

## Oxygen Atom Adsorption and Diffusion on Pd Low-index Surfaces and (311) Stepped Surface

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The 5-parameter Morse potential (5-MP for short) of the interaction system between an oxygen atom and palladium surface clusters was constructed. The adsorption and diffusion of an oxygen atom on low index surfaces Pd (100), Pd (111), Pd (110) and Pd (311) stepped surface were investigated in detail with 5-MP. It is found that fcc and hcp sites on the (111) surface and (111) microfacets are equivalent. The calculation results show that O atom adsorbs in the three-fold hollow site, and the long-bridge site is a stable site both in regular Pd (110) surface and in the (1×2) missing-row reconstruction structure. Moreover, in the study of O-Pd (311) surface system, We conclude that there are two stable adsorption states (four-fold site:  $H_4$ , three-fold site:  $H_h$ ) on O-Pd (311) surface and the three-fold site ( $H_f$ ) is the metastable adsorption. At low coverage oxygen atom favors the four-fold hollow site ( $H_4$ ).

**Keywords**      5-MP, O adsorption on Pd surface, step defect surface, O/Pd (311) system

### Introduction

Atom adsorption on transition metal surfaces has attracted special attention as a base for understanding the fundamental processes of oxidative catalysis. Particularly interesting is the adsorption and diffusion of oxygen on well-defined metal surfaces. An oxygen covered palladium surface, for example, plays a central role in several important reactions such as oxidation of carbon monoxide and ammonia. In particular, the (100), (111), (110) surfaces and the interactions with oxygen have been studied extensively with many surface science techniques.

About O-Pd (100) system, several authors have suggested that oxygen atoms located in the four-fold site,<sup>1,4,9</sup> and observed the reconstructed Pd (100)–( $\sqrt{5} \times \sqrt{5}$ ) R27°–O structure.<sup>10,11</sup> The Pd atoms tightly array in Pd (111), which makes the Pd (111) is the most tranquil in the Pd low-index surface. Oxygen adsorption and diffusion on Pd (111) attract more interest.<sup>12-19</sup> Steltenpohl and Memmel have reported scanning tunneling microscopy and low-energy ion scattering studies of adsorption of atomic oxygen on Pd (111).<sup>13</sup> According to their analysis the hcp site is the preferred adsorption site. The experimental<sup>15,17-19</sup> and theoretical<sup>14,16</sup> results show that the fcc site is the most favorable one. The surface phase of oxygen on Pd (110) exhibits considerable complexity, which has attracted special attention for understanding the adsorption of oxygen on the (110) surface.<sup>20-28</sup> Yagi *et al.*<sup>21</sup> assigned oxygen atoms to be located in the fcc (111) sites to form Pd-O zig-zag chains along the  $[\bar{1}10]$  rows. Therefore, the

result could not be reconciled to the long-bridge adsorption site.<sup>20</sup> The high-temperature oxygen exposure phase of  $c(2 \times 4)$  with its half-monolayer oxygen coverage was suggested to consist of  $[\bar{1}10]$  added rows of Pd atoms with two oxygen atoms adsorbed in the upper-layer hcp (111) sites per every other Pd atom.<sup>23</sup> Zig-zag chains of oxygen atoms located in second-layer fcc (111) sites might also be populated at low temperature oxygen exposure. The oxygen atoms were also observed in the fcc sites on the Pd (110)  $c(2 \times 4)$ –O phase and the Pd (1×3) missing-row reconstruction surface. Although the missing-row nature of these reconstructions has been confirmed by the STM,<sup>24,25</sup> the local location of oxygen adatoms is a controversial problem.

Though the adsorption of oxygen on palladium surfaces has been intensively investigated in the last several decades, it is lacking of investigation about the more “open” Pd (311). The structure of O adsorbed at transition metal surfaces is an interesting topic. It is well known that O preferentially adsorbs at the highest-coordinated site available on the surface. For example, It adsorbs at the fourfold sites of fcc (100)<sup>2,3</sup> surfaces and at the threefold sites of fcc (111)<sup>12-17</sup> surface. These surfaces contain only one kind of high-coordinated site, whereas some open surfaces offer both threefold and fourfold sites. The question arises then at which site the adsorption occurs. Farías<sup>29</sup> was interested in the more open and rough Pd (311) surface. They made a study of the interaction of oxygen with a Pd (311) surface by means of He diffraction and thermal

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desorption spectroscopy (TDS). The formation of a  $(2 \times 4)$ pg structure was observed, and the existence of zig-zag chains on Pd (311) would require the occupation of three- as well as four-fold sites. But they could not conclude whether the O atoms occupied three-fold or four-fold hollows when forming the  $(2 \times 4)$ pg phase on Pd (311).

From the information above we can see that an entire study about the characteristics of critical points including some specialities should be carried out so as to thoroughly understand the interaction of the O-Pd surface system. In order to achieve the purpose, the five-parameter Morse potential (5-MP) method was put forward which has been performed on H—Ni,<sup>30</sup> C—Ni,<sup>31</sup> N—Ni<sup>32</sup> and O, CO—Ni<sup>33</sup> surface systems recently. Here, we study further the low-index surface system of O-Pd and the stepped surface system of O-Pd (311) using the 5-MP and obtain the characteristics of all the critical points.

## Calculation method and model of surface clusters

### 5-MP

It is assumed that the metal cluster is frozen, namely the metal atoms of the surface layer are fixed, and the approximation is adopted for the whole surface cluster. So the interaction energy  $U_i(\bar{R})$  between an adsorbed atom (its coordinate is specified by  $\bar{R}$ ) and the  $i$ -th atom in the metal surface cluster (its coordinate is specified by  $\bar{r}_i$ ) can be written in the following form of Morse function:

$$U_i(\bar{R}) = D_i \left\{ \exp[-2\beta(R_i - R_0)] - 2\exp[-\beta(R_i - R_0)] \right\} \quad (1)$$

In Eq. (1),  $R_i$  is the distance between the adsorbed atom and the  $i$ -th atom in the surface cluster, namely,  $R_i = |\bar{R} - \bar{r}_i|$ ,  $\beta$ ,  $R_0$  are the parameters for vibration and equilibrium distance respectively.  $D_i$  is binding energy and can be described as:

$$D_i = D \left( \frac{h_i + Q_1}{R_i + Q_2} \right) \quad (2)$$

where,  $D$  is a simulating energy parameter,  $h_i$  is the vertical distance between the adsorbed atom and the surface where the  $i$ -th metal atom lies,  $Q_1$  and  $Q_2$  are two simulating parameters. We employ such a method to deal with the binding energy in order to take account of the orientation effect of d electrons of transition metals.

So the total potential energy  $V(\bar{R})$  for the adsorbed atom and the whole surface cluster constructed by  $n$  metal atoms can be expressed as the sum of pair-potential  $U_i(\bar{R})$  as follows:

$$V(\bar{R}) = \sum_{i=1}^n U_i(\bar{R}) \quad (3)$$

We have constructed that the potential function  $V(\bar{R})$  consists of only 5 parameters:  $D$ ,  $\beta$ ,  $R_0$ ,  $Q_1$  and  $Q_2$ . Apparently,  $V(\bar{R})$  is closely relative to the metallic surface structure.

An adatom has three degrees of freedom when it moves on the cluster surface. The 5-MP  $V(\bar{R})$  gives out a potential hypersurface of four-dimensionality. The second derivative of  $V(\bar{R})$  with respect to  $\bar{R}$  in the critical point composes a Hessian matrix of  $3 \times 3$  dimensionality. Then there are four kinds of critical points for the potential hypersurface. We apply the number of negative eigenvalues of Hessian, and denote as  $\lambda$  to characterize the nature of critical points. The critical point of  $\lambda=0$  is the minimum point corresponding to atomic surface adsorption state. The one of  $\lambda=1$  is the saddle point which corresponds to surface diffusion transitional state. The one of  $\lambda=2$  or  $\lambda=3$  is the maximum point, and the one of  $\lambda=2$  corresponds to surface diffusion maximum point (the case of  $\lambda=3$  does not exist on the cluster surface). Namely, our calculation can directly give out the adsorption state, transitional state *etc.* for the adatom on the cluster surface by  $\lambda$  of critical points. Moreover, eigenvalues from Hessian matrix are relevant to the frequency and model of vibration for the adatom on the cluster surface. And, the adsorption geometry is also determined by the information of adsorption state.

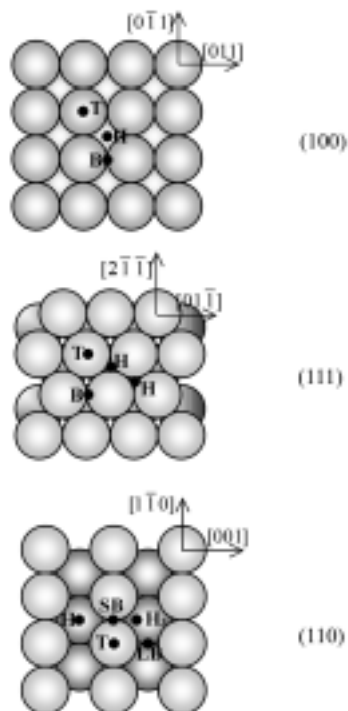
The key step is how to adjust the parameters. We employed the experimental data of three low index palladium surfaces (100), (111) and (110) to adjust the five parameters at the same time. And so the kinetic characteristics of adsorption for the adatom on three low index palladium surfaces can be recurred through our theoretical method, such as the adsorption sites, adsorption geometry, binding energy, eigenvibration and so on. Obviously, the potential function  $V(\bar{R})$  constructed by the optimum seeking parameters may be applicable to deal with the atom adsorption system on low-index palladium surfaces (100), (111) and (110). Further more  $V(\bar{R})$  is also applicable to the adsorption system on the stepped surfaces that are constructed of low index surfaces mentioned above. In fact,  $V(\bar{R})$  (called 5-MP) is the potential function of the interaction between the adatom and surface cluster. The main characteristic of 5-MP is independent of structure for the surface clusters.

### Cluster models for palladium surfaces

Metal palladium belongs to fcc lattice with the lattice constant  $a_0 = 0.3883$  nm. Considering both the local geometrical symmetry in a point group for a surface cluster cell and the whole surface lattice displacement symmetry, we simulate the Pd surface cluster with at least 5 (high) layers of cell atoms and every layer contains at least 6 (length)  $\times$  6 (wide) atoms, which contains about 400—500 palladium atoms. The

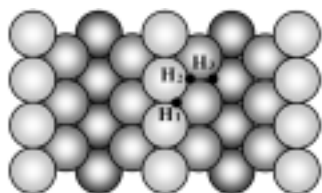
size of the cluster is defined by the principle that there is no boundary effect in our calculation.

Figure 1 shows cluster models and adsorption sites (dark dots) for the three low-index surfaces of Pd (100), Pd (111) and Pd (110). The adsorption sites are denoted the hollow site (H), bridge site (B) and top site (T) for Pd (100) surface; fcc hollow site (H) and hcp hollow site (H') for Pd (111) surface; the pseudo-3-fold hollow site (H<sub>3</sub>), long-bridge site (LB), short-bridge site (SB) and the transitional state (S) between LB and H<sub>3</sub> for Pd (110) surface, respectively.



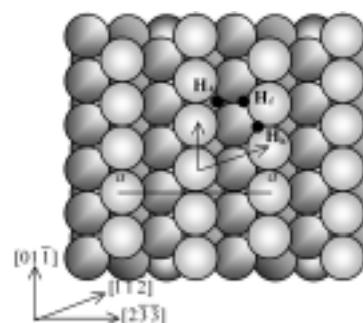
**Figure 1** Cluster models and adsorption sites for low index surface.

Figure 2 shows the cluster model and adsorption sites for the (1×2) missing-row reconstructed structure. There are more three-fold hollow sites (H<sub>1</sub>, H<sub>2</sub> corresponding to the fcc and the hcp of the upper-layer and the second-layer fcc (H<sub>3</sub>)) compared with Pd (110) in Figure 1.



**Figure 2** Cluster model and adsorption sites for (110) surface missing-row reconstruction.

Figure 3 shows the cluster model and adsorption sites for Pd (311) stepped surface. Two non-equivalent three-fold sites are denoted by H<sub>f</sub> for fcc and H<sub>h</sub> for hcp respectively and four-fold site by H<sub>4</sub>. Other adsorption sites see below.



**Figure 3** Cluster model and adsorption sites for (311) stepped surface.

## Results and discussion

In O-Pd surface interaction systems, 5 optimum parameters are listed in Table 1 and then the analytical 5-MP is obtained. Using 5-MP, we calculated O-Pd (100), O-Pd (111), O-Pd (110) low-index surfaces systems and O-Pd (311) stepped surface system and obtained the whole critical characteristics. The results are summarized in Table 2 and Table 3. In Tables, N denotes the number of nearest neighbor [ $R_{O-Pd} \leq 0.2$  nm] between the O atoms at critical points and the surface Pd atoms.  $\lambda$  denotes the number of the negative eigenvalues from Hessian matrix,  $E_b$ ,  $f$ ,  $R_{O-Pd}$  and  $z$  denote binding energies, eigenvibration frequencies ( $f_{//}$ : parallel vibration model  $f_{\perp}$ : perpendicular model), bond length to nearest neighboring Pd atoms and the vertical distance between O atoms and the cluster surface, respectively. To further verify the characteristic for the critical points of the rough stepped system O-Pd (311) and the O-Pd (110) missing-row structure, the results are also listed in Table 2. The comparison between our results and the values from literatures are listed in Table 3.

**Table 1** 5 Parameters for O-Pd system

System	$D$ / eV	$\beta$ / $\text{\AA}^{-1}$	$R_0$ / $\text{\AA}$	$Q_1$ / $\text{\AA}$	$Q_2$ / $\text{\AA}$
O-Pd	1.25	2.1	1.95	1.35	0.25

The calculation results about the Pd (100) surface in Table 2 show the top site T ( $\lambda=2$ ) is the surface diffusion maximum point, the bridge site B ( $\lambda=1$ ) is the surface diffusion transition state, and the four-fold hollow site H<sub>4</sub> ( $\lambda=0$ ) is the surface adsorption state that has a  $C_{4v}$  local geometrical symmetry. The binding energy 5.65 eV agrees with the data of experiments,<sup>2,3</sup> the perpendicular vibration model of 41.89 meV agrees well with 41.04 meV<sup>4-6</sup> of the HREELS spectrum for the O-Pd (100) in the low coverage ( $\theta < 0.25$  ML). The bond length of 1.95  $\text{\AA}$  (0.195 nm) in this paper coincides with the experimental results 1.98  $\text{\AA}$  (0.198 nm) and 2.02  $\text{\AA}$  (0.202 nm).<sup>34</sup> Evidently, the results sustained experimental guess that oxygen atoms adsorb on four-fold hollow sites (H<sub>4</sub>)<sup>1,4-6</sup> and it is hardly

possible that the oxygen diffuse on Pd (100) plane under the potential energy barrier of 1.90 eV corresponding to the diffusion channel on the H—B—H.

### O-Pd (111) system

The Pd (111) is the most compact surface in the low-index palladium surfaces and the crystal cell has a  $C_{3v}$  local geometrical symmetry. There are four kinds of non-equivalent critical points in this system (as shown in Figure 1). In Table 2, it shows that the three-fold hollow sites fcc (H) and hcp (H') are both surface adsorption states with  $\lambda=0$ , the bridge site (B) is the surface diffusion transitional state between H and H' sites, and the top site (T) is the surface diffusion maximum point. From the calculation, the difference between H and H' in their critical characteristics is very little, such as nearly the same  $f$ ,  $R_{O-Pd}$ ,  $Z_{O-Pd}$  and a considerably low discrepancy of 0.02 eV in binding energy (H: 4.80 eV; H': 4.78 eV). The perpendicular vibration model of 58.00 meV for H & 57.85 meV for H' agree well with the HREELS data 58.6 meV<sup>35</sup> &

58.89 meV<sup>36</sup> and the calculated results of 60.78 meV (fcc) & 57.02 meV (hcp).<sup>19</sup>

From other aspects of critical points, the bond length of 1.95 Å (0.195 nm) for H and H' accords with the experimental data 1.97 Å (0.197 nm),<sup>15</sup> 1.98 Å (0.198 nm)<sup>34</sup> and 2.02 Å (0.202 nm)<sup>34</sup> which are all little lower than the calculation results of bond length [fcc: 2.06 Å (0.206 nm); hcp: 2.05 Å (0.205 nm)]<sup>16</sup> and vertical distance [fcc: 1.24 Å (0.124 nm); hcp: 1.34 Å (0.134 nm)].<sup>16</sup> It is easy to see that the calculated results of the critical points for the H and H' tally with the results of experiments. From the structure of the Pd (111) surface, H and H' are different types of stable adsorption sites, but from the calculations and the above analysis the difference between their critical characteristics is very little. So fcc (H) and hcp (H') can be considered equivalent approximately. From the discussion about the oxygen atom locating at fcc (H) or hcp (H') in the former experiments and calculations, we consider it is of no significance in reality because H and H' are

**Table 2** Critical characteristics of O-Pd surface systems

System	Site	$N$	$\lambda$	$E_b$ /eV	$f$ /meV		$R_{O-Pd}$ /Å	$Z$ /Å
					//	⊥		
O-Pd (100)	H	4	0	5.65	62.3×2	41.89	1.954	0.13
	B	2	1	3.75	64.8	63.08	1.92×2	1.35
	T	1	2	2.48		75.98	1.90	1.90
O-Pd (111)	H <sub>f</sub>	3	0	4.78	55.25×2	58.00	1.95×3	1.13
	H <sub>h</sub>	3	0	4.80	55.83×2	57.85	1.95×3	1.13
	B	2	1	4.18	68.41	65.47	1.91×2	1.13
	T	1	2	2.65		77.17	1.89	1.89
O-Pd (110)	H	1	2	4.35		76.05	1.92	0.54
	H <sub>3</sub>	3	0	4.69	43.96, 42.93	64.66	1.96×3	0.50
	LB	4	0	5.30	61.28, 48.65	53.90	1.95×2, 1.99×2	0.07
	SB	2	1	3.55	64.90	62.43	1.93×2	1.34
	T	1	2	2.29		74.06	1.91	1.89
	S	2	1	4.51	41.32	70.48	1.97	0.47
Missing-row (110)	H <sub>1</sub>	3	0	4.37	53.21, 52.78	59.55	1.92×2, 1.97	0.47
	H <sub>2</sub>	3	0	4.42	51.49, 56.28	58.13	1.89, 1.92×2	0.02
	H <sub>3</sub>	3	0	4.77	44.58, 46.07	62.45	1.96×3	-0.90
	LB	4	0	5.34	61.02, 48.49	54.12	1.99×2, 1.95×2	-1.31
O-Pd (311)	H <sub>4</sub>	4	0	6.87	70.33, 70.06	74.85	1.95×2, 1.94×2	-0.62 (0.04)
	H <sub>f</sub>	3	0	4.77	36.91, 55.70	59.08	1.98×2, 1.96	0.22 (1.16)
	H <sub>h</sub>	3	0	4.56	51.73, 51.53	61.14	1.94×2, 1.96	0.60 (1.24)
	S	2	1	4.09	55.69	70.08	1.91, 1.92	0.60
	B	2	1	3.49	63.66	61.54	1.92×2	1.24
	B'	2	1	3.81	49.52	69.20	1.94, 1.93	0.64
	B''	2	1	4.69	58.35	60.93	1.95×2	0.19
	T	1	2	2.26		73.68	1.91	1.83

Table 3 Comparison between our results and literature

	System	Site	Experiment date	Theoretical calculated	This work
$R_{\text{O-Pd}}/\text{\AA}$	Pd (110)	H	2.01, <sup>26</sup> 2.02, <sup>19</sup> 2.11 <sup>20</sup>		1.96
	Pd (100)		1.98, 2.02 <sup>34</sup>		
	Pd (111)	fcc	1.97 <sup>15</sup>	2.06 <sup>6</sup>	1.95
$Z/\text{\AA}$		hcp		2.05 <sup>16</sup>	1.95
	Pd (111)		0.9, <sup>13</sup> 1.16 <sup>15</sup>	1.17, <sup>15</sup> 1.34 <sup>16</sup>	1.13
	Pd (111)	H' (hcp)	1.22 <sup>12</sup>	1.24 <sup>16</sup>	1.13
$E_b/\text{eV}$		fcc			
	Pd (100)		0.92 <sup>5</sup>		
	Pd (100)		5.7 <sup>1</sup>		5.65
	Pd (110)	H	5.9 <sup>21</sup>	4.5—6.5 <sup>21</sup>	4.69
		H <sub>3</sub>	3.77 <sup>5</sup>		
	Pd (111)			5.0—6.0 <sup>26</sup>	4.78
$f/\text{meV}$	Pd (100)	H	48.33 <sup>4</sup>		
			41.03 <sup>4-6</sup>		41.89
	Pd (110)	H //	68 <sup>18</sup>		44.58, 46.07
		$\perp$	62 <sup>18</sup>	51.4 <sup>18</sup>	62.45
		$\perp$	59.5, <sup>18</sup> 59.6 <sup>19</sup>	62 <sup>18</sup>	64.66
	Pd (111)	fcc	60.02 <sup>37</sup>		58.00
		hcp		60.78 <sup>37</sup>	57.85
Pd (111)	$\perp$	58.89, <sup>17</sup> 58.6 <sup>35</sup>	57.02 <sup>37</sup>	58.00	

equivalent and they are difficult to be identified in experiments.

### O-Pd (110) system

The Pd (110) surface is a relatively more complex surface, which is a zig-zag surface constituted by two (111) facets colliding each other top to top, and has symmetrical zig-zag along the  $[1\bar{1}0]$  direction. In Table 2, the calculations show there are six kinds of non-equivalent critical points on this surface (as shown in Figure 1). Among them, LB and H<sub>3</sub> both are surface adsorption states with  $\lambda=0$ ; SB is the surface diffusion transitional state between two H<sub>3</sub> sites; H and T sites are surface diffusion maximum points; S (non-denoted in Figure 1) is the surface diffusion transitional state between the two non-equivalent adsorption states LB and H<sub>3</sub>. It can be seen that the oxygen atom locates at the H<sub>3</sub> ( $\lambda=0$ ) site with the perpendicular vibration frequency of 64.66 meV in accord with the experimental date of 59.5 meV,<sup>18</sup> 59.6 meV,<sup>19</sup> 62 meV,<sup>22</sup> and with the binding energy 4.96 eV which accords with calculation value of 4.5—6.5 eV<sup>21</sup> and the experimental data of 5.9,<sup>21</sup> 3.77 eV.<sup>5</sup> We also can see that the oxygen atom locates at the LB ( $\lambda=0$ ) site with one parallel vibration frequency of 61.28 meV and the binding energy of 5.30 meV which is consistent well with the experimental data. So we hold out that oxygen atoms locate at H<sub>3</sub> sites, and at the same time, find out the LB is the adsorption site. On account for the complex of the Pd (110) surface, the adsorbate-induced reconstructions of the Pd (110) have been studied by ARUPS,<sup>21,26</sup> EELS<sup>18</sup> and STM<sup>23,25,28</sup> etc., and the Pd (110)  $c(2\times 4)$ —O surface with the  $(1\times 2)$  missing-row substrate reconstruction structure where the oxygen atoms located

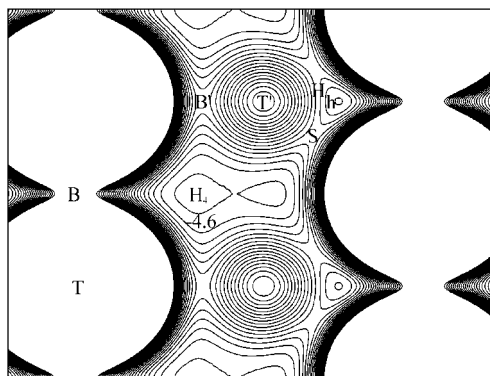
at the three-coordinated (fcc or hcp) sites has been investigated mainly by them.

Here, we make a calculation of the missing-row substrate reconstruction structure of the O-Pd (110) surface by the 5-MP method. As shown in Figure 2, this surface is also a symmetrical zig-zag along the  $[1\bar{1}0]$  direction. There are three kinds of three-fold hollow sites (as shown in Figure 2) and one LB site (non-denoted) and the characteristics of them is list in Table 2. It is easy to be seen that the four critical points are all the adsorption states with  $\lambda=0$ . Among them, there are few differences between the characteristics of H<sub>1</sub> and H<sub>2</sub>. For example, the binding energy of 4.37 eV & 4.42 eV and the perpendicular vibration frequency of 59.55 meV & 58.13 meV are respectively for H<sub>1</sub> & H<sub>2</sub>, which is difficult to distinguish in experiments. So we consider they are equivalent as in Pd (111) surface. In three hollow sites the second-layer fcc H<sub>3</sub> is the favored adsorption site with the binding energy of 4.77 eV and the stretching vibration frequency of 62.45 meV, while the LB is stable with the binding energy of 5.34 eV and one parallel vibration frequency of 62.01 meV. Moreover, these characters of H<sub>3</sub> and LB agree well with the former experimental data. Therefore, we approve of the conclusions<sup>22,23,27,28</sup> that oxygen atoms adsorbed in three-fold hollow sites not only in regular Pd (110) surface but also in the  $(1\times 2)$  missing-row reconstruction structure, and we consider LB is also the stable adsorption state. So the result of Jo *etc.*<sup>20</sup> is worth taking into account, and we expect more full-blown experiments to bear our results. About the view of Takagi<sup>22</sup> that the O atoms adsorbed at the three-coordinated sites of the (111) microfacets with the perpendicular vibration frequency of 62 meV and the

parallel of 68 meV, it is not supported by our results. In Table 2, the parallel vibration frequencies are lower than the perpendicular vibration frequencies of all the three-fold hollow sites in (111) surfaces and (111) microfacets. Furthermore, the view conflicted with the estimated values ( $\perp$ : 62 meV,  $\parallel$ : 51.04 meV) the author obtained by the nearest-neighbour central force field model. The author dealt with the O-Pd (111), O-Pt (111), Rh (110)—O and Pt (110)—O surfaces by the same means, however, the results answered well with the experimental values (the vibrational energy of the  $\parallel$  mode is lower than that of the  $\perp$  mode). The two losses originally come from the broad loss peak observed at 58—62 meV depending on the heating temperatures, so we consider the observed values the author obtained are the perpendicular vibration energy of an atom located at the  $H_3$  site or the parallel vibration energy of an atom located at the LB site.

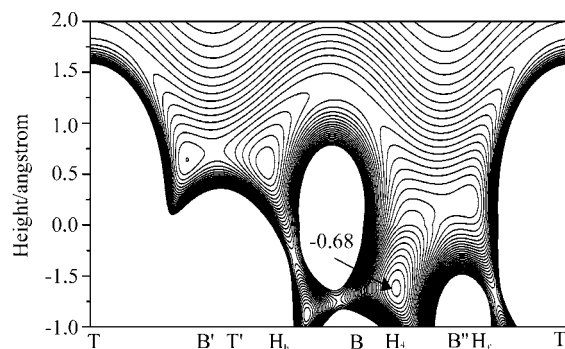
### O-Pd (311) system

Similar with the low-index (110) surface, the (311) surface is a zig-zag surface constituted by a (100) facet and a (111) facet colliding each other side to side. That is to say, it forms unsymmetrical zig-zag groove along [01 $\bar{1}$ ] direction, in short, it is a more rough and open step surface. The crystal cell of Pd (311) has a  $C_1$  local geometrical symmetry, namely, it has not any symmetrical elements except for the identical elements. There are nine kinds of non-equivalent critical points on this surface (see Figures 3—5). Among them, four-fold hollow site  $H_4$  and three-fold  $H_f$ ,  $H_h$  are surface adsorption states with  $\lambda=0$ ; the top site T on the first layer and the top site T' in the second layer are the surface diffusion maximum points with  $\lambda=2$ ; B, B' and B'' are bridge sites and they are diffusion transitional state with  $\lambda=1$ ; S is the surface diffusion transitional state with  $\lambda=1$  between the two threefold adsorption states  $H_f$  and  $H_h$ . The characteristics of each critical point for oxygen atom adsorbing and diffusing on Pd (311) are gathered in Table 2.



**Figure 4** PES contour of disorption and diffusion of oxygen atom on Pd (311).

From Table 2, it is easy to see, the binding energy of 6.87 eV for the four-fold  $H_4$  site is bigger than the 4.77 eV for the three-fold  $H_f$  site and 4.56 eV for the  $H_h$  site.



**Figure 5** PES contour of disorption and diffusion of oxygen atom on Pd (311) along T-T section.

So, the four-fold hollow site ( $H_4$ ) is the stablest adsorption state. The geometrical symmetry of four-fold adsorption states is the slightly distorted  $C_{4v}$  point group, and we can classify the eigenvibration according to the irreducible representation in the  $C_{4v}$  group. We determine that our 74.85 meV eigenvibration [perpendicular to the (100) facet] corresponds to the full-symmetrical  $A_1$  irreducible representation, and our 70.33 meV and 70.06 meV eigenvibration [parallel to the (100) facet] corresponds to the two-dimension degenerate irreducible representation  $E$ . Owing to the influence of the step, these characteristics of the four-fold hollow site ( $H_4$ ) change a lot compared with the O-Pd (100) surface system.

For thoroughly analyzing our results about the O-Pd (311) surface system, we display the PES contour figure of adsorption and diffusion of O atom on Pd (311) surface crystal cell at the height of 0.03 Å (0.002 nm) above the surface and show it in Figure 4 (with the contour interval energy of 0.2 eV). The surface positions and characteristics of nine non-equivalent critical points are clearly stated in it. Along the [2 $\bar{3}$ 3] direction at section a-a, we scan the PES contour figure of adsorbing and diffusion of O atoms at the height above the surface from -1.0 Å (-0.10 nm) to 2.0 Å (0.2 nm) (as shown in Figure 5). The PES (in Figure 5) contains eight critical points and the positions are denoted at the horizontal coordinate, the lowest energy points are at the four-fold  $H_4$  site, the lowest energy contour is -6.80 eV and the contour interval energy is 0.2 eV. From the analysis of the Figures 4, 5 and our calculation results in Table 2, we can see there is a lowest-energy diffusion channels between two adsorption states  $H_4$  and  $H_f$  along [2 $\bar{3}$ 3] direction [ $H_4$ —B''— $H_f$  (2.18 eV, 0.075 eV)]. The potential barrier is only 0.075 eV from  $H_f$  to  $H_4$ , while it is 2.18 eV from  $H_4$  to  $H_f$ . That is to say, there is a competition between the four-fold site ( $H_4$ ) and the near neighbor three-fold site ( $H_f$ ), which leads to the  $H_f$  becoming the metastable adsorption site on Pd (311) surface. So, it can be concluded that there are two stable adsorption states (four-fold site:  $H_4$ , three-fold site:  $H_h$ ) on O-Pd (311) surface and the three-fold site ( $H_f$ ) is the metastable adsorption. At low coverage oxygen atom favors the

four-fold hollow site ( $H_4$ ). Thus, we answer clearly the question proposed by Fari *et al.*<sup>29</sup> whether the O atoms occupied three-fold or four-fold hollows. We expect that the exhaustive experiments bear out our calculation results, at the same time, we provide more valuable reference for the investigation about the O-Pd system.

## Conclusion

In this paper, the 5-MP to deal with O-Pd (100), (111), (110) three low-index surfaces and O-Pd (311) stepped surface were applied. The results agree well with the experiments, and the conclusions were brought forward as follows:

(1) On the O-Pd (111) surface system, we find that fcc(H) and hcp(H') can be considered equivalent approximately in (111) surfaces and (111) microfacets.

(2) In the investigation of the O-Pd (110) surface system and its (1 × 2) missing-row reconstruction surface system, the calculation results show that O atom adsorbs at the three-fold hollow site and the long-bridge is also stable site. The parallel vibration frequencies are lower than the perpendicular vibration frequencies of all the three-fold hollow sites in (111) surfaces and (111) microfacets.

(3) By studying the O-Pd (311) surface system, the thorough characteristic of the critical points on the stepped surface was obtained. We conclude that there are three adsorption states (two three-fold sites:  $H_f$  and  $H_h$ , one four-fold site:  $H_4$ ) on O-Pd (311) surface. There is a competition between the four-fold site ( $H_4$ ) site and the near neighbour three-fold site ( $H_f$ ), finally, the three-fold site ( $H_f$ ) becomes the metastable adsorption site. At low coverage oxygen atom favors the four-fold site ( $H_4$ ).

On account of the influences of the relaxation and reconstruction or other factors, and the investigation of the O-Pd system, especially the calculation results about the stepped surface, we expect to be supported further by the theoretical and experimental studies.

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