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Size effect of Pd clusters on hydrogen adsorption

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Abstract

The size effect of Pd clusters on hydrogen adsorption was investigated by density functional theory calculations. From molecular dynamics simulations, we found that the hydrogen molecules were dissociatively adsorbed on the Pd clusters; the most stable adsorption site was the hollow site. We also found that the adsorption energy increased as the size of Pd clusters decreased. These results were in good agreement with experimental findings. By analyzing the electronic structure, we found that the d-band center shifted toward the Fermi energy as the size of the Pd cluster decreased. This shift resulted in stronger hydrogen bonding.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen adsorption on platinum group metal clusters [1–17] is an important process in fuel cell systems including hydrogen storage and heterogeneous catalysis. In proton exchange membrane fuel cells, platinum (Pt) is the most widely used catalyst. However, carbon monoxide binds more strongly on Pt surfaces than hydrogen. Due to the high adsorption energy for CO on Pt surfaces, CO is hardly removed from Pt catalysts [18]. Therefore, adsorption of CO would reduce the active sites for hydrogen. This is the so-called CO poisoning effect. On the other hand, palladium (Pd) has similar chemical reactivity to Pt but with a weaker binding energy for CO. This difference suggests that taking CO away from a Pd surface would be easier than taking it from a Pt surface. Thus, Pd clusters are an alternative choice as a catalyst, and they have attracted many studies. For example, Pd–H alloy clusters have been suggested as a new type of hydrogen storage material [5–9]. Moreover, Pd cluster-doped carbon material now has a high potential as a hydrogen storage material [2]. The storage of atomic hydrogen in carbon material operates through the spillover mechanism [2–4], which involves several steps: (1) a hydrogen molecule dissociates on a metal cluster, (2) atomic hydrogen migrates from a metal cluster to the carbon surface, and (3) atomic hydrogen diffuses on the carbon surface. Among these steps, it is clear that the dissociative adsorption of hydrogen on a cluster is the major step in the

spillover process. The chemical reactivity of the dissociative adsorption of hydrogen would depend on the size and shape of the cluster. Thus, it is possible to control the activity of the catalyst by changing the cluster's size or shape.

Recently, Huang *et al* [17] have shown that when the diameter of Pd clusters was smaller than 2 nm, the adsorption energy of hydrogen on Pd clusters increased drastically as the size of Pd clusters decreased. To explain this phenomenon, three different kinds of effects have been proposed: (1) special sites at the particle–support interface provide more active sites; (2) the surface atoms have lower average coordination number for smaller particles and thus increased activity; (3) the size effect of the electronic structures, especially the d-orbit of the Pd particles. In order to shed some light on the size effect, we performed systematic studies of hydrogen adsorption on free icosahedral Pd₁₃, Pd₅₅, and Pd₁₄₇ clusters. Hydrogen adsorption on a clean Pd(111) surface was also calculated as a reference. Although the icosahedron is not the most stable structure of a Pd₁₃ cluster [19], its binding energy is very close to the lowest one. Furthermore, icosahedral Pd₅₅ and Pd₁₄₇ clusters were found to be the most stable structures among several highly symmetrical structures [20]. Because the free icosahedral clusters are in atomic shell closure, we could exclude the effects from the support and interface, and minimize the effect of defect sites or special sites of the clusters (e.g., step site, kink site, etc). Using this approach, we were able to focus on the size effect of the Pd clusters themselves.

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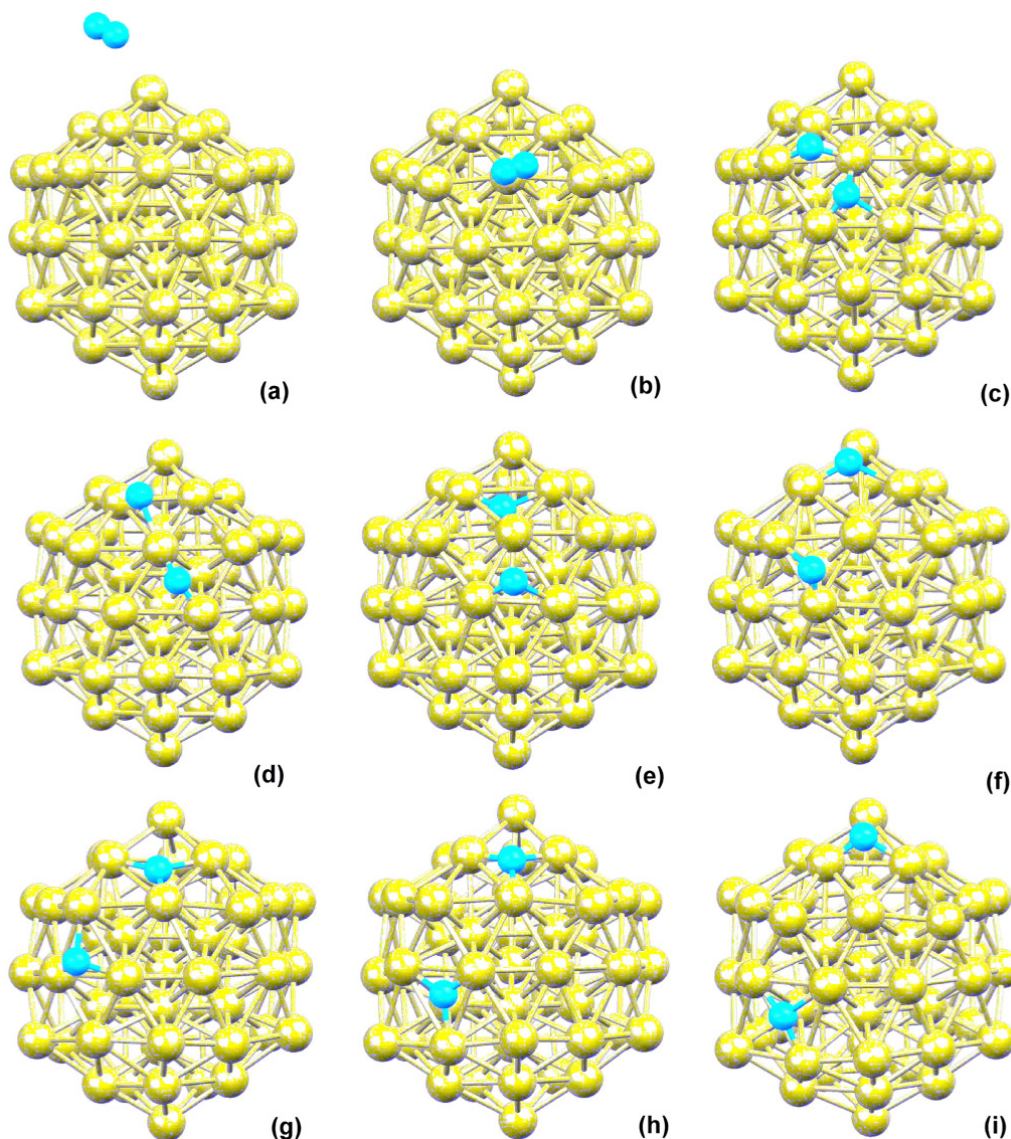


Figure 1. Snapshots of *ab initio* molecular dynamics simulation for the process of dissociative adsorption of hydrogen on an icosahedral Pd₅₅ cluster.

2. Computational details

All the calculations in this study were based on density functional theory (DFT) and were performed using the Vienna *ab initio* simulation package (VASP) [21]. The Kohn–Sham equations were solved using the plane wave basis set with a kinetic energy cutoff of 250.925 eV. For the exchange–correlation functional, we used the spin-polarized generalized gradient approximation [22]. The interactions between the ions and valence electrons were described by the projected augmented wave (PAW) method [23, 24]. The vacuum spaces were more than 10 Å in all calculations to avoid image interactions. The Pd(111) surface was simulated by a repeating slab of six atomic layers (the bottom three layers are kept at the bulk positions) with hexagonal (3 × 3) surface unit cell in the lateral directions. K-point sampling was constructed by a (5 × 5 × 1) Monkhorst–Pack mesh [25] for the Pd(111) surface and only a gamma point for free clusters, respectively.

The structures were fully optimized until the force on each atom was smaller than 0.02 eV Å⁻¹. In order to investigate the dynamical process of hydrogen adsorption on Pd clusters, we carried out finite-temperature ($T = 300$ K) molecular dynamics (MD) simulations. The atomic motion was described by using the Nosé dynamics within a canonical ensemble, and the time step used for integrating the atomic equations of motion was one femtosecond.

3. Results and discussion

Some of the snapshots from the MD simulation for H₂/Pd₅₅ are shown in figure 1. The initial state for MD simulation is shown in figure 1(a), where the hydrogen molecule was initially far away from the Pd₅₅. During the MD runs, the hydrogen molecule moved toward the Pd₅₅ cluster and adsorbed on it as shown in figure 1(b). In figure 1(c), the hydrogen molecule

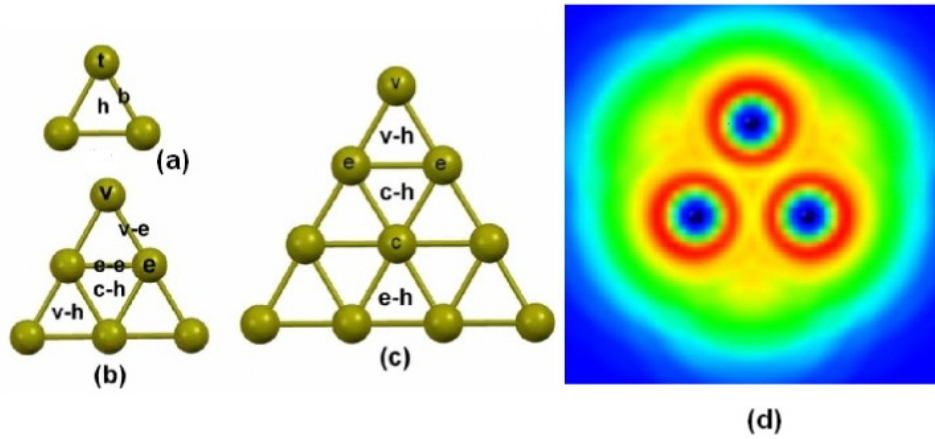


Figure 2. Available adsorption sites for atomic hydrogen on icosahedral (a) Pd₁₃, (b) Pd₅₅, and (c) Pd₁₄₇ clusters. (d) The localized charge density for the Pd₁₃ cluster. Only one of the 20 symmetry equivalent triangular facets on the icosahedron is shown.

Table 1. Adsorption energy (eV) at the atop, bridge, and hollow sites for atomic hydrogen on icosahedral Pd clusters and a Pd(111) surface. The averaged surface Pd–Pd distances ($d_{\text{Pd-Pd}}$) and the H–Pd distances ($d_{\text{H-Pd}}$) at the most stable hollow site are also shown in the last two columns (in units of Å).

Size	Atop	Bridge	Hollow	$d_{\text{Pd-Pd}}$	$d_{\text{H-Pd}}$
Pd ₁₃	—	2.94(b)	3.00(h)	2.79	1.83
Pd ₅₅	—	2.83(v-e)	2.93(v-h), 2.89(c-h)	2.80	1.82
Pd ₁₄₇	—	—	2.85(v-h), 2.85(c-h), 2.90(e-h)	2.81	1.82
Pd(111)	2.32	2.68	2.82(fcc), 2.68(hcp)	2.75	1.82

disassociated into two atomic hydrogens on the cluster. Then, in figures 1(d)–(i), the two atomic hydrogens diffused freely on the surface of the Pd₅₅ cluster and departed from each other. This process is easily understood by the competition bond effect [26]; the two atomic hydrogens repel each other to reduce correlation among adsorbates [27]. Therefore, in the following calculations, we focused on the adsorption energy of atomic hydrogen on Pd clusters and surfaces.

The adsorption energy of atomic hydrogen, E_{ads} , is defined as

$$E_{\text{ads}} = (E(\text{Pd}_n) + E(\text{H})) - E(\text{Pd}_n\text{H}), \quad (1)$$

where $E(\text{Pd}_n)$ refers to the total energy for either Pd_n clusters or Pd(111) slab, $E(\text{Pd}_n\text{H})$ represents the total energy for atomic hydrogen adsorbed on Pd_n clusters or Pd(111) surface, and $E(\text{H})$ is the total energy of a free hydrogen atom. Considering the symmetry of the icosahedral cluster and fcc(111) surface, the adsorption sites could be grouped into atop, bridge, and hollow sites. On the Pd(111) surface, atomic hydrogen preferred the fcc hollow site with the adsorption energy of 2.82 eV (table 1). Our results have also been confirmed by other calculations [28, 29].

For the icosahedral Pd₁₃ cluster, there was one atop (t), one bridge (b), and one hollow site (h) for hydrogen adsorption as shown in figure 2(a). Among these sites, we found that the hollow site was the most stable adsorption site with an adsorption energy of 3.00 eV (table 1), which is consistent with a previous DFT result (2.969 eV) [20]. Moreover, we found that the atop site was not a stable adsorption site for atomic hydrogen, and it would relax to the hollow site or bridge site

with an adsorption energy of 2.94 eV (table 1). This might due to the closed-shell d¹⁰ electronic configuration of Pd. From figure 2(d) (for Pd₁₃) we can see that most of the electrons are localized around the Pd atoms (the red rings) with some charges (orange) distributed at the hollow site as well as the bridge site. Therefore, the hollow site is more stable while the top site is not favored.

On the icosahedral Pd₅₅ cluster, as shown in figure 2(b), there were two kinds of atop sites (on top of the vertex (v) and edge (e) atoms), two kinds of bridge sites (bridge between the vertex and edge atoms (v-e), a bridge between two edge atoms (e-e)), and two kinds of hollow sites (hollow site with a nearby vertex atom (v-h), and hollow site at the center of the three edge atoms (c-h)). In spite of the six different sites shown in figure 2(b) for H/Pd₅₅, we found only three stable adsorption structures: vertex-bridge (v-e), vertex-hollow (v-h), and center-hollow (c-h). The most stable site was the vertex-hollow with an adsorption energy of 2.93 eV (table 1).

There are ten symmetry unrelated sites (three atop, four bridge, and three hollow sites) on icosahedral Pd₁₄₇ clusters. However, based on the results for Pd₁₃, Pd₅₅ clusters and the Pd(111) surface mentioned above, the hollow sites were preferred for hydrogen adsorption rather than the bridge and atop sites. We restricted our attention to the hollow sites. Among the three hollow sites, the edge-hollow (e-h) site (see figure 2(c)) had the highest adsorption energy for atomic hydrogen. All the calculated adsorption energies, the H–Pd distance at the most stable hollow site and the averaged surface Pd–Pd distance are listed in table 1.

In order to compare the experimental results, the dissociative adsorption energy of a hydrogen molecule was

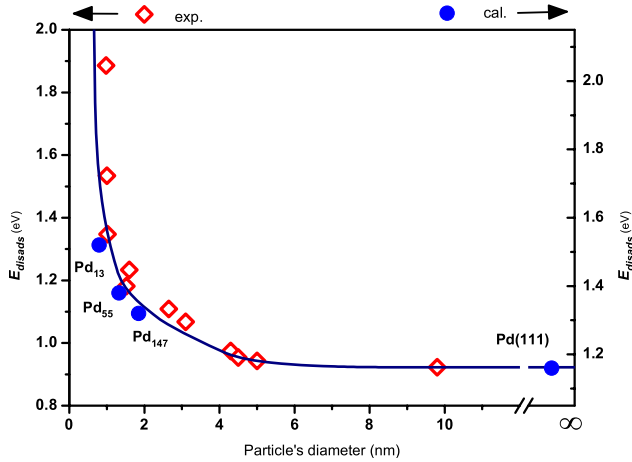


Figure 3. Dissociative adsorption energy as a function of the size of clusters. The experimental data are taken from [17]. The line is a guide for the eye only.

defined as

$$E_{disads} = 2|E_{ads}| - |E_{b,H_2}|, \quad (2)$$

where E_{ads} is the adsorption energy of atomic hydrogen at the most stable site, and E_{b,H_2} is the binding energy of a hydrogen molecule (the calculated binding energy and bond length were 4.48 eV and 0.745 Å). Here, we assumed that the two dissociated hydrogen atoms diffused far away from each other and the competition bond effect could be ignored. Our MD simulation for the dissociative adsorption of the hydrogen molecule on an icosahedral Pd₅₅ cluster supported the assumption.

The theoretical and experimental dissociative adsorption energies as a function of the size of clusters are plotted in figure 3. In this plot, the energy scales for the theoretical and experimental results are on the left and right axes, respectively, and the two axes have the same energy ranges (1.2 eV). As shown in the figure, DFT calculations usually overestimate the adsorption energy on transition metal surfaces. However, the major theme of this study was to find the relative trend of the adsorption energies as a function of the cluster size and to try to understand the physical origin of the trend. As shown in figure 3, the relative trend of the calculated adsorption energies

was in good agreement with the experimental results. For example, when the diameter of the cluster was smaller than 2 nm, the adsorption energy increased sharply as the size of the cluster decreased. Notice that our calculated results were based on free Pd clusters (without support). Therefore, the size effect should mostly come from the clusters themselves. Furthermore, for Pd₅₅ and Pd₁₄₇ clusters, the local geometry of the most stable adsorption site (hollow site) for atomic hydrogen was very similar and had the same coordination number, while the adsorption energy for Pd₅₅ was much higher than Pd₁₄₇. Thus, the size effect of hydrogen adsorption on Pd clusters should mainly come from the electronic structures, especially the d electrons of Pd.

The d-band center model was proposed by Hammer and Nørskov [30] to explain the trend of the catalytic reactivity on the surfaces of many transition metal based catalysts [31–36]. The model suggests that the d-band width of the catalyst could be broadened or narrowed by combination of another kind of metal. Because of the change in the d-band width, the d-band center would shift toward or away from the Fermi energy. If the d-band center moves toward the Fermi energy, the adsorbate binds more strongly on the transition metal surfaces. Recently, by investigating the behavior of oxygen adsorption on the Pd clusters, Tang and Henkelman have shown that the d-band model was not only suitable for surfaces but also for clusters [37]. The d-band center (E_d) and the d-band width (W_d) were described as

$$E_d = \frac{\sum \epsilon D_d(\epsilon)}{\sum D_d(\epsilon)}, \quad (3)$$

$$W_d^2 = \frac{\sum (\epsilon - E_d)^2 D_d(\epsilon)}{\sum D_d(\epsilon)}, \quad (4)$$

respectively, where ϵ is the energy with respect to the Fermi energy (E_f), $D_d(\epsilon)$ is the density of states (DOS) of the d electrons of the surface atoms. The d-band centers of the Pd clusters, the Pd(111) surface and their corresponding root mean square band widths are illustrated in figure 4(a). We can see from this figure that the relationship between the root mean square d-band width and d-band center was almost linear. The d-band width was proportional to the interaction between the d states. By the constant filling of the d-band and a simple rectangle model, the d-band center would shift toward the Fermi energy when the band width was narrowed. The

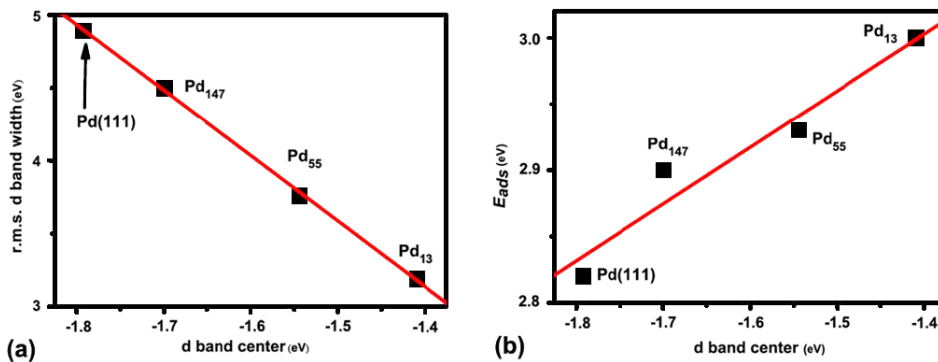


Figure 4. (a) Relationship between the rms d-band width and the d-band center; (b) relationship between the d-band center and the adsorption energy. The lines are a guide for the eye only.

relationship between d-band center and adsorption energy is plotted in figure 4(b). There was a roughly linear relationship between the adsorption energy and the d-band center. The adsorption energy increased as the d-band center shifted toward the Fermi energy. The d-band center moving toward the Fermi energy would cause more d electrons to bind the hydrogen atoms and thus increase the adsorption energy.

4. Conclusions

In conclusion, we have used density functional theory calculations to study the behavior of hydrogen adsorption on free Pd clusters. From *ab initio* molecular dynamics simulations, we found that the hydrogen molecules would dissociate on the Pd clusters. The dissociated hydrogen atoms prefer to adsorb on the hollow sites. The adsorption energy increased as the diameter of the cluster decreased, and the trend was consistent with experimental results. Notice that our calculated results were based on free Pd clusters (without support), and the local geometry of the most stable adsorption site (hollow site) was similar. Therefore, the size effect of the adsorption energy in this study should mainly come from the electronic structures. From the analysis of the d-band model, we found that while the diameter of the Pd cluster decreased, the adsorption energy increased as the d-band center shifted toward the Fermi energy. That is, the d-band center played a significant role for hydrogen adsorption on Pd clusters.

Acknowledgments

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