

# Theoretical Study of Adsorption Site and State for Hydrogen Atom on Pd(311)

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Received: May 15, 2004; In Final Form: September 14, 2004

The adsorption of hydrogen atom on open, rough Pd(311) stepped surface is investigated by the five-parameter Morse potential (5-MP) method in detail. Calculated results demonstrate that the frequency of 62.37 meV (56 meV in a HREELS experiment) is attributed to the vibration parallel to the fcc-like 3-fold site along the [233] direction. The other calculated results are in good accord with HREELS experiments. Meanwhile, we also obtain the critical characteristics of the subsurface adsorption sites.

## 1. Introduction

The (311) surfaces of fcc (face-centered cubic) metals are of special interest for the study of adsorption phenomena, because there are 3-fold as well as 4-fold hollow sites due to the existence of (111) and (100) microfacets that are distributed with equal density through the whole surface. This situation leads to an interesting competition in the case of adsorbates such as hydrogen or oxygen, which are known to prefer adsorption in the high coordination sites to optimize the H-metal bond.

About the system H/Pd(311),<sup>1–4</sup> experimental scientists have made plenty of investigations to ascertain the adsorption states of hydrogen atoms. In 1996, Farias et al.<sup>1</sup> studied hydrogen adsorption on Pd(311) by He-diffraction experiments and detected the formation of (2×1)H, (2×1)2H, (2×1)3H, and c(1×1) phases with coverage of 0.25, 0.50, 0.75, and 1 monolayer (ML), respectively. However, whether 3- or 4-fold hollow sites were occupied was undetermined. Later, they made further investigations<sup>2</sup> and assumed that in all four ordered phases the hydrogen atoms occupied the same kind of adsorption sites, 3-fold hollow sites, and the disorder of the layers led to the occupation of the 4-fold hollow sites only for coverage larger than 0.5 ML.

Recently,<sup>3,4</sup> they concluded that the first two phases—(2×1)H and (2×1)2H—mainly occupied the 4-fold sites and found hydrogen atoms led to two kinds of adsorption sites—3-fold and 4-fold—by means of high-resolution electron energy loss spectroscopy (HREELS) with increasing the coverage ( $\theta > 0.5$  ML). For hydrogen chemisorption, there existed studies on the similar system of H/Rh(311).<sup>5,6</sup> In these papers, Rieder et al. found that H adsorbed on Rh(311) on 3-fold coordinated site, in contrast to adsorption on Pd(311).

Recently,<sup>7</sup> we have studied the adsorption for hydrogen atom on Pd(311) above the topmost layer and have not found 4-fold hollow site and subsurface sites. In this work, we present a further study on the H/Pd(311) system using the five-parameter Morse potential (5-MP) method again. And we find not only a 4-fold adsorption site, which is below the topmost layer, but

also subsurface sites. In our previous work, we discovered the oxygen atom adsorbed on the 4-fold site above the topmost layer on Pd(311) surface, and 3-fold sites are annihilated.<sup>8</sup> That is in good agreement with experiment.<sup>9</sup> The 5-MP method adopted in this paper has been successfully used in the investigations of O-Cu;<sup>10</sup> O-Ni<sup>11</sup> low index surface; and O-Cu(211), -(410),<sup>10</sup> O-Ni(510), -(115),<sup>11</sup> and O-Cu(311)<sup>12</sup> stepped surface systems, and we obtained the good results that agreed well with the experimental data.

## 2. Theoretical Calculated Method and Surface Cluster Model

**2.1. Theoretical Calculated Method—5-MP.** The 5-MP method has been introduced in detail in refs 10–12. Briefly, on the assumption that the metal cluster is frozen, the interaction energy  $U(\vec{R})$  between an adsorbed atom and the whole metal surface cluster can be written with the following equation

$$U(\vec{R}) = D \sum_{i=1}^{\text{cluster}} \left( \frac{h_i + Q_1}{R_i + Q_2} \right) \{ \exp[-2\beta(R_i - R_0)] - 2 \exp[-\beta(R_i - R_0)] \}$$

where  $\vec{R}$  and  $\vec{r}_i$  specify the coordinate of adsorbed atom and the  $i$ th metal surface atom, respectively.  $R_i$  is the distance between the atom and the  $i$ th metal surface atom and is denoted as  $R_i = |\vec{R} - \vec{r}_i|$ .  $h_i$  is the vertical distance between the atom and the surface where the  $i$ th metal atom is.

The summation runs over all the atoms of the metal surface cluster and the potential function  $U(\vec{R})$  we have constructed only consists of five parameters:  $D$ ,  $\beta$ ,  $R_0$ ,  $Q_1$ , and  $Q_2$ . The main characteristic of 5-MP is that the parameters are independent of surface cluster structure; that is, the 5-MP theory is applicable not only to adsorption systems of low-index surfaces but also to the stepped surfaces. Once the parameters are ascertained, the analytical 5-MP of the corresponding system is constructed successfully.

Note that TDS data<sup>3</sup> suggested that no pairing-row reconstruction was induced by hydrogen on Pd(311), at least not at coverage  $< 1$  ML. And the work function measurement<sup>3</sup> also

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**TABLE 1: Five Parameters of the H–Pd System<sup>14</sup>**

| system | $D/\text{eV}$ | $\beta/\text{\AA}^{-1}$ | $R_0/\text{\AA}$ | $Q_1/\text{\AA}$ | $Q_2/\text{\AA}$ |
|--------|---------------|-------------------------|------------------|------------------|------------------|
| H–Pd   | 1.1306        | 1.70                    | 1.74             | 0.4565           | 0.225            |

indicated that the dipole moment remained constant until the final hydrogen structure was completed, which strongly suggested that the substrate remained unreconstructed while hydrogen adsorbed on the surface. So the frozen approximation we employ in this paper is reasonable.

In the investigations of H–Pd low-index surface systems, we have determined five optimum parameters, as shown in Table 1. Parts of the calculated results are listed in Table 2. And good results in agreement with experiments are obtained as shown in Table 3.

In this paper we will make a further study on the H–Pd(311) system using the same set of parameters. We determine critical points according to  $\lambda$ , which denotes the number of the negative eigenvalues from the Hessian matrix and can be used to represent the critical characteristics of potential energy surfaces. In the atom–surface adsorption system, there are three kinds of critical points corresponding to different  $\lambda$  values. Among them,  $\lambda = 0$  corresponds to the surface adsorption state for adsorbed atoms,  $\lambda = 1$  corresponds to the surface diffusion transitional state, and  $\lambda = 2$  corresponds to the surface diffusion maximum point.

**2.2. Surface Cluster Model.** Considering the local geometrical symmetry in a point group and the displacement symmetry for a surface crystal cell as well as the boundary effect of adatoms, we simulate the metal cluster with at least 10 layers of cell atoms, and each layer contains at least 10 (length)  $\times$  10 (wide) atoms. Figure 1 shows a schematic diagram of the surface cluster model and surface adsorption sites of Pd(311) stepped surface. Here,  $H_f$  and  $H_h$  represent the two nonequivalent fcc- and hcp (hexagonal-close packed)-like 3-fold adsorption sites and  $H_4$  represents the 4-fold hollow site. The top sites on the top layer and on the second layer are denoted by T and T' and the two bridge sites in the (100) facet denoted by B and B'. Figure 2 is the sketch map of adsorption sites of hydrogen atom on the Pd(311) stepped surface.  $H_1$  represents the tetrahedral subsurface site below the 2-fold bridge site and  $H_2$  represents the octahedral subsurface site between the second and third layers below the pseudo-4-fold site. To show the subsurface sites clearly, we cut two Pd atoms in the topmost layer, which are over the subsurface sites (see Figure 2).

### 3. Calculation Results and Analysis

Systemic investigations were conducted using the 5-MP method on the adsorption systems for the hydrogen atoms on Pd(311) stepped surfaces and obtained the whole critical characteristics shown in Table 2. There,  $N$  denotes the coordinated number of the adsorbed hydrogen atom at critical points.  $E_b, f, R_{H-Pd}$ , and  $h$  denote binding energies, vibration frequencies ( $\parallel, \perp$  denote parallel vibration and perpendicular vibration, respectively), bond length to nearest neighboring metal atoms, and the vertical distance between the adsorbed hydrogen atom and the cluster surface, respectively.

The (311) surface of the fcc metal is a rough and open stepped plane, and the crystal cell of the Pd(311) surface exhibits  $C_3$  local geometrical symmetry. There are eight kinds of non-equivalent critical points on the surface (see Figure 3). Among them, both 3-fold  $H_f$  and  $H_h$  as well as 4-fold states are surface adsorption states with  $\lambda = 0$ . The difference between the critical characteristics of the two 3-fold states is very small but can be distinguished by vibration frequencies. T and T' are the surface diffusion maximum points with  $\lambda = 2$ . B and B' are the surface diffusion transitional states with  $\lambda = 1$ . And S is the surface diffusion transitional state between the two 3-fold adsorption states  $H_f$  and  $H_h$  with  $\lambda = 1$ . Due to the existence of the competition between the 4- and 3-fold sites, the 4-fold site of the Pd(311) stepped surface is much different from the one of the Pd(100) plane, and it is below the topmost layer. The critical characteristics of the fcc-like 3-fold site also show some changes, especially the parallel vibration frequency along the  $[2\bar{3}3]$  direction in contrast to the fcc-like 3-fold site of the (111) plane. As to the hcp-like 3-fold site, such an effect is small, and the critical characteristics of this site are almost the same as those of the (111) surface. The adsorption geometries of the hydrogen atom on the three adsorption sites are shown in Figure 2.

Our calculations show that the frequency of  $\sim 82$  meV is the vibration parallel to the 4-fold site, and the frequencies of 90–96 and 117.35, 121.86 meV are the parallel and perpendicular vibration in 3-fold sites, respectively. These are well in accord with the experiments by Farias et al.<sup>3</sup> However, as to the adsorption of 56 meV that corresponds to 62.37 meV in this paper, there are some disparate ideas. Nicol<sup>13</sup> assigned a mode at 58 meV observed in his experiment to subsurface hydrogen. But Schilbe et al.<sup>4</sup> thought the peak at 56 meV resulted from hydrogen in a 4-fold site. Later, in their HREELS experiment,<sup>3</sup> they found that above 0.3 layer the peaks at 80 and 96 meV

**TABLE 2: Critical Characteristics of the H–Pd(311) System**

| system                  | site  | N | $\lambda$ | $E_b/\text{eV}$ | $f/\text{meV}$   |         | $R(\text{H–Pd})/\text{\AA}$                | $h/\text{\AA}$ |
|-------------------------|-------|---|-----------|-----------------|------------------|---------|--|----------------|
|                         |       |   |           |                 | $\parallel$      | $\perp$ |  |                |
| H–Pd(311)               | $H_4$ | 5 | 0         | 3.86            | 82.84<br>82.98   | 216.00  | $1.84 \times 2, 2.10 \times 2, 1.68$       | –0.76          |
|                         | $H_f$ | 3 | 0         | 2.67            | 62.37<br>96.10   | 117.35  | $1.87 \times 3$                            | 0.08           |
|                         | $H_h$ | 3 | 0         | 2.65            | 91.19<br>90.20   | 121.86  | $1.82 \times 2, 1.85$                      | 0.42           |
|                         | $H_1$ | 4 | 0         | 4.01            | 148.27<br>151.75 | 227.46  | $1.72 \times 2, 1.65 \times 2$             | –0.93          |
|                         | $H_2$ | 6 | 0         | 4.91            | 93.24<br>87.51   | 160.98  | $1.98 \times 2, 1.91 \times 2, 1.99, 1.90$ | –1.83          |
|                         | S     | 2 | 1         | 2.54            | 107.62           | 153.90  | 1.75, 1.79                                 | 0.39           |
|                         | B     | 2 | 1         | 2.30            | 144.52           | 117.02  | $1.73 \times 2$                            | 0.78           |
|                         | B'    | 2 | 1         | 2.43            | 96.41            | 157.67  | 1.77, 1.76                                 | 0.41           |
|                         | T     | 1 | 2         | 1.75            |                  | 198.11  | 1.68                                       | 1.59           |
|                         | T'    | 1 | 2         | 2.33            |                  | 188.15  | 1.72                                       | 0.54           |
|                         | H     | 4 | 0         | 2.71            | $52 \times 2$    | 69      | $2.01 \times 4$                            |                |
|                         | H     | 3 | 0         | 2.86            | $95 \times 2$    | 119     | $1.86 \times 3$                            |                |
| H–Pd(111) <sup>14</sup> | H'    | 3 | 0         | 2.88            | $98 \times 2$    | 117     | $1.85 \times 3$                            |                |

**TABLE 3: Comparison between the Experiments and the Calculations**

| system                | site                   | $f/\text{meV}$                         |                |
|-----------------------|------------------------|--|----------------|
|                       |                        | exptl data                             | this work      |
| Pd(100) <sup>15</sup> | H $\perp$              | 64 <sup>16,17</sup>                    | 69             |
| Pd(110) <sup>15</sup> | H <sub>3</sub> $\perp$ | 120 <sup>18</sup>                      | 124            |
|                       | LB $\perp$             | 98 <sup>18</sup>                       | 102            |
| Pd(111) <sup>15</sup> | H $\parallel$          | 96, <sup>19</sup> 94, <sup>520</sup>   | 95, 98         |
|                       | H $\perp$              | 124, <sup>19</sup> 120.7 <sup>20</sup> | 119, 117       |
| Pd(311)               | H <sub>3</sub>         | 90–94                                  | 90–96          |
|                       |                        | 120–126 <sup>3,4</sup>                 | 117–121, 62.37 |
|                       | H <sub>4</sub>         | 50–85 <sup>3,4</sup>                   | ~82, 216       |

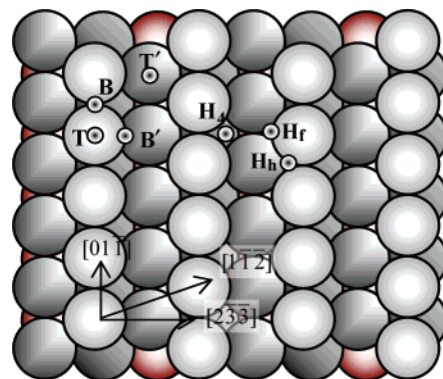
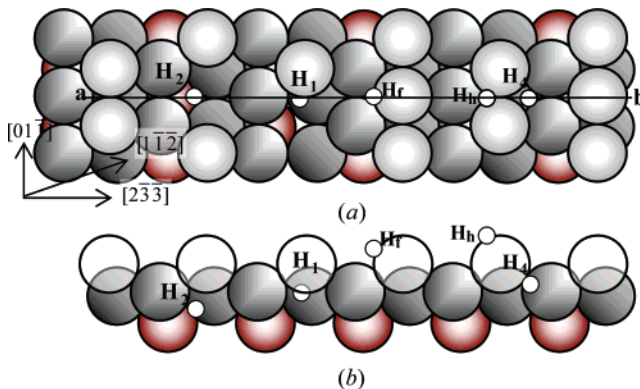
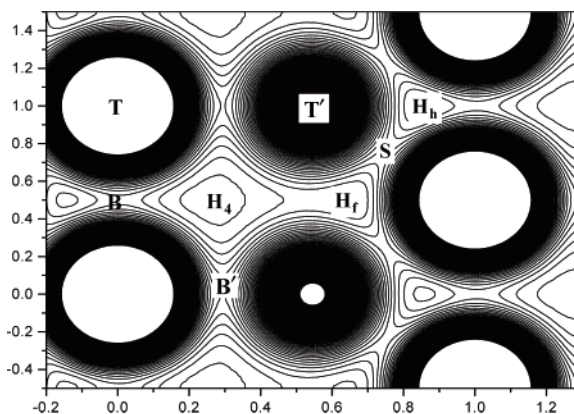
moved closer together so that they were not well resolved, but the peak at 56 meV could be seen in all off-specular spectra for almost all exposures. The peaks at 50–56 and 85 meV should therefore not result from hydrogen in the same site. On the other hand, the peak at 50–56 meV had the same or even a higher intensity as the other hydrogen peaks from the HREELS results, and it was in contradiction with the expectation that peaks from subsurface vibrations should have low intensity. Our calculated results indicate that the frequency of 62.37 meV (56 meV in the HREELS experiment) corresponds to the parallel vibration in the fcc-like 3-fold site along the  $[2\bar{3}3]$  direction.

In addition, we also find two different highly coordinated subsurface adsorption states with  $\lambda = 0$  (i.e., the tetrahedral state H<sub>t</sub> and the octahedral state H<sub>o</sub>). Such results support the conclusion from the HREELS experiment.<sup>3</sup> The adsorption geometries of the two adsorption states have been shown in Figure 2.

In the octahedral subsurface site, we obtain the perpendicular vibrational frequency of 160.98 meV and two parallel vibrational frequencies of 93.24 and 87.51 meV. In the tetrahedral subsurface site, the perpendicular vibrational frequency is 227.46 meV and the two parallel vibrational frequencies are 148.27 and 151.75 meV.

On the basis of our calculated results, which are in good agreement with the HREELS experimental results.<sup>3</sup> The adsorption mechanism could be speculated as follows: a hydrogen molecule dissociates directly on the Pd(311) surface, and the dissociative atoms tend to adsorb in the most stable site. From Table 2, we can see the adsorption energy values for the octahedral subsurface site and the tetrahedral site are the lowest (i.e., 4.91 eV for octahedral site and 4.01 eV for tetrahedral site). From this viewpoint, the subsurface sites should be preferred. However, the channels of the hydrogen atom migrating into the subsurface sites are devious. So we conclude that dissociative hydrogen atoms will mainly occupy the 4-fold hollow surface sites at low coverage. And because the H<sub>4</sub> site of Pd(311) surface is under the topmost layer and actually is a five-coordinated site, its perpendicular vibration is high in frequency and low in intensity. Therefore, the peak at 216 meV is possible to ignore by experiment. We expect that it is observed in the new experiment. With increasing coverage, 3-fold sites are also occupied. Due to the influence of the adjacent 4-fold site, the parallel vibration energy of the H<sub>f</sub> site declines to 62.37 meV (corresponding to the 56 meV in experiment) along the  $[2\bar{3}3]$  direction, whereas the perpendicular one as well as parallel one along the  $[01\bar{1}]$  direction are familiar with the (111) surface.

To analyze visually our calculated results, we scan the potential energy surface (PES) contour figure of adsorption and diffusion of hydrogen atom on the Pd(311) surface at the height of 0.3 Å under the surface, as shown in Figure 3. The surface positions and characteristics of seven nonequivalent critical points are clearly labeled on it. From the PES, one can see that

**Figure 1.** Cluster model and adsorption sites for (311) stepped surface.**Figure 2.** The sketch map of adsorption sites of hydrogen atom: (a) top view, (b) side view along the line of  $a-b$ ;  $\circ$  represents the hydrogen atom.**Figure 3.** PES sketch map for adsorption and diffusion of hydrogen atom on Pd(311) at the height of 0.3 Å under the topmost layers.

there are more rumples between H<sub>h</sub> and H<sub>4</sub> than between H<sub>f</sub> and H<sub>4</sub>. Namely, the diffusion between H<sub>f</sub> and H<sub>4</sub> is much easier.

#### 4. Conclusions

The adsorption and diffusion of hydrogen atom on open, rough Pd(311) stepped surface are investigated in detail using the 5-MP method. Our theoretical results suggest the following.

(1) There are 3-fold as well as 4-fold hollows as possible surface adsorption sites. From the binding energy we demonstrate that the 4-fold site is the most stable adsorption site for hydrogen atom adsorption on Pd(311) surface and it is dominantly occupied at low coverage. With the coverage increasing, 3-fold sites are also occupied. These are in accord with recent experiment studies.<sup>3</sup> The frequencies of ~82 and 216 meV associate with the parallel and perpendicular vibrations in the

4-fold site and the frequencies of  $\sim 90$  and  $121$  meV are the vibrations parallel and perpendicular to the  $H_h$  site.

(2) Owing to the influence of the neighbor 4-fold site, the parallel vibration energy in the  $H_f$  site falls to  $62.37$  meV along the  $[2\bar{3}3]$  direction, but the perpendicular one as well as the parallel one along the  $[01\bar{1}]$  direction is familiar with the (111) surface.

(3) We also find two subsurface adsorption sites. One is the octahedral site between the second and third layers below the pseudo-4-fold site; the other is the tetrahedral site below the 2-fold bridge site. And these are in favor of the conclusion by Farias et al. in ref 3.

The existence of the subsurface hydrogen atoms should influence some characteristics of surface sites, but how large is the influence? From our present data we cannot estimate. In future work, we will make a further investigation.

**Acknowledgment.** We express our thanks to the Community of Shandong Nature Science Foundation (No. Y2002B09) for their support.

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