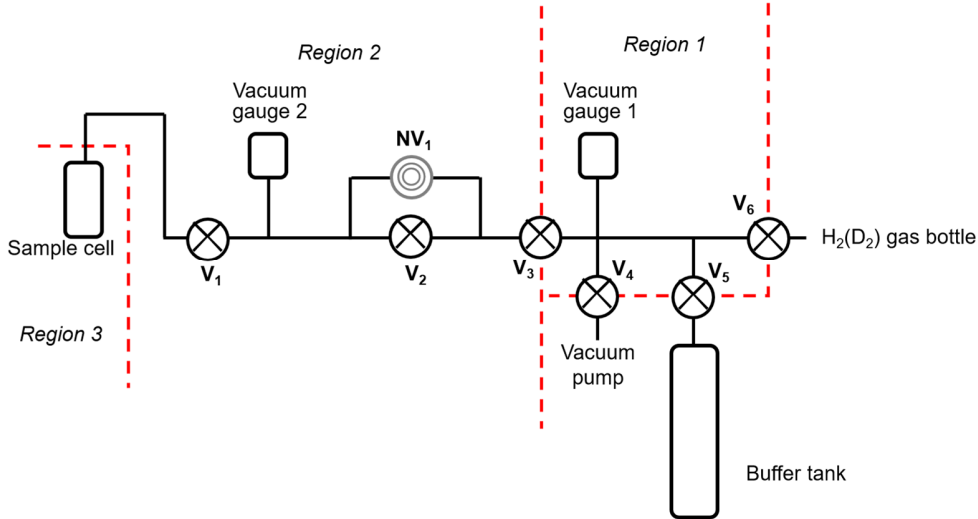


Figure S2. A schematic of the gas line equipped with the calorimeter.

The absorbed molar amount of H or D at the n th step, ΔN_n , can be calculated by the temperature and pressure change of each region, based on ideal gas approximation:

$$\Delta N_n = \frac{2}{R} \left[\left(\frac{^1P_n^i}{^1T_n^i} - \frac{^1P_n^f}{^1T_n^f} \right) + \left(\frac{^2P_n^i}{^2T_n^i} - \frac{^2P_n^f}{^2T_n^f} \right) + \left(\frac{^3P_n^i}{^3T_n^i} - \frac{^3P_n^f}{^3T_n^f} \right) \right]$$

Here, $(^1T_n^i, ^1P_n^i)$, $(^2T_n^i, ^2P_n^i)$, and $(^3T_n^i, ^3P_n^i)$ are the temperature and pressure of each region before opening V_3 , and $(^1T_n^f, ^1P_n^f)$, $(^2T_n^f, ^2P_n^f)$, and $(^3T_n^f, ^3P_n^f)$ are those at the equilibrium.

On the other hand, at thermal equilibrium, a slight incompleteness of the adiabatic condition causes a

temperature drift, which can be observed as the constant slope. Taking account of this, the temperature change at the n th step, ΔT_n , was estimated as shown in Figure 1b in the main text.

Absorption speed at each step

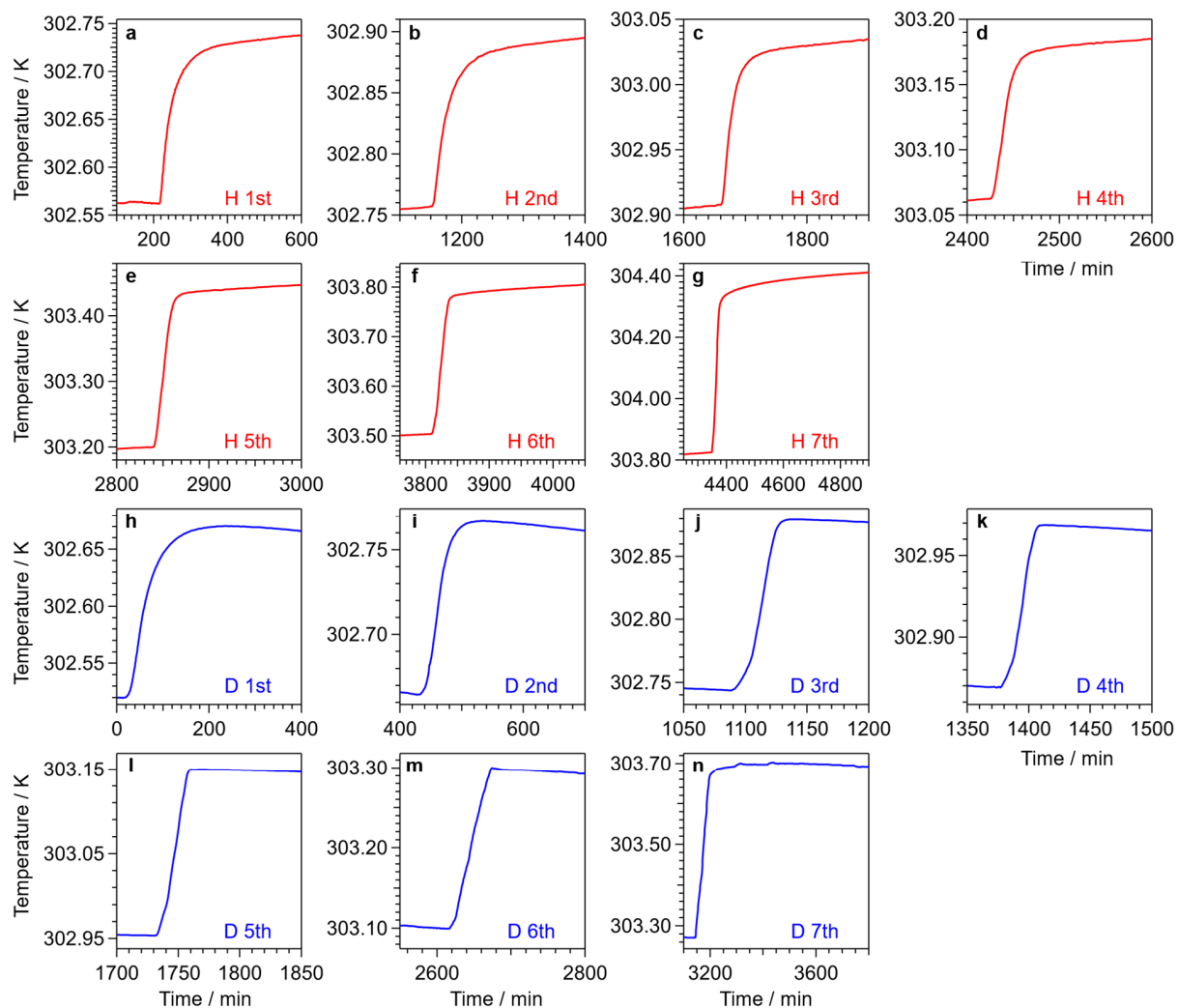


Figure S3. Expanded figures of (a)–(g) Figure 2a and (h)–(n) Figure 2b at each step in the main text, respectively.

Calculation of the enthalpy change

The enthalpy change for each step was calculated by following equation (the same equation as in the main text).

$$-\Delta H_n = (C_{p_{\text{cell}}} + C_{p_{\text{Pd}}} + C_{p_{\text{H}_2}}) \times \Delta T_n - V\Delta P$$

The value of $C_{p_{\text{cell}}} + C_{p_{\text{Pd}}}$ was measured at several temperatures, as shown in Figure S4. We estimated $C_{p_{\text{cell}}} + C_{p_{\text{Pd}}}$ at the measurement temperature at each step, taken from the midpoint of ΔT_n by a linear fit of the measured $C_{p_{\text{cell}}} + C_{p_{\text{Pd}}}$ data.

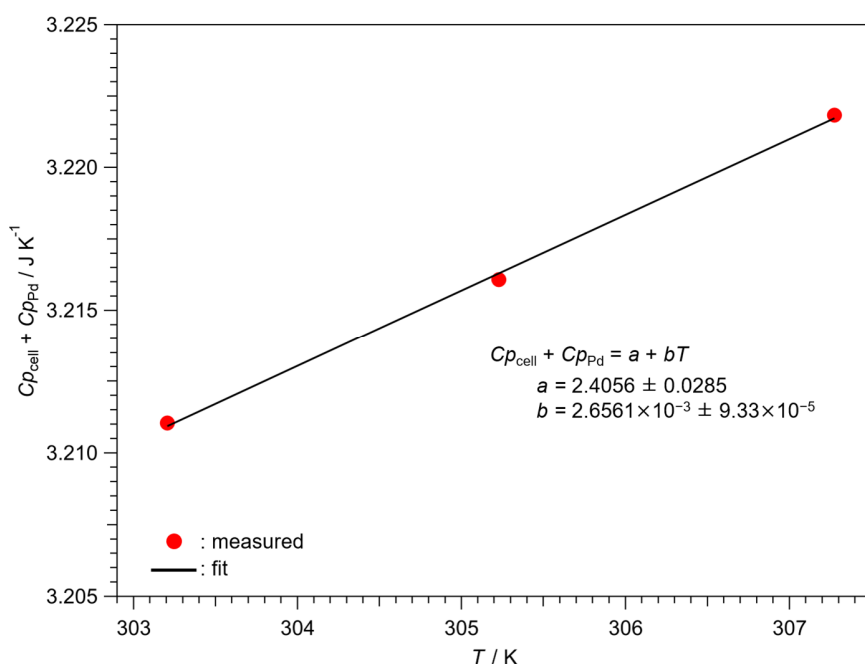


Figure S4. The $C_{p_{\text{cell}}} + C_{p_{\text{Pd}}}$ values measured at several temperatures plotted with the fitting line.

The value of $C_{p_{\text{H}_2}}$ (or $C_{p_{\text{D}_2}}$ for D) was calculated by the Shomate equation:

$$C_{p_{\text{H}_2}} \left(\frac{T}{1000} \right) = A + B \left(\frac{T}{1000} \right) + C \left(\frac{T}{1000} \right)^2 + D \left(\frac{T}{1000} \right)^3 + E \left(\frac{T}{1000} \right)^{-2}$$

where the parameters A , B , C , D , and E are taken from literature.³

Correction of the enthalpy changes to the values at standard temperature (298.15 K)

The enthalpy change at each equilibrium temperature and at the standard temperature can be written as follows (the same way can be applied for both H and D).

$$H_{\text{PdH}_x}(T_f) + \frac{y-x}{2} H_{\text{H}_2}(T_f) = H_{\text{PdH}_y}(T_f) - \Delta H_n(T_f) \quad (\text{S1})$$

$$H_{\text{PdH}_x}(298.15 \text{ K}) + \frac{y-x}{2} H_{\text{H}_2}(298.15 \text{ K}) = H_{\text{PdH}_y}(298.15 \text{ K}) - \Delta H_n(298.15 \text{ K}) \quad (\text{S2})$$

From (S1)–(S2) and $C_p = \left(\frac{\partial H}{\partial T}\right)_p$:

$$\begin{aligned} \int_{298.15 \text{ K}}^{T_f} C_{p,\text{PdH}_x} dT + \frac{y-x}{2} \int_{298.15 \text{ K}}^{T_f} C_{p,\text{H}_2} dT &= \int_{298.15 \text{ K}}^{T_f} C_{p,\text{PdH}_y} dT - \Delta H_n(T_f) + \Delta H_n(298.15 \text{ K}) \\ -\Delta H_n(298.15 \text{ K}) &= -\Delta H_n(T_f) + \int_{298.15 \text{ K}}^{T_f} (C_{p,\text{PdH}_y} - C_{p,\text{PdH}_x}) dT - \frac{y-x}{2} \int_{298.15 \text{ K}}^{T_f} C_{p,\text{H}_2} dT \\ &\approx -\Delta H(T_f) + \int_{298.15 \text{ K}}^{T_f} (y-x) C_E(T) dT - \frac{y-x}{2} C_{p,\text{H}_2}(298.15 \text{ K}) \times (T_f - 298.15 \text{ K}). \end{aligned}$$

Here, $C_E(T)$ is the Einstein heat capacity

$$C_E(T) = 3R \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left(e^{\frac{\Theta_E}{T}} - 1\right)^2},$$

where Θ_E is the Einstein temperature of H or D in the α phase or the β phase. We used the Θ_E values, 789 K and 557 K for H and D in the α phase, and 658 K and 464 K for H and D in the β phase, respectively.⁴ The value of C_{p,H_2} and C_{p,D_2} was calculated as $28.837 \text{ J K}^{-1} (\text{mol H}_2)^{-1}$ and $29.193 \text{ J K}^{-1} (\text{mol D}_2)^{-1}$, by the Shomate equation.³

Sample temperature of the other runs

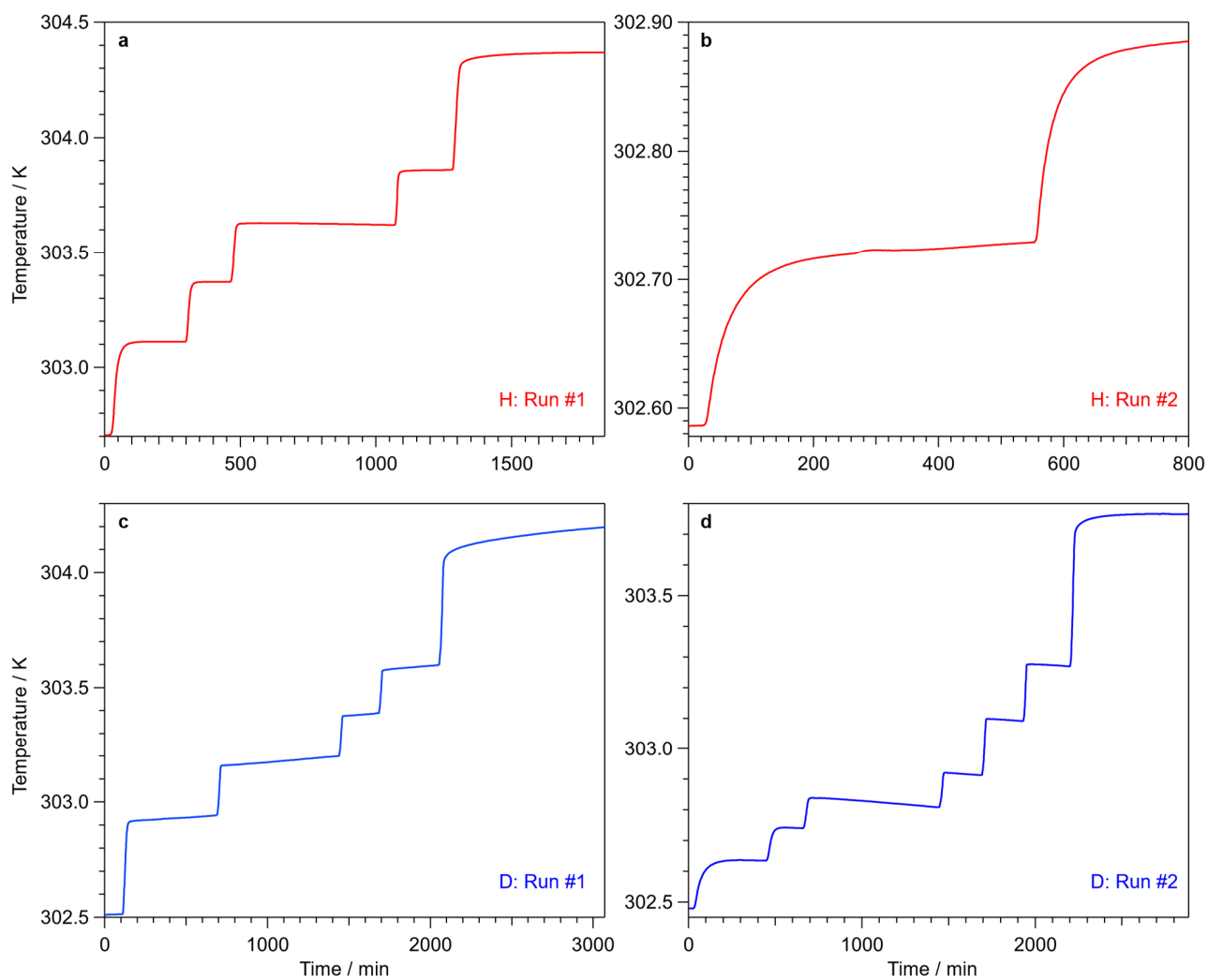


Figure S5. (a)–(d) The sample temperature in the other runs of the measurements. Three runs were measured for both H and D. Run #3 for H and D is shown in Figure 2a and 2b in the main text.

H₂(D₂) pressure–composition (PC) isotherms at 303 K

The H₂ and D₂ PC isotherms of bulk Pd were measured from 10^{−3} up to 101.3 kPa by a volumetric technique, using a PCT apparatus (BELSORP-max, Microtrac BEL Corp.).

Figure S6 shows the H₂ and D₂ PC isotherms of bulk Pd measured at 303 K. The pressure plateau corresponding to the α – β phase transition appears at around H(D)/Pd = 0.03 (Figure S6b). Thus, the α – β phase boundary exists at H(D)/Pd = 0.03.

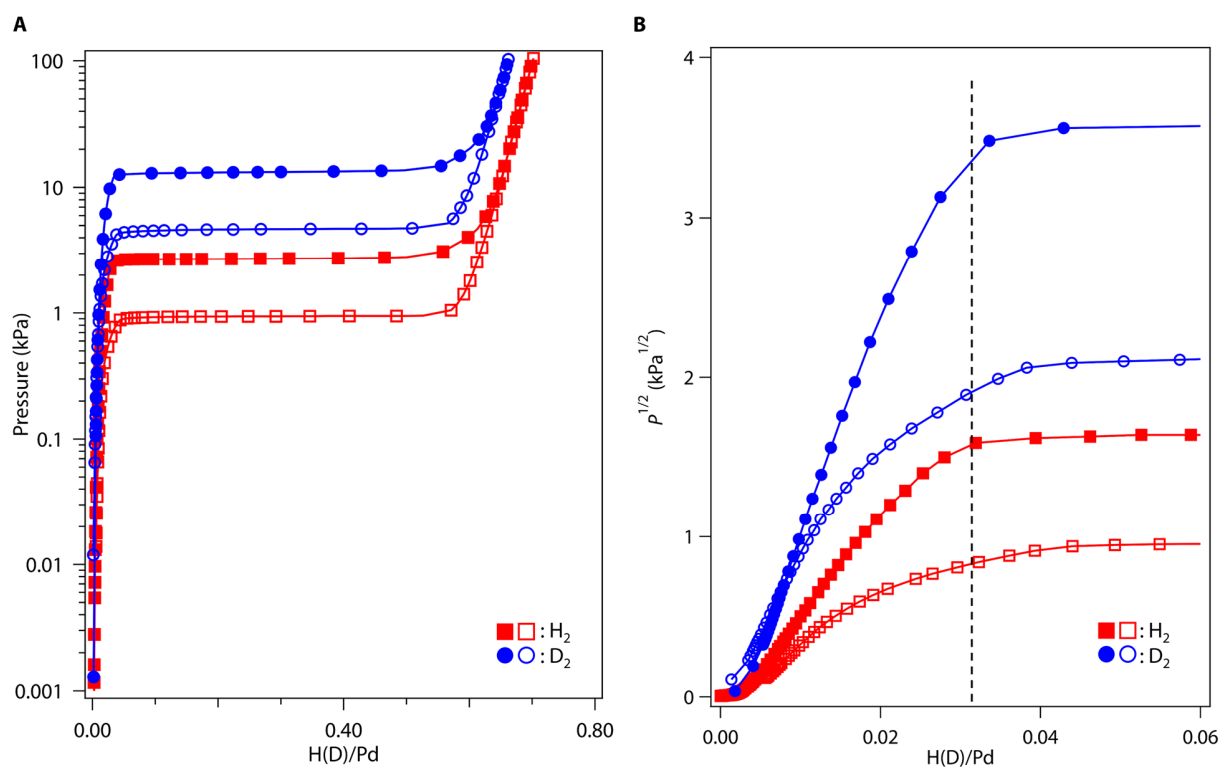


Figure S6. H₂(D₂) pressure–composition isotherms of bulk Pd. (a) H₂ (red squares) and D₂ (blue circles) sorption isotherms measured at 303 K (closed: absorption, open: desorption). (b) The expanded figure in the α -phase region on absorption process. Dashed line shows the α – β phase boundary.

References

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