

## Theoretical Studies on Adsorption and Diffusion of Hydrogen Atom on Pd(311) and Ni(311) Stepped Surface

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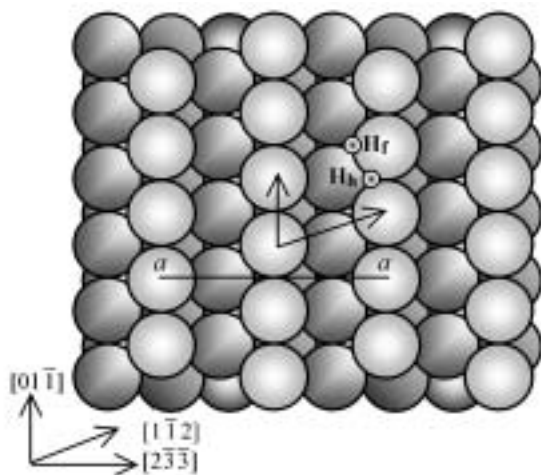
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The adsorption and diffusion of hydrogen atom on open rough Pd(311) and Ni(311) stepped surface were investigated in detail using 5-parameter Morse Potential (5-MP for short) method. The results on theoretical studies indicate that only threefold adsorption states exist at low coverage, and fourfold states are annihilated on the top layer which become the diffusion channels between threefold adsorption states due to strong competition and repulsion between hydrogen adatoms.

**Keywords**    5-MP, adsorption, diffusion, structure of potential energy surface

### Introduction

Considering the investigations of ordered adsorbed phases for the adsorption atoms on surface, it is necessary to clarify firstly the dominations of adsorption sites, especially adsorption systems on stepped surface, which, however, has been puzzling experimental scientists. The (311) surfaces of fcc metals (Figure 1) are of special interest for the study of adsorption phenomena because there are threefold as well as fourfold hollows due to the existence of (111) and (100) microfacets, which are distributed with equal density through the whole surface. This situation leads to an interesting competition in the case of adsorbates like hydrogen or oxygen because they tend to adsorb in highly coordinated sites.



**Figure 1** Cluster model and adsorption sites for (311) stepped surface.

With respect to H/Pd(311),<sup>1-4</sup> H/Rh(311)<sup>5,6</sup> and

H/Ni(311)<sup>7,8</sup> systems, experimental scientists have made plenty of investigations about the ascertainment of 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) plane phases with coverages of 0.25, 0.50, 0.75 and 1 monolayer (ML), respectively. However, whether threefold or fourfold 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—threefold hollows, and the disorder of the layers led to the occupation of the fourfold hollows only for coverages 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 fourfold sites and with the increasing of coverages ( $\theta > 0.5$  ML) hydrogen atoms led to two kinds of adsorption sites, threefold and fourfold sites by means of He-atom scattering (HAS), high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and work function measurements. However, TDS and HAS experimental results<sup>3</sup> indicated that only one single adsorption site should be occupied. In order to account for this contradiction, two explanations were put forward. The first one is that by analogy with the c(2×4)4H phase on Co(10 $\bar{1}$ 0) they thought two different domains resulted in the c(1×1) structure, which differed in the occupation of threefold or fourfold sites, respectively. The second one is based on the HREELS observation<sup>4</sup> that the peak at 85 meV disappeared at high exposures, therefore, the peak at 50 meV should not result from hydrogen in a fourfold site. However, they could not judge which explanation was the correct one.

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Concerning H/Ni(311) system, Rieder *et al.*<sup>7</sup> concluded that the hydrogen preferred to occupy the threefold coordinated sites on the (111)-facets instead of the competing fourfold sites on the (100) facets by He-diffraction experiment. But Schilbe *et al.*<sup>8</sup> noted the first stage of adsorption behavior on the Ni(311) surface by HREELS: occupation of the threefold sites on the (111)-facets, and that with the increasing of the exposures, fourfold sites simultaneously appeared.

Although H-Pd(311) and H-Ni(311) systems have been investigated a lot, whether threefold or fourfold sites are occupied is still inconsistent in experiments.<sup>1-4,7,8</sup> Therefore the theoretical study of adsorption sites and adsorption states for the (311) stepped adsorption systems is a very significant task. However, these theoretical studies are comparatively deficient. The 5-MP of interaction between the adatoms and metal surface has been performed recently on low-index surface adsorption systems such as H-Ni,<sup>9</sup> H-Pd,<sup>10</sup> C-Ni,<sup>11</sup> O-Pd,<sup>12</sup> O-Ni,<sup>13</sup> O-Cu<sup>14</sup> as well as stepped surface adsorption systems: O-Pd(311),<sup>10</sup> O-Cu(211),<sup>14</sup> O-Cu(410),<sup>14</sup> H-Ni(510),<sup>15</sup> H-Ni(997),<sup>15</sup> H-Pd(997).<sup>16</sup> All the calculated results are supported very well by available theoretical calculations and experimental data. In this paper, adsorption sites and adsorption states for the H-Pd(311) and H-Ni(311) stepped surface adsorption systems are studied by 5-MP theoretical method, respectively.

## Theoretical calculation method and surface cluster model

### Theoretical calculated method—5-MP

The 5-MP method has been introduced in detail in Refs. 9—16. Here we just simply illuminated as follows.

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 in 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 adatom and the  $i$ th metal surface atom and denoted as  $R_i = |\vec{R} - \vec{r}_i|$ ,  $h_i$  is the vertical distance between the adatom 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 5 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 those of the stepped surfaces constructed of low-index surfaces. Once the parameters are ascertained, the analytical 5-MP of the corresponding system is constructed successfully. In the investigations of H-Pd and H-Ni low-index surface systems, we have determined 5 optimum parameters<sup>9,10</sup> as shown in Table 1. In this paper we will make a further study on H-Pd(311) and H-Ni(311) systems.

**Table 1** 5 parameters of H-Ni system and H-Pd system

System	$D/\text{eV}$	$\beta/0.1 \text{ nm}^{-1}$	$R_0/0.1 \text{ nm}$	$Q_1/0.1 \text{ nm}$	$Q_2/0.1 \text{ nm}$
H-Ni <sup>9</sup>	1.08806	1.78	1.58	0.329877	0.075
H-Pd <sup>10</sup>	1.1306	1.70	1.74	0.4565	0.225

We determine critical points according to  $\lambda$ , which denotes the number of the negative eigenvalues from 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, the one  $\lambda=0$  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.

### 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 the surface cluster model and adsorption sites of Pd(311) stepped surface, and the two non-equivalent fcc- and hcp-like threefold adsorption sites are denoted by  $H_f$  and  $H_h$ , respectively. Other adsorption sites will be defined in the following explanations. It is worthy to point out that, due to the similar characteristics of H-Ni(311) and H-Pd(311) systems, only the sketch of Pd(311) appears in this paper.

## Calculation results and analysis

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

**Table 2** The whole critical characteristics of H-Pd(311) and H-Ni(311) systems as well as corresponding low-index (100) and (111) surfaces of H-Pd and H-Ni systems

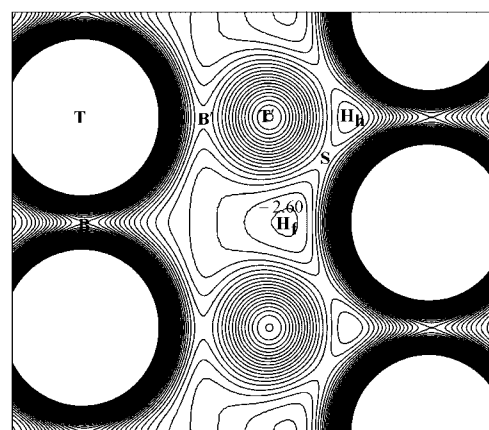
System	Site	$N$	$\lambda$	$E_b/\text{eV}$	$f/\text{meV}$		$R(\text{H-M})/\text{nm}$	$h/\text{nm}$
					//	$\perp$		
H-Pd(311)	H <sub>f</sub>	3	0	2.67	62.37, 96.10	117.35	0.187×3	0.008 (0.099)
	H <sub>h</sub>	3	0	2.65	91.19, 90.20	121.86	0.182×2, 0.185	0.042 (0.091)
	S	2	1	2.54	107.62	153.90	0.175, 0.179	0.039
	B	2	1	2.30	144.52	117.02	0.173×2	0.078
	B'	2	1	2.43	96.41	157.67	0.177, 0.176	0.041
	T	1	2	1.75		198.11	0.168	0.159
	T'	1	2	2.33		188.15	0.172	0.054
H-Ni(311)	H <sub>f</sub>	3	0	2.68	60.11, 93.60	124.63	0.172, 0.171×2	0.010 (0.094)
	H <sub>h</sub>	3	0	2.67	91.85, 88.45	128.05	0.166×2, 0.169	0.040 (0.085)
	S	3	1	2.57	108.85	158.36	0.159, 0.162	0.036
	B	2	1	2.35	146.91	121.85	0.157×2	0.070
	B'	2	1	2.47	96.24	164.16	0.161, 0.160	0.038
	T	1	2	1.83		212.58	0.151	0.145
	T'	1	2	2.40		197.24	0.156	0.049
H-Pd(111) <sup>10</sup>	H <sub>f</sub>	3	0	2.86	95×2	119	0.186×3	0.095
	H <sub>h</sub>	3	0	2.88	98×2	117	0.185×3	0.094
H-Pd(100) <sup>10</sup>	H	4	0	2.71	52×2	69	0.201×4	0.048
H-Ni(111) <sup>9</sup>	H <sub>f</sub>	3	0	2.85	95×2	126	0.169×3	0.089
H-Ni(100) <sup>9</sup>	H	4	0	2.70	51×2	80	0.184×4	0.053

between hydrogen atom and the (111)-microfacet), respectively. In this paper, we mainly analyzed the H-Pd(311) system due to similar properties of H-Pd(311) and H-Ni(311) systems.

### H-Pd(311) system

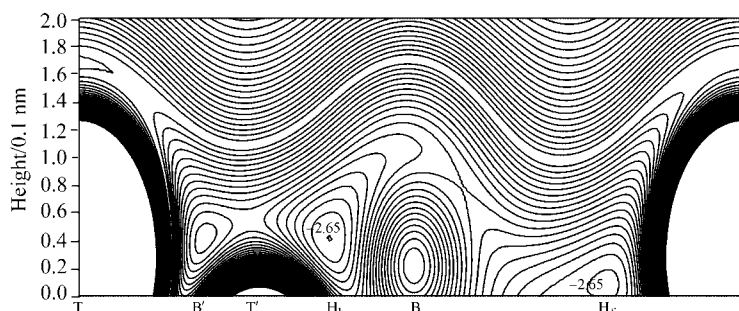
The (311) surface of fcc metal is a more rough and open stepped plane. The crystal cell of Pd (311) belongs to  $C_1$  local geometrical symmetry, that is to say, it has not any other symmetrical elements except for the identical element. There are seven kinds of non-equivalent critical points on the surface (see Figure 2, Figure 3). Among them, both threefold hollow sites H<sub>f</sub> and H<sub>h</sub> are surface adsorption states with  $\lambda=0$ . The difference between the critical characteristics of the two sites is very little but can be distinguished by vibration frequencies. The top site T on the top layer and the top site T' on the second layer are the surface diffusion maximum points with  $\lambda=2$ . B and B', used to distinguish the two bridge sites in the (100) facet, are the surface diffusion transitional states with  $\lambda=1$ , and S is the surface diffusion transitional state between the two threefold adsorption states H<sub>f</sub> and H<sub>h</sub> with  $\lambda=1$ .

Our calculation results shown in Table 2 suggest that H-Pd(311) system has two non-equivalent threefold



**Figure 2** PES contour figure of adsorption and diffusion of hydrogen atoms on Pd(311) surface at the height of 0.02 nm above the surface with energy interval of 0.05 eV.

adsorption sites: H<sub>f</sub> and H<sub>h</sub>. The geometrical symmetries of both threefold adsorption states belong to the distorted  $C_{3v}$  point group. The eigenvibration of 117.35 meV for the stable adsorption state H<sub>f</sub> corresponding to the full-symmetrical  $A_1$  irreducible representation is perpendicular to the surface. Because of distortion, the E



**Figure 3** PES contour figure of adsorbing and diffusion of H atoms at the height of 0–0.2 nm above the surface with energy interval of 0.05 eV.

irreducible representation decays and splits into two one-dimension irreducible representations  $\Gamma$  of 62.37 meV and 96.10 meV. The former corresponding to the peak 56 meV in Ref. 3 is the one parallel to the surface for hydrogen atom along  $[2\bar{3}\bar{3}]$  direction, while 96.10 meV corresponding to the peak 94 meV in Ref. 3 is the vibration mode parallel to the surface for hydrogen atom along  $[01\bar{1}]$  zigzag groove direction. The perpendicular vibration frequency for hydrogen atom on the adsorption state  $H_h$  is 121.86 meV corresponding to 120–126 meV in Ref. 3, and the parallel vibration frequencies are 91.19 meV and 90.20 meV which correspond to 80–85 meV in Ref. 3.

To compare further with Ref. 3, our previous results<sup>9</sup> on Pd(100) and Pd(111) planes are also gathered in Table 2. Clearly, the vibration energies on Pd(100) are less than 80 meV and those of Pd(111) are more than 90 meV, which correspond to perpendicular and parallel energy ranges and are in good agreement with those in Ref. 3. However, with respect to Pd(311), the results in this work indicate that the data of threefold states have an Einstein shift and the vibration energies are lower than those of low-index Pd(111) surface system due to the distortion. Therefore it is unreasonable to determine adsorption states only according to a simple comparison of vibration energies among different surfaces and likely leads to wrong conclusions.

Although all our calculation results are well supported by the experimental result of HREELS,<sup>3,4</sup> there appeared a divarication about the explanation of the origination of the data. Farias *et al.*<sup>4</sup> attributed the peaks 94 and 120–126 meV to the parallel and perpendicular vibrations in threefold states, which was in accordance with our calculation results. However, they attributed 56 meV and 80–85 meV to the vibrations perpendicular and parallel to fourfold microfacets, respectively. But we can not find fourfold adsorption states. And moreover they did not give reasonable explanation as mentioned in the introduction.

In order to resolve this perplexity and thoroughly analyze our calculated results, we scanned the potential energy surface (PES) contour figure of adsorption and diffusion of hydrogen atom on Pd(311) surface at the height of 0.02 nm above the surface and the results are shown in Figure 2. The surface positions and character-

istics of seven non-equivalent critical points are clearly stated in it. Simultaneously, at the a-a section in Figure 1, the PES contour figure of adsorbing and diffusion of hydrogen atom is also scanned at the height of 0–0.2 nm above the surface, which consists of six critical points denoted at the horizontal coordinates as shown in Figure 3.

Two lowest-energy diffusion channels between two adjacent  $H_f$  adsorption states for hydrogen atom along  $[01\bar{1}]$  zigzag groove direction are shown in Figure 3. The one along the  $H_f-B'-H_f$  is a direct diffusion channel with a diffusion potential barrier of 0.24 eV, and the other along the  $H_f-S-H_h-S-H_f$  is also a low-barrier diffusion channel with diffusion potential barriers of 0.13 and 0.11 eV, respectively. Compared with the diffusion of hydrogen atom along  $[01\bar{1}]$  zigzag direction, the one of hydrogen atom along  $[2\bar{3}\bar{3}]$  direction is not smoother and easier. On the one hand, the surface diffusion potential barrier of hydrogen atom along the  $H_f-B-H_f$  diffusion channel is 0.37 eV, which is much higher than 0.24 eV on the  $[01\bar{1}]$  orientation. On the other hand, soon it meets with a very high potential barrier, and the diffusion channel is hindered. The analysis above indicates that the surface diffusion of hydrogen atom on Pd(311) possesses distinct anisotropy, that is, the diffusion of hydrogen atom along  $[01\bar{1}]$  zigzag groove direction possesses two low-energy channels which are easier for the diffusion of the hydrogen adatoms, but the one of hydrogen atom along  $[2\bar{3}\bar{3}]$  direction is more difficult. In addition, the interaction between adatoms is predominantly repulsive in the low coverage regime,<sup>1</sup> therefore, we believe that because of strong competition and repulsion between hydrogen adatoms, fourfold states are annihilated on the top layer and become the diffusion channels between threefold adsorption states. And these conclusions are urgent to expect further experimental and theoretical support.

#### H-Ni(311) system

With respect to H-Ni(311) system, we adopted the same method and obtained the results similar to H-Pd(311) (see Table 2). The eigenvibration of 124.63 meV for the stable adsorption state  $H_f$  corresponds to the full-symmetrical  $A_1$  irreducible representation,

which is perpendicular to the surface. Due to the distortion, the E irreducible representation decays and splits into two one-dimension irreducible representations  $\Gamma$  of 60.11 meV and 93.60 meV. The vibration mode of 60.11 meV is the one parallel to the surface for hydrogen atom along  $[2\bar{3}\bar{3}]$  direction, while the 93.60 meV is the one parallel to the surface for hydrogen atom along  $[01\bar{1}]$  zigzag groove direction. The perpendicular vibration frequency for hydrogen atom on the adsorption state  $H_h$  is 128.05 meV, and the parallel ones are 91.85 meV and 88.45 meV, respectively. But we can not find fourfold adsorption state the same as H-Pd(311) system.

In order to determine the adsorption sites, Schilbe *et al.*<sup>8</sup> analysed the vibration mode of H-Ni(311) using HREELS method. They advisably attributed the peak 60 meV to the vibration mode of threefold adsorption site parallel to the surface by comparing with those of low-index surface system, and claimed that at low coverage hydrogen atoms occupied threefold sites. From our calculation results, 60 meV obtained from experiments should be the parallel mode of threefold adsorption state for hydrogen atoms along  $[01\bar{1}]$  zigzag groove direction, which is in agreement with that by Stocker *et al.*<sup>7</sup> Whereas Schilbe *et al.*<sup>8</sup> synchronously claimed that there were fourfold adsorption states. Unfortunately, our calculation results do not support this assumption.

## Conclusions

We adopted 5-MP method to study the adsorption and diffusion properties of H-Pd(311) and H-Ni(311) systems, and confirmed that only threefold adsorption states appeared. Because of strong competition and repulsion of the hydrogen adatoms between threefold and fourfold sites, fourfold states on the top layer are not found and become the diffusion channels between two

threefold adsorption states. However, whether the sub-surface adsorption sites are also in existence at higher coverage will make a further study in the future.

## References

- 1 Farias, D.; Troger, H.; Patting, M.; Rieder, K. H. *Surf. Sci.* **1996**, 352—354, 155.
- 2 Farias, D.; Patting, M.; Rieder, K. H. *Phys. Status. Solidi.* (a) **1997**, 159, 255.
- 3 Farias, D.; Schilbe, P.; Patting, M.; Rieder, K. H. *J. Chem. Phys.* **1999**, 110, 559.
- 4 Farias, D.; Schilbe, P.; Rieder, K. H. *Surf. Rev. Lett.* **1998**, 5, 473.
- 5 Payne, S. H.; Kreuzer, H. J.; Frie, W.; Hammer, L.; Heinz, K. *Surf. Sci.* **1999**, 421, 279.
- 6 Nichtl-Pecher, W. *Phys. Rev. B* **1991**, 43, 6946.
- 7 Rieder, K. H.; Stocker, W. *Chem. Phys. Lett.* **1986**, 126, 297.
- 8 Schilbe, P.; Siebentritt, S.; Pues, R.; Rieder, K. H. *Surf. Sci.* **1996**, 360, 157.
- 9 Wang, Z.-X.; Hao, C.; Zhang, J.-S.; Han, E.-S.; Chen, Z.-G. *Acta Chim. Sinica* **1993**, 51, 417 (in Chinese).
- 10 Zhang, J.-S.; Zhang, W.-X.; Wang, Z.-X. *Acta Phys.-Chim. Sin.* **1996**, 12, 773.
- 11 Zhang, W.-X.; Qiao, Q.-A.; Chen, S.-G.; Cai, M.-C.; Wang, Z.-X. *Chin. J. Chem.* **2001**, 19, 325.
- 12 Wang, Z.-X.; Jia, X.-F.; Tian, F.-H.; Chen, S.-G. *Chin. J. Chem.* **2004**, 22, 152.
- 13 Wang, Z. X.; Qiao, Q. A.; Chen, S. G.; Zhang, W. X. *Surf. Sci.* **2002**, 517, 29.
- 14 Wang, Z. X.; Tian, F. H. *J. Phys. Chem. B* **2003**, 25, 6153.
- 15 Wang, Z.-X.; Zhang, J.-S.; Yu, X.-A.; Hao, C.; Chen, Z.-G.; Zhou, Y.-Q. *Chin. J. Chem.* **1994**, 52, 209.
- 16 Wang, Z.-X.; Hao, C.; Zhang, F.; Zhang, W.-X.; Chen, Z.-G. *Acta Phys.-Chim. Sin.* **1994**, 10, 121 (in Chinese).