



Oxygen Atom Adsorption and Diffusion on Pd(110) and Missing-Row (110) Surfaces

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The adsorption and diffusion of an oxygen atom on Pd (110) and its missing-row surfaces were investigated in detail with five-parameter Morse potential (5-MP). 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.

Key Words: Oxygen atom, five-parameter Morse potential, Adsorption, Diffusion, Pd surface, Step surfaces.

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 (110) and (311) surfaces and the interactions with oxygen have been studied extensively with many surface science techniques. 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) surface¹⁻⁹. Yagi *et al.*² assigned oxygen atoms to be located in the fcc (111) sites to form Pd-O zig-zag chains along the [110] rows. Therefore, the result could not be reconciled to the long-bridge adsorption site¹. The high-temperature oxygen exposure phase of c(2 × 4) with its half-monolayer oxygen coverage was suggested to consist of [110] added rows of Pd atoms with two oxygen atoms adsorbed in the upper-layer hcp (111) sites per every other Pd atom⁴. 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 × 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^{5,6}, the local location of oxygen adatoms is a controversial problem.

From the information above it is observed 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-Ni¹⁰, C-Ni¹¹, N-Ni¹², O, CO-Ni¹³ and NO-Pd¹⁴ surface systems recently. Here, we study further the oxygen atom adsorption and diffusion on Pd(110) and missing-row (110) surfaces.

EXPERIMENTAL

Extended LEPS constructed by five-parameter Morse potential and cluster models: The extended LEPS method was put forward by McCreedy and Wolken firstly, which was used to investigate the interaction of the diatomic molecule and metal surface cluster. Now, the extended LEPS has developed to a built-up potency. Analyzed from the mathematical physics, the extended LEPS potential deduced by valence bond theory is constructed by three pair-potential function: one for a gaseous diatom and the other two for a single atom and surface cluster, respectively. The pair-potential functions for a gaseous diatom can be obtained from spectroscopic data, whereas the other two should be constructed by other means; therefore, the latter is the brilliant part of the extended LEPS method. In this paper, the extended LEPS constructed by the 5-MP is the pair potential for an atom adsorption on surface clusters.

Five-parameter Morse potential has been explicated in the literatures¹⁰⁻¹⁴. On the assumption that the metal cluster is

frozen, so the interaction energy $U(\vec{R})$ as the 5-MP between an atom, which coordinate is specified by \vec{R} and the whole surface cluster can be written in the following equation:

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

In eqn. 1, \vec{r}_i specifies the coordinate of the 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 surface where the i th metal atom. The adjuster parameters, D , β , R_0 , Q_1 and Q_2 . (in eqn. 1), have been described in detail in the literatures¹⁰⁻¹⁴. The main characteristic of 5-MP is that the parameters are independent of the surface cluster structure. So we can use the same set of optimized parameters in the interaction of an atom, whether it is a single one or one of a molecule, with the same metal surfaces including low-index and stepped surfaces.

Fig. 1 shows the cluster model and adsorption sites for (110) and the (1×2) missing-row reconstructed structure. There are more three-fold hollow sites (H_1 , H_2 corresponding to the fcc and the hcp of the upper-layer and the second-layer fcc (H_3)) on the missing-row (110) than on the Pd (110).

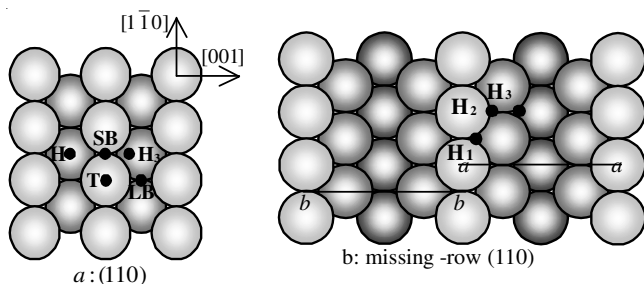


Fig. 1. Adsorption sites for (110) (a) and missing-row (110) (b) surfaces reconstruction

RESULTS AND DISCUSSION

The results are summarized in Table-1. In table, N denotes the number of nearest neighbor [$RO-Pd \leq 0.2$ nm] between the O atoms at critical points and the surface Pd atoms. l denotes the number of the negative eigenvalues from Hessian matrix, E_b , f , R_{O-Pd} and z denote binding energies, eigen vibration

frequencies, bond length to nearest neighboring Pd atoms and the vertical distance between O atoms and the cluster surface, respectively.

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 $[1\hat{1}0]$ direction. In Table-1, the calculations show there are six kinds of non-equivalent critical points on this surface (Fig. 1). Among them, LB and H_3 both are surface adsorption states with $\lambda = 0$; SB is the surface diffusion transitional state between two H_3 sites; H and T sites are surface diffusion maximum points; S (non-denoted in Fig. 1) is the surface diffusion transitional state between the two non-equivalent adsorption states LB and H_3 . It can be seen that the oxygen atom locates at the H_3 ($\lambda = 0$) site with the perpendicular vibration frequency of 64.66 meV in accord with the experimental date of 59.5 meV¹⁵, 59.6 meV¹⁶, 62 meV and with the binding energy 4.96 eV which accords with calculation value of 4.5-6.5 eV and the experimental data of 5.9, 3.77 eV⁵. One can also 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_3 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^{2,7}, EELS¹ and STM^{4,6,9} *etc.* and the Pd (110) $c(2 \times 4)$ -O surface with the (1×2) 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 Fig. 1, this surface is also a symmetrical zig-zag along the $[1\hat{1}0]$ direction. There are three kinds of three-fold hollow sites (as shown in Fig. 1) and one LB site (non-denoted) and the characteristics of them is list in Table-1. 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_1 and H_2 . For example, the binding energy of 4.37 and 4.42 eV and the perpendicular vibration frequency of 59.55 and 58.13 meV are, respectively for H_1 and H_2 , 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_3 is the favoured adsorption site with the binding energy of 4.77 eV

TABLE-1
CRITICAL CHARACTERISTICS OF O-Pd SURFACE SYSTEMS

System	Site	N	λ	E_b (eV)	f (meV)		R(O-Ag) (Å)	Z (Å)
					\parallel	\perp		
O-Pd (110)	H	1	2	4.35	–	76.05	1.92	0.54
	H_3	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	$1.95 \times 2, 1.99 \times 2$	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_1	3	0	4.37	53.21, 52.78	59.55	$1.92 \times 2, 1.97$	0.47
	H_2	3	0	4.42	51.49, 56.28	58.13	$1.89, 1.92 \times 2$	0.02
	H_3	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	$1.99 \times 2, 1.95 \times 2$	-1.31

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 H₃ and LB agree well with the former experimental data. Therefore, it is concluded^{3,4,8,9} that oxygen atoms adsorbed in three-fold hollow sites not only in regular Pd (110) surface but also in the (1 × 2) missing-row reconstruction structure and we consider LB is also the stable adsorption state. So the result of Jo, is worth taking into account and we expect more full-blown experiments to bear our results. About the view of Yasui *et al.*³ 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 present results. In Table-1, 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 H₃ site or the parallel vibration energy of an atom located at the LB site.

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-1, the calculations show there are six kinds of non-equivalent critical points on this surface (as shown in Fig. 1). Among them, LB and H₃ both are surface adsorption states with $\lambda = 0$; SB is the surface diffusion transitional state between two H₃ sites; H and T sites are surface diffusion maximum points; S (non-denoted in Fig. 1) is the surface diffusion transitional state between the two non-equivalent adsorption states LB and H₃. It can be seen that the oxygen atom locates at the H₃ ($\lambda = 0$) site with the perpendicular vibration frequency of 64.66 meV in accord with the experimental data of 59.5 meV¹⁵, 59.6 meV¹⁶, 62 meV and with the binding energy 4.96 eV which accords with calculation value of 4.5-6.5 eV and the experimental data of 5.9, 3.77 eV. 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 H₃ 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^{2,7}, EELS¹ and STM^{4,6,9} *etc.* and the Pd (110) c(2 × 4)-O surface with the (1 × 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 Fig. 1,

this surface is also a symmetrical zig-zag along the [1 $\bar{1}$ 0] direction. There are three kinds of three-fold hollow sites (Fig. 1) and one LB site (non-denoted) and the characteristics of them is list in Table-1. It is easy to observe that the four critical points are all the adsorption states with $\lambda = 0$. Among them, there are few differences between the characteristics of H₁ and H₂. For example, the binding energy of 4.37 and 4.42 eV and the perpendicular vibration frequency of 59.55 and 58.13 meV are, respectively for H₁ and H₂, 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 H₃ is the favoured 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 H₃ and LB agree well with the former experimental data. Therefore, we approve of the conclusions^{3-4,8,9}, that oxygen atoms adsorbed in three-fold hollow sites not only in regular Pd (110) surface but also in the (1 × 2) missing-row reconstruction structure and we consider LB is also the stable adsorption state. So the result of Jo *etc.* is worth taking into account and we expect more full-blown experiments to support present results. According to the view of Yasui *et al.*³ 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-1, 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 H₃ site or the parallel vibration energy of an atom located at the LB site.

Conclusion

In this paper, the 5-MP to deal with O-Pd (110) surface and its missing-row surfaces. The results agree well with the experiments and the conclusions were brought forward as follows: 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.

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