A Theoretical Study of the In Situ Structural Reconstruction of \( \text{Pd}_n \) \((n = 6, 19, 44)\) Clusters for Catalytic Hydrogen Evolution

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Abstract: How in situ structural reconstructions affect the hydrogen evolution reaction (HER) activity of small Pd clusters is a long-standing problem in the field of heterogeneous catalysis. Herein, we reveal the structural evolution of Pd\(_n\) \((n = 6, 19, 44)\) clusters under the HER environment via stochastic global potential energy surface searching. We theoretically demonstrated that the HER activity of Pd\(_n\) clusters first increases and then decreases under long-term working conditions. The intrinsic nature of these phenomenon includes interior H formations and structural reconstructions caused by the supersaturated adsorption of H atoms. This proves that carefully adjusting the hydrogenation degree of Pd clusters is a good strategy for improving the HER's catalytic performance.

Keywords: hydrogen evolution reaction; palladium cluster; structural reconstruction; density functional theory calculation

1. Introduction

The application of clean hydrogen energy is one of the most promising methods for reducing carbon emissions and for coping with global climate change [1,2]. As a key component of water splitting, catalytic hydrogen evolution reaction (HER, \(2H^+ + 2e^- \rightarrow H_2\)) is critical for the achievement of highly efficient hydrogen production on a large-scale [3–5]. Among all the transition metals, due to the higher energy efficiency and faster kinetics, platinum nanoparticles have long been used as commercial catalysts for this reaction [6,7]. However, in order to develop the hydrogen industry and solve renewable energy problems, finding catalysts with a comparative or superior performance as Pt is still a long-term pursuit [8].

In the past decades, other platinum group elements and their compounds, as catalysts with the most potential to replace platinum, have been widely studied in both theory and experiments [9–12]. Among them, Pd has similar hydrogen adsorption energy with Pt [13], which is a prerequisite for improved HER performance. However, the HER kinetics of Pd is much slower than that of Pt [9,14]. This is generally attributed to the in situ formation of palladium hydride, which suppresses the subsequent hydrogen evolution reaction [14,15]. However, the formation of palladium hydride was also recognized to promote hydrogen evolution kinetics in the recent experimental study of Zou and his coworkers [16]. They reported that Pd nanoparticles with a size of \(~10\) nm achieved the optimum catalytic activity after 130,000 CV cycles, in which the activity is superior to that of initial Pd and even outperformed commercial Pt/C. Thus far, whether the hydrogenation increases or decreases the HER activity of Pd remains quite unclear. Recently, Long and his coworkers used the stochastic collision electrochemistry method to study the HER activity of a single Pd nanoparticle. They observed a 2–5 orders of magnitude enhancement of the HER activity of Pd nanoparticles under different working conditions [17]. Therefore, the critical problem here is to reveal the effect of the in situ reconstruction of Pd clusters on their catalytic performance.
Considering the influences of real reaction conditions on the structure of Pd-based catalysts, the active site’s transformation generally includes changes in size, morphology, and compositions [18,19]. In this paper, we focused on small-sized Pd$_n$ clusters, which are more significantly affected by the reaction environment. The cluster size of Pd$_n$ clusters was selected to be Pd$_6$, Pd$_{19}$, and Pd$_{44}$. Pd$_6$ and Pd$_{19}$ clusters represent the ultra-small sub-nano-sized Pd cluster, and the Pd$_{44}$ cluster corresponds to a Pd nanoparticle with a size of about 1 nm. All these clusters have an octahedral shape and the same face-centered cubic (fcc)-packing mode as bulk Pd. The in situ structural reconstructions of these Pd clusters under HER condition (standard conditions of 1 atm H$_2$ pressure, 298 K) were studied by the stochastic surface walking (SSW) global optimization method [20,21] and grand canonical ensemble Monte Carlo (GCMC) simulations [22]. The HER kinetics was further investigated via first-principle based density functional theory calculations. We revealed that the initial hydrogenation of Pd clusters is helpful for promoting the hydrogen evolution reaction, while the supersaturated surface H atoms adsorbed under HER working conditions will lead to the reconstruction of highly active apex-sites of Pd clusters, which is the intrinsic reason for the reduction in catalytic activity.

2. Calculation Methods

The most stable structures of Pd$_n$H$_m$ ($n = 6, 19, 44$) were determined by Neural Network Stochastic Surface Walking (NN-SSW) [20,21] structure searches. The Hydrogen content and the equilibrium structures were obtained via the grand canonical Monte Carlo (GCMC) simulation [22]. In the GCMC simulations, we evaluate the chemical potential of adsorbed H atom with respect to that of H in the gas phase, $\Delta G_{\text{ad}}$, in Equation (1) based on the current most stable configuration. According to the value $\Delta G_{\text{ad}} < 0$, we will decide to accept or refuse the current most stable configuration:

$$\Delta G_{\text{ad}} = \Delta E_{\text{ad}} + \text{ZPE} - \frac{1}{2} G(\text{H}_2)$$

where $\Delta E_{\text{ad}}$ and ZPE are the differential adsorption energy and the zero-point energy of the newly arrived H atom on the cluster, and $G(\text{H}_2)$ is the free energy of H$_2$ in the gas phase at the standard state.

All density functional theory (DFT) calculations were performed using VASP 6.2.1 packages [23] with projected augmented wave (PAW) pseudo-potentials [24,25]. The exchange-correlation energy was treated based on the generalized gradient approximation (GGA) by using Perdew–Burke–Ernzerhof (PBE) functional [26]. The plane-wave cutoff energy was set to 400 eV. The Monkhorst–Pack scheme with a k-point separation length of 0.05 Å$^{-1}$ was utilized for sampling the first Brillouin zone [27]. Transition states (TSs) were searched using the constrained Broyden-based TS-searching methods [28,29] and the Double-Ended Surface Walking (DESW) method [21]. Liu’s group implemented these TS searching methods and the global optimization methods in a neural-network computing program (LASP, www.lasphub.com, accessed on 1 January 2022). LASP can interface with VASP for all functionalities. All atoms are fully relaxed in the calculations. The Quasi-Newton l-BFGS method is used for geometry relaxation until the maximal force on each degree of freedom is less than 0.05 eV/Å.

To derive the reaction energy profile, the large entropy term of gaseous molecules at 298 K has also been taken into account. We utilize the standard thermodynamic data [30] to obtain the temperature and pressure contributions for the G of the gaseous H$_2$, which is $-0.31$ eV compared to the total energy of the corresponding free molecule (E, 0 K) [31]. The Gibbs free energy change ($\Delta G$) of each reaction step was obtained after ZPE correction. The calculated zero-point energies (ZPE) of different H species are listed in Table S1.
3. Results
3.1. Structure Reconstruction of Pdₙ (n = 6, 19, 44) Clusters under HER Environment

To investigate the structure reconstruction of small Pd clusters, here, we selected the three smallest Pdₙ (n = 6, 19, 44) clusters with octahedral structure as the research object. Firstly, their most stable structures were searched by the SSW-NN global optimization and then determined by the first-principle-based DFT calculations. The effect of surface hydrogen adsorption on the structure of Pdₙ clusters in a real HER environment was further studied by grand canonical ensemble Monte Carlo simulation. The interaction energies (ΔE_int) of PdₙH₂ clusters referring to a single Pd atom and gaseous H₂ molecule are listed in Table S2. Not surprisingly, the hydrogen adsorption and cluster size increase are generally exothermic. As shown in Figure 1, we found that before hydrogen adsorption, the global minimum (GM) structures of all three Pdₙ clusters (low-lying isomers can be found in SI, Figure S1) remain as highly symmetrical (Oₙ) octahedrons. However, with the increase in hydrogen adsorption on the surface, all three clusters finally undergo significant structural reconstruction.

![Figure 1](image-url)  
**Figure 1.** The optimized most stable structures of Pdₙ and PdₙHₘ (n = 6, 19, 44) clusters. (a) Pd₆ and Pd₆H₂; (b) Pd₁₉ and Pd₁₉H₉; (c) Pd₄₄ and Pd₄₄H₁₄. The symmetry group of the Pd sub-structure of each cluster was labeled. The structures of the core Pd atoms of representative Pd₁₉H₉ and Pd₄₄H₁₄ clusters were illustrated in the inserted small squares. The relative formation energies (ΔG_f) relative to the GM of pure Pd cluster and gaseous H₂ are listed at the bottom-right corners of the structure. Dark blue balls: Pd; small white balls: H.
3.1.1. Pd₆

As shown in Figure 1a, we can find that even the initial hydrogen adsorption would lead to the structural distortion of the Pd₆ cluster. The average adsorption energy (ΔG_{ad}) of the first two H atoms is −0.34 eV. These H atoms prefer to adsorb on the opposite edge sites of the Pd₆ octahedron. For such a small Pd cluster, the formation of Pd-H bonds weakens the bonding ability of bonded Pd atoms, which also results in the connection between the top and bottom Pd atoms of the Pd₆ octahedron, and forms a capped trigonal bipyramid structure with C₃v symmetry. In this structure, all Pd atoms are located in three Pd₄ tetrahedrons with shared triangle facets. From Pd₆H₂ to Pd₆H₇, the ΔG_{f} of the cluster decreased to −2.52 eV with the increase in H. In this process, the C₃v structure of the cluster is maintained well, and most adsorbed H atoms are uniformly distributed on bridge sites of the cluster. We noticed that the cluster reaches the equilibrium H adsorption amount on Pd₆H₇ under HER conditions. Furthermore, by adding an H atom into the system, the hydrogen evolution reaction begins to occur on the cluster of Pd₆H₈. The adsorption free energy of the additional H is positively 0.18 eV. Except for the two coupling H atoms reacting on an apex site, all other H atoms sit on the edge sites of Pd₆H₈.

3.1.2. Pd₁₉

Figure 1b shows the most stable structures of the Pd₁₉ cluster with different H adsorption amounts. We can find that the adsorbed H atoms prefer to uniformly adsorb on the 3-fold hollow sites on the surface of the Pd₁₉ octahedron at the initial stage. The average ΔG_{ad} of the first eight H atoms on the Pd₁₉H₈ cluster is −0.68 eV, which is much larger than that on the Pd₆ cluster. With the additional H adsorption, from Pd₁₉H₁₀ to Pd₁₉H₂₂, the structures of Pd clusters were reconstructed into a rod-like structure with D₃d symmetry. To expose more free 3-fold surface sites, the core structure of this rod-like structure turns to be a two-atom dimer. At this stage, the differential H adsorption energy gradually decreased from −0.44 eV to −0.12 eV. The surface H-H coupling on the Pd₁₉ cluster surface was first observed when the H amount reaches Pd₁₉H₂₂, in which the reacting H atoms were located at the apex of one end of the nanorod. If the hydrogen content continues to increase, although the hydrogen adsorption energy becomes slightly positive (0.08 eV), the supersaturated adsorbed hydrogen triggers further structural reconstructions to accommodate more H atoms. During the reconstruction, one of the Pd atoms in the core of the Pd₁₉H₂₂ cluster moves back to the surface in the most stable structures of the Pd₁₉H₂₄ cluster. The ΔG_{f} of Pd₁₉H₂₄ of further reduced to −12.21 eV. This implies that the reconstruction is thermodynamically irreversible under the HER environment. The cluster reached the equilibrium H adsorbed structure under HER conditions at Pd₁₉H₂₈. One subsurface H can be found in the structure of the Pd₁₉H₂₈ cluster. The additional H adsorption energy on Pd₁₉H₂₈ increases to positive 0.26 eV, preventing the subsequent H adsorption.

3.1.3. Pd₄₄

For the cluster of Pd₄₄, as shown in Figure 1c, the most stable structure of the cluster maintained the initial octahedron in a wide range of H content. Similarly to that on the surface of the Pd₁₉ cluster, most surface H atoms are distributed uniformly on the surface 3-fold hollow sites. Increasing the number of H atoms, from Pd₄₄ to Pd₄₄H₅₆, the average H adsorption energy gradually reduced from −0.42 eV to −0.34 eV, which is close to that reported on the Pd single crystal surface [32]. Compared with the smaller Pd₁₉ cluster, the larger Pd₄₄ cluster can accommodate more (up to five) hydrogen atoms into its interior region before it undergoes an obvious structural reconstruction. The first subsurface H was observed after the H content reached Pd₄₄H₄₀. The interior H is located at the center of the [Pd₄] octahedron core of the Pd₄₄ cluster. According to GCMC simulations, the surface H-H coupling on Pd₄₄ starts from Pd₄₄H₄₅, in which the reacting H atoms were located at the apex site of the octahedron. From Pd₄₄H₄₅ to Pd₄₄H₅₆, along with the formation of the H₂ molecule, the number of the subsurface H atoms also increased from one to five. It should
be mentioned that the differential H adsorption energy between Pd$_{44}$H$_{56}$ and the Pd$_{44}$H$_{57}$ (the molecular H$_2$ adsorbed state) is only $-0.09$ eV, which is very close to the ideal H adsorption energy for the HER. This will be discussed in the later parts of this manuscript. Being similar to that of the Pd$_{19}$ cluster, the H content of Pd$_{44}$H$_{56}$ to Pd$_{44}$H$_{60}$ increases, and the supersaturated adsorbed H also results in the thermodynamically irreversible structural reconstruction with a free energy change of $-1.00$ eV. The Pd$_{44}$H$_{60}$ cluster has an ellipsoidal low symmetry (C$_1$) structure, in which three additional H atoms are embedded into the interior of the cluster. To accommodate these newly embedded H atoms, the core Pd structure unit of the Pd$_{44}$H$_{60}$ cluster also transferred from a [Pd$_6$] octahedron to [Pd$_7$]-capped triangular prism. The cluster reaches the equilibrium structure at Pd$_{44}$H$_{61}$ under HER conditions, and the core Pd structure unit finally turned into a [Pd$_7$] double penta-pyramid. Additional H adsorption on the Pd$_{44}$H$_{61}$ cluster could not further reduce the free energy of the cluster, and the number of hydrogen atoms in the cluster remains at 8.

For all the Pd$_n$ clusters, we found the adsorbed H atoms can not only embed into the interior of the clusters but also induce significant structural reconstructions under HER conditions. We also observed that no matter whether the cluster structure is reconstructed or not, the hydrogen evolution reaction can take place on the surface of the Pd$_n$ cluster. Therefore, for the purpose of understanding the HER mechanisms of Pd$_n$ clusters under real reaction conditions, studying how these structural reconstructions affect the catalytic performance is critical.

### 3.2. Effects of Structural Reconstruction on HER Activity

Here, we mainly focused on the cluster of Pd$_{19}$ and Pd$_{44}$, which may have significant structural reconstruction. The possible candidates for the intermediate structure of the Pd$_n$ cluster in the process of in situ structural evolution were selected to study the effect of structural reconstruction on HER catalytic performance. Under the HER conditions, the reaction is most likely to occur when the differential $\Delta G_{ad}$ of hydrogen is close to zero. The number of H atoms in the cluster was, thus, determined by calculating the differential $\Delta G_{ad}$ (see Figure S2) of newly added H atoms.

There are two possible reaction routes for HER: One is the reaction of surface H with a proton (Heyrovsky route: H$_{ad}$ + H$^+$ + e$^-$ → H$_2$), and the other is the coupling of two surfaces H (Tafel route: 2H$_{ad}$ → H$_2$). Our previous studies [33–35] have shown that the Tafel mechanism is a key pathway for platinum group metal-based HER catalysts, and the free energy barrier of H-H coupling ($\Delta G_{H-H}$) is a good indicator for comparing the activities of different HER catalysts. In Figure 2, it shows the reaction profiles of H-H coupling reactions on representative H-adsorbed Pd$_{19}$ and Pd$_{44}$ clusters under reaction conditions. For all these clusters, the reaction takes place between a surface adsorbed hydrogen atom and an additional hydrogen atom adsorbed on the surface with positive $\Delta G_{ad}$. The Volmer step occurs first with one proton from the solution to adsorb on the surface (Sur states) and with a simultaneous electron transfer, $* + H^+ + e^- \rightarrow H^*$, to form an additional H atom adsorbed state (H$_{ad}$). Moreover, this additional H reacts with the nearby surface H to achieve the transition state (TS). The TS is a [H-H] complex nearby the Pd catalytic site with the H-H distance in the range of 0.80–1.40 Å. It should be mentioned that the reaction barriers of the structural reconstruction are generally $-1$ eV higher than the H-H coupling. Therefore, HER will take place preferentially in kinetics, but the reconstruction of the cluster is still possible under long-term reaction conditions. As an example, the reaction profiles of the first structural reconstruction step of the octahedral Pd$_{44}$H$_{60}$ cluster are shown in Figure S3.
For Pd$_{19}$, as shown in Figure 2a, the $\Delta G_{a\mathrm{H\text{-H}}}$ on the rod-like Pd$_{19}$H$_{21}$ cluster is only 0.30 eV, which is much lower than the 0.53 eV on the reconstructed Pd$_{19}$H$_{28}$ cluster. By comparing the free energy of the additional H adsorbed (H$_{\text{ad}}$) state and the transition state (TS), we found that the surface H-H coupling becomes easier when there are more adsorbed H atoms. However, at the same time, the structural reconstruction significantly increased the adsorption energy of the additional adsorbed reacting H atoms (from 0.04 eV to 0.40 eV), resulting in an increase in the overall reaction barrier by 0.23 eV. The structures of the key reaction intermediates can be found in Figure S4. On the cluster of Pd$_{19}$H$_{21}$, the reacting H atoms are located at the 3-fold hollow sites nearby the apex of the cluster. At the TS, the H-H distance is reduced from 2.32 Å to 1.18 Å and eventually forms the molecular H$_2$ at the apex site. On the Pd$_{19}$H$_{28}$ cluster, due to the denser distribution of surface H atoms, the newly adsorbed H atom must share a surface square hollow site with other surface H atoms at the H$_{\text{ad}}$ state. The H-H distance of the reacting H atoms at the H$_{\text{ad}}$ state is 2.27 Å, and then it is reduced to 1.18 Å at the TS. These results clearly show that the reconstruction of Pd$_{19}$ clusters allows the cluster to accept more adsorbed H atoms, but it also leads to a rapid increase in H adsorption energy with the increase in H adsorption and inhibits HER activities.

With respect to the clusters of Pd$_{44}$H$_{m}$, the optimized structures of the reaction intermediates are shown in Figure 3. The reaction processes on Pd$_{44}$H$_{45}$ and Pd$_{44}$H$_{56}$ are very similar. An additional adsorbed H is first adsorbed as the act of the cluster; then, it reacts with the H nearby the apex site. The apex Pd atom bonds with four surface hydrogen atoms. At the TSs, one of the reacting H moves to the top site on the apex of the cluster. The $\Delta G_{\text{ad}}$ of additional adsorbed H on Pd$_{44}$H$_{45}$ is 0.35 eV and the $\Delta G_{a\mathrm{H\text{-H}}}$ on Pd$_{44}$H$_{45}$ is 0.42 eV. It corresponds to the situation that the hydrogen evolution reaction only started to take place on the cluster’s surface. The substructure of Pd maintains the octahedral structure of the Pd$_{44}$ cluster. There are 44 H atoms adsorbed on the cluster’s surface, and only one interior H atom sat at the core of cluster Pd$_{44}$H$_{45}$. The Pd$_{44}$H$_{56}$ cluster corresponds to the H-saturated octahedral Pd$_{44}$. Structurally, the fcc packing mode of Pd clusters and the octahedral shape of the cluster is maintained well in the structure of Pd$_{44}$H$_{56}$. The major difference between the structures of Pd$_{44}$H$_{45}$ and Pd$_{44}$H$_{56}$ is the boosted interior H content (increased from one to eight) of Pd$_{44}$H$_{56}$. From Pd$_{44}$H$_{45}$ to Pd$_{44}$H$_{56}$, due to the expansion of the Pd lattice caused by subsurface H insertion, the number of surface H atoms slightly increased from 44 to 48. On cluster Pd$_{44}$H$_{56}$, the free energy change between the Sur state and H$_{\text{ad}}$ state reduced to 0.13 eV and $\Delta G_{a\mathrm{H\text{-H}}}$ also decreases to 0.27 eV. This clearly shows that the interior H can render additional H adsorptions easier on the Pd

**Figure 2.** The reaction profiles of H-H coupling reactions on H covered Pd$_m$ clusters. (a) On Pd$_{19}$H$_{21}$ and Pd$_{19}$H$_{28}$ clusters. (b) On Pd$_{44}$H$_{45}$, Pd$_{44}$H$_{56}$, and Pd$_{44}$H$_{61}$ clusters. The calculated free energy barriers were also illustrated in the graphs.
cluster with the fcc Pd substructure and, thus, promote the surface H-H coupling. Excess H adsorption on the Pd_{44}H_{56} cluster will lead to the reconstruction of the octahedron structure. After the reconstruction, the energy cost for the additional H adsorption and the H-H coupling on Pd_{44}H_{56} once again increases to 0.29 eV and 0.35 eV, respectively. At the TS, the reacting H atoms are both located at a bridge site on the ellipsoidal cluster surface. The coordination number of Pd atoms at the active center is also higher than that on the clusters without reconstitution.

In summary, the high active sites for HER on these Pd clusters are generally at the apex sites of the cluster. The increase in H content at the interior of the clusters is helpful for reducing barriers to the H-H coupling reaction, while the reconstruction of the Pd substructure will eliminate the highly active sites on the surface of clusters and, thus, inhibit the HER. The calculated ΔG_{a H-H} on Pd_{3}H_{y} clusters are in the range of 0.27~0.53 eV. In contrast, according to our previous study [22], ΔG_{a H-H} on Pt nanoparticles with a size of about 1 nm and crystalline Pt(111) surface is 0.48 eV and 0.78 eV, respectively. The results show that small Pd clusters do have the potential to exhibit outstanding catalytic performance for HER.

4. Discussion

Since the structural reconstruction of the Pd clusters significantly affects their HER activity, we examined the local structural features of the Pd clusters. In Figure 4, we plotted the Pd-Pd distance distribution function of representative Pd clusters at different stages of the in situ structural reconstruction. For comparison, each plot was normalized according to the area of the first Pd-Pd distance peak at ~2.80 Å, which corresponds to the shortest Pd-Pd bond length (L).

At the early stage of HER, the Pd-Pd distance peaks of the octahedral Pd_{44}H_{45} cluster are at 2.80, 3.95, 4.83, 5.58, 6.24, and 6.83 Å, corresponding to 1L, √2L, √3L, 2L, √5L, and √6L (L = 2.80 Å), respectively. Then, as adsorbed H atoms are gradually embedded into the Pd lattice, for Pd_{44}H_{56}, all peaks significantly widened, and the Pd-Pd bond length.

Figure 3. Optimized structures of the key reaction intermediates of HER on Pd_{44}H_{m} (m = 45, 56, 61) clusters. Dark blue balls: Pd; small white balls: surface H; small yellow balls: interior H; small pink balls: reacting H.
increased to 2.84 Å. This reflects that the interior hydrogen atoms weaken Pd-Pd bonds in the cluster, which leads to the lattice expansion of the cluster. Finally, under the working conditions of long-term hydrogen evolution reaction, excess H adsorption will eventually cause the collapse of the Pd\(_{44}\) octahedron. The shape of the Pd\(_{44}H_{61}\) cluster changes from octahedron to quasi-ellipsoid. At this stage, one immediate observation is that the peak around \(\sqrt{2}L\) (\(L = 2.75\) Å) is diminished for Pd\(_{44}H_{61}\). Interestingly, although the cluster contains more interior H atoms, the major peak of the Pd-Pd bond shortened to 2.75 Å. This can be attributed to the transformation of the core structural unit from the rigid [Pd\(_6\)] octahedron to the more flexible [Pd\(_7\)]. Similarly, for the Pt\(_{19}\) clusters, the same attenuation of the \(\sqrt{2}L\) peak also occurs (Figure S5). These structural features are consistent with the structural versatility of small Pd nanoparticles.

![Figure 4. Pd-Pd distance distributions for Pd\(_{44}H_{45}\), Pd\(_{44}H_{56}\), and Pd\(_{44}H_{61}\).](image)

The effects of hydrogenation and in situ reconstruction can be summarized as follows: (i) The early-stage hydrogenation of the Pd cluster can improve HER activity, which is consistent with the experiment that the catalytic performance of HER improves after hydrogen diffuses into the subsurface layer of bulk Pd [16]; (ii) the apex of Pd cluster is the active site for HER. Under long-term HER working conditions, the structural reconstruction allows the adsorption of additional interior H atoms but will reduce the number of surface high active sites, eventually inhibiting the HER activity.

5. Conclusions

In this study, we present a systematic approach to reveal the in situ structural reconstructions of small-sized Pd\(_n\) \((n = 6, 19, 44)\) clusters for catalytic HER. The H adsorption on ultra-small Pd\(_6\) quickly leads to the decomposition of the cluster. For the Pd\(_{19}\) and Pd\(_{44}\), the structural evolution of the Pd clusters undergoes three stages. The H-H coupling can occur at all three stages. The first stage is surface H adsorption. At this stage, H atoms are adsorbed on the surface of the Pd cluster. In the second stage, saturated surface hydrogen atoms gradually enter the interior of the cluster. The Pd lattice is expanded in this stage. Meanwhile, the surface H adsorption energy decreases, which helps improve the HER’s activity. At the last stage, excess H adsorption further results in the substantial reconstruction of the Pd cluster to accommodate more hydrogen atoms. The reduced number of surface high active sites inhibits HER activity. These results reveal the intrinsic properties of the
catalytic performance evolution of small Pd clusters under the HER reaction environment. It proves that carefully adjusting the hydrogenation degree of Pd clusters is a good strategy for improving the HER’s catalytic performance.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/sym14091753/s1, Figure S1: the low-lying isomers; Figure S2: differential H adsorption energies; Figure S3: reaction profiles of the initial structural reconstruction; Figure S4: optimized structures of the key reaction intermediates of HER on Pd$_{11}$H$_{2n}$ ($n = 21$ and 28) clusters; Figure S5: Pd-Pd distance distributions of Pd$_{11}$H$_{6}$, Pd$_{11}$H$_{12}$, and Pd$_{12}$H$_{28}$ clusters; Figure S6: DOS and pDOS of Pd$_{44}$H$_{45}$ and Pd$_{44}$H$_{56}$; Table S1. Calculated zero-point energies of different H species; Table S2. Interaction energies per Pd atom ($\Delta E^{\text{int}}$) of Pd$_{11}$H$_{6}$ clusters and bulk Pd.

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**References**

19. Newton, M.A.; Belver-Coldeira, C.; Martinez-Arias, A.; Fernandez-Garcia, M. Dynamic in situ observation of rapid size and shape change of supported Pd nanoparticles during CO/NO cycling. Nat. Mater. 2007, 6, 528–532. [CrossRef]