Dynamic Study of O_2 Adsorption and Dissociation on Pd Low-Index Surfaces

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The extended LEPS constructed by 5-MP (the 5-parameter Morse potential) is performed. At low coverage, O_2 prefers to dissociate on the Pd(100) and (110) surfaces; however, at high coverage, it can stably adsorb in the H−B−H site on the Pd(111) surface and more molecular states are found. The calculation results agree well with the experimental results, especially, the results of O_2 on Pd(111) explain well the three precursor states (the superoxo-like state, the peroxo-like and second peroxo-like state) of HREELS and EELS results. Simultaneously, the conceptions of the molecular dissociation limit and the surface dissociation distance are brought forward first, which illuminate the dissociation mechanism of the O_2 on the low-index surfaces and offer the answer to the question why is it more difficult for O_2 to dissociate on the (111) surface than on the (100) and (110) surfaces?

1. Introduction

The adsorption and dissociation of an oxygen molecule on a metal surface plays a central role such as in catalytic oxidation of CO and NO on transition metal surfaces. So, the interaction of O_2 and Pd surfaces is always an interesting topic.[1−17]

The initial adsorption of oxygen on Pd(100) dissociated at low coverage, but a molecular state was stable upon additional exposure to O_2,[8] the 90 meV(726 cm^{-1}) loss peak was observed and identified as the intramolecular O−O stretch vibration. Stuve and Madix[9] studied the adsorption and coadsorption of oxygen on Pd(100) and observed the molecular state characterized by the O−O stretching frequency of 96 meV (775 cm^{-1}). About the system of O_2−Pd(110), the adsorption of O_2 on the surface is more complex, and the reconstruction and the dissociation of O_2 on the Pd(110) surface were found in the literatures.[10−12] Thermal desorption spectra (TDS)[13,14] revealed three major peaks: a low-temperature peak (α) being from molecular adsorbates and the other two high-temperature peaks (β_1 and β_2) from atomic oxygen. The studies of O_2−Pd(111) showed that the molecular oxygen could exist.[15−17] Early in 1986, Imbihl and Demuth[15] studied the oxygen adsorption on a Pd(111) surface by HREELS and LEED. At 30 K, they presumed that oxygen adsorption led to the parallel occupation of two chemisorbed molecular adsorption states characterized by vibrational losses at 850 and 1035 cm^{-1} and these losses assigned to the O−O stretching frequency of molecularly adsorbed oxygen in a peroxo-like state and a superoxo-like state, respectively. Upon warming the sample above 80 K, an additional loss feature at 650 cm^{-1} developed which was assigned to a second peroxo-like molecular species. The peroxo-like state at 805 cm^{-1} and the second peroxo-like at 635 cm^{-1} were observed, indicating the presence of molecular oxygen on the surface; a small feature was noticeable at approximately 950 cm^{-1} that probably corresponds to a small population of superoxo-like oxygen.[16] Recently ab initio studied the O_2 precursor states on the Pd(111) surface.[12] The authors calculated several adsorption trajectories for O_2 on Pd(111) and found three geometrically distinct precursor states: O_2 located at top-bridge-top (TBT), top-hcp-bridge (TH′B), and top-fcc-bridge (THB) sites, which respectively had the vibrational frequencies of 1026, 855, and 876 cm^{-1}. However, they did not find the third precursor state that had been identified to have a stretching frequency of 650 cm^{-1} in the experiment.[15]

Basing on the former experiences and the analyses of the diatomic molecular adsorption and dissociation on metal surface, we find that there is an queer dynamic phenomenon about the O_2 dissociation and adsorption on the low-index surfaces of face-centered cubic (FCC) metals; the dissociation of O_2 on the compact (111) surface is more difficult than on the (100) and (110) surfaces. Even the sticking probability is lower than 10^{-5} about the oxygen atom on the Ag and Cu(111) surfaces;[18] it is similar about the N_2 adsorption and dissociation on the body-centered cubic (BCC) Fe(111) surface.[19] Why is it difficult to dissociate about the O_2 on the (111) surface? Which surface structure is beneficial to the dissociation? These are universal surface dynamic phenomena, and many people try to solve them. For the system of O_2−Pd though, the former experiments offered a great deal of dynamic information, which was less to open out the puzzling question. It is necessary to make a full study of the microcosmic dynamic mechanism of the adsorption and dissociation in theory. The extended LEPS constructed by 5-MP is the credible potential function based on the experimental information from the interaction of O_2 and Pd. We have studied the systems of O−Pd,[20] O−Ni,[21] and O−Cu[22,23] using the 5-MP method (the 5-parameter Morse potential function) and obtained the good results that agreed well with the experimental data. The extended LEPS constructed by 5-MP has been successfully used in the systems of CO−Ni[21] and H_2−Ni.[24] Here, based on the study of oxygen atom adsorbing and diffusing on Pd low-index and (311) stepped surfaces,[20] we make a further study of the adsorption and dissociation of O_2 on Pd low-index surfaces with the extended LEPS.

2. Extended LEPS Constructed by 5-MP and Cluster Models

The extended LEPS method was first put forward by McCreey and Wolken,[25,26] which is the technique frequently

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TABLE 1: Five Parameters for the O−Pd System

system	D/eV	β/Å^{-1}	R_0/Å	Q_1/Å	Q_2/Å
O−Pd	1.25	2.1	1.95	1.35	0.25

used in investigating the interaction of the diatomic molecule and metal surface cluster. Analyzed from the mathematical physics, the extended LEPS potential deduced by valence bond theory is constructed by three pair-potential functions: one for a gaseous diatom and the other two for a single atom and a 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.

2.1. 5-MP Function. 5-MP has been explicated in the literature.[20−24] On the assumption that the metal cluster is frozen (before ascertaining the potential function, the relaxation of the Pd cluster is considered and obtained by parameters Q_1 and Q_2, and once the parameters are confirmed, the cluster is assumed frozen), the approximation is adopted for the whole surface cluster. So the interaction energy $U(\vec{R})$ as the 5-MP between an atom, which coordinate is specified by $\vec{R}$, and the whole metal surface cluster can be written in the form of a Morse potential

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

In eq 1, $\vec{r}_i$ specifies the coordinate of the adsorbed atom and the ith metal surface atom, respectively; R_i is the distance between the adatom and the ith metal surface atom and denoted as $R_i = |\vec{R} - \vec{r}_i|$; the adjustable parameters, D, β, R_0, Q_1, and Q_2 (in eq 1), have been described in detail in the literature.[20−23] The five adjustable parameters of the O−Pd obtained from the literature[20] are listed in Table 1. The main characteristic of 5-MP is that the parameters are independent of the structure for the surface clusters, so we use the same set of optimized parameters. The adsorption systems of an adatom on a low-index surface are easy to deal with at one time, and the adsorption systems on the stepped surface constituted by the low-index surfaces are also easy to carry out.

2.2. Extended LEPS Constructed by 5-MP. The 5-MP (1) is regarded as the bonded interaction potential; thus, the antibonded interaction potential between the adatom and the metal surface cluster can be expressed as

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

here, $D^{+} = 0.5D(1 - \Delta)/(1 + \Delta)$, where Δ is so-called Sato parameter. Thus, the Coulomb integral J and the exchange integral K for a special point can be obtained from eqs 1 and 2. Finally, the extended LEPS potential energy surface of a diatomic molecule (AB) and metal (M) surface can be expressed as

$$E = J_{AB} + J_{AM} + J_{BM} + [K_{AB}{}^{2} + (K_{AM} + K_{BM})^{2} - K_{AB}(K_{AM} + K_{BM})]^{1/2} \quad (3)$$

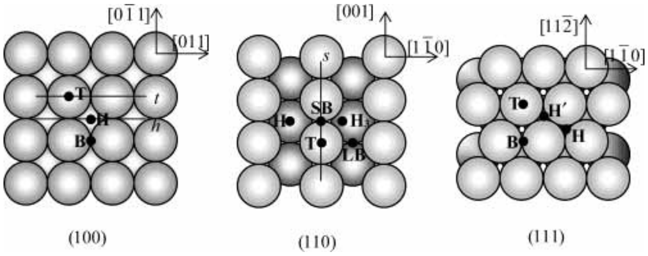

Figure 1. Cluster models and adsorption sites for a low-index surface.

In eq 3, J_{AB} and K_{AB} are Coulomb integral and exchange integral for the diatom AB while J_{iM} and K_{iM} are (Coulomb integral and exchange integral) for atom and the metal cluster (i = A or B). For the interaction of O_2 and Pd surfaces (O═A═B), the potential function includes two adjustable *sato* parameters (Δ_{O-O} and Δ_{O-Pd}). Just like the five parameters mentioned above in the 5-MP, we also adjust them simultaneously according to the experimental data of three low-index (100), (110), and (111) surfaces. Therefore, our extended LEPS is also independent of the structure of the surface clusters. Obviously, the same set of optimum of the *sato* parameters can be used both in the adsorption of diatom molecule on the metal low-index surfaces and the stepped defect metal surfaces.

2.3. Construction of Cluster Models for Palladium Surfaces. Metal palladium belongs to fcc lattice with the lattice constant a_0 = 0.3883 nm. Considering the local geometrical symmetry in a point group and the lattice displacement symmetry for the crystal cell as well as the boundary effect of adatoms, we simulate the Pd surface cluster with at least 5 (high) layers of cell atoms, and every layer contains at least 10 (length) × 10 (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, which means: "The cluster simulated must have certain size. For the same adsorption site, the critical characteristics of adsorption atom at the boundary are different slightly from that of in the interior of the cluster surface, which is the so-called boundary effect. To ignore the boundary effect, the range of the surface cluster is simulated at least two unit cells from the center to boundary."

Figure 1 shows cluster models and adsorption sites for the three low-index surfaces of Pd(111), Pd(100), and Pd(110). They are the top site (T), the hollow site (H), and the bridge site (B) for the surfaces; fcc hollow site (H) and hcp hollow site (H′) for Pd(111) surface; the long-bridge site (LB), the short-bridge site (SB), and the pseudo-3-fold hollow site (H_3) for Pd(110) surface, respectively.

Commonly, the zero-point of the coordinate is orientated on the top atom, the x and y axes respectively corresponding with the crystal axis as shown in Figure 1, the z axis point to vacuum, and the distance of the nearest two lines (or two rows) is regarded as the unit length of x and y axes, which is so-called the lattice coordinate. There are six degrees of freedom in the movement of the diatomic molecule, and there are several definitions about the coordinate. We adopt the lattice coordinates for the centroid of the diatomic molecule to denote the orientation of molecule on the cluster surface, and adopt the polar coordinates for the diatomic molecule itself. Here, θ shows the angle between O−O bond and surface normal (z axis), whereas φ is the angle between the projection of O−O bond and x axis. $E(x, y, z, r, \theta, \varphi)$; the systemic potential function includes six variables that constitute seven dimensions energy hypersurface. The critical point is the one with the first derivative being zero on the hypersuface, and the second derivatives of the critical points form the Hessian matrix. The

TABLE 2: Critical Characteristics of the O_2−Pd Surface System

system	site	λ	E_b (eV)	f_{O-O} (cm^{-1})	Z_{O1-Pd} (Å)	Z_{O2-Pd} (Å)	R_{O-O} (Å)	R_{O2-Pd} (Å)	θ (deg)	
O_2−Pd(100)	H1	1	4.09	727	−0.17	1.23	1.40	0.53	0	0
	H2	1	2.58	380	1.19	1.19	1.51	1.19	90	0
	BHB	2	2.29		1.34	1.34	2.73	1.34	90	0
O_2−Pd(110)	H_3−H−H_3	0	3.69	671	0.49	0.49	1.50	0.49	90	0
	LB	1	2.55	653	−0.19	1.20	1.39	0.50	0	0
	H_3	1	0.96	939	0.44	1.74	1.31	1.08	14	0
	H_3-LB1	1	3.96		0.48	0.49	2.53	0.485	81.8	71.3
	H_3-LB2	1	3.95		0.48	0.49	2.38	0.485	81.8	87.2
O_2−Pd(111)	H	1	0.76	861	1.08	2.40	1.31	1.74	0	0
	H′	1	0.77	857	1.08	2.40	1.31	1.74	0	0
	H−B−H	0	4.21	565	1.14	1.14	1.67	1.14	90	90
	B	1	0.19	1067	1.44	2.70	1.26	2.07	0	0
	H−BB−H	1	3.73		1.13	1.33	1.24	1.23	80.7	19.1

TABLE 3: Comparison between Our Results and Those of the Literature

	system	experiment date	theoretical calculated	this work
f_{O-O} (cm^{-1})	O_2−Pd(100)	726,[8] 775[9]		727
	O_2−Pd(111)	1035(superoxo)[15]	1026[17]	1067
		850(peroxo-I)[15]	855(H), 876(H′)[17]	861(H), 857(H′)
		805[16]		
		650(peroxo-II)[15]		565
		635[16]		
R_{O2-Pd} (Å)	O_2−Pd(111)	1.63[10]	2.0(B)[17]	2.07(B)
			1.79(H), 1.81(H′)[17]	1.74(H,H′)
R_{O-O} (Å)	O_2−Pd(111)	1.33(superoxo)[15]	1.32(B)[17]	1.26(B)
		1.44(peroxo)[15]	1.36(H), 1.37(H′)[17]	1.31(H, H′)
				1.67 (H−B−H)
	O_2−Pd(110)	1.50[11]		1.50(H_3−H−H_3)
				1.39(LB)
				1.31(H_3)

number (denoted as λ) of negative eigenvalues of Hessian matrix characterizes the nature of critical points. The critical point of $\lambda = 0$ corresponds to the stable state of the system and the one with $\lambda = 1$ corresponds to the trans-state, to which we pay more attention. There are two stable states with $\lambda = 0$: one is the adsorption state of diatomic molecule on the surface and the other is the adsorption state of dissociated atom on the surface. The former one is mainly concerned about, and also the latter has been made systemic study.[20] About the diatomic molecular adsorption system, there are also two trans-states with $\lambda = 1$: the diffusion trans-state forms when the negative eigenvalue of the Hessian matrix appears in the critical point of lattice coordinates (x, y, z), and the construction trans-state forms when the negative engenvalue of Hessian matrix appears in the critical point of polar coordinates (θ,φ). It is the dissociation trans-state only when the negative engenvalue of Hessian matrix appears in the critical point of bond length (r) in the polar coordinates. In this paper, we study about the adsorption and dissociation of O_2 molecule on the low-index surfaces of Pd, so just pay attention to the critical points with $\lambda = 0$ or $\lambda = 1$.

3. Result and Discussion

According to the experimental data, we get the optimization of the Sato parameters O−Pd = 0.14 and O−O = 0.16 by calculating and adjusting. From the spectrum data, the O−O bond length of 1.208 Å and the vibration frequency of 1580 cm^{-1} for gas molecules have been given.[27] Then, we calculate all critical characteristics (listed in Table 2) of O_2−Pd low index plane. E_b represents the binding energy, and f_{O-O} is the intramolecular O−O stretch vibration frequency. Z_{O1-Pd} and Z_{O2-Pd} are the height of the close O atom and the far O atom to the surface, respectively. R_{O-O} represents the O−O bond length and R_{O2-Pd} is the distance of the center of mass of O_2 above the surface. The same meaning of λ, θ, and φ is as mentioned in the former. The comparison between our results and the values from literatures is listed in Table 3.

3.1. O_2 Dissociation and Adsorption on Pd(100). First, we search for the adsorption state of O_2 on Pd(100) surface. It is a pity that the oxygen molecular adsorption state with $\lambda = 0$ does not be found. Whereas we find two trans-states in the 4-fold hollow site (H), which are defined as H1 and H2 states. The H1 state is the construction trans-state with the negative engenvalue in θ. Its critical characteristics show the following: the oxygen molecule uprightly adsorbs in the hollow site (H) with the binding energy of 4.09 eV, the O−O bond is stretched to 1.40 Å, and the stretching frequency of O−O is 727 cm^{-1} with the weakening of the O−O bond. The frequency agrees with the oxygen molecular vibration fingerprint of 726[8] and 775 cm^{-1}.[9] The H2 state is the diffusion trans-state with the negative engenvalue in x. Its critical characteristics show the following: oxygen molecule paralleling the surface lies in the hollow site (H) with the binding energy of 2.58 eV, the O−O bond is stretched to 1.51 Å, and the stretching frequency of O−O falls to 380 cm^{-1} with the weakening of the O−O bond. The abnormally low frequency indicates that the trans-state is not stable. That is to say there is no O_2 molecular adsorption state on the Pd(100) surface at low coverage, and only the dissociation atomic states can be found with the two dissociated atoms adsorb in 4-fold hollow sites of the nearest crystal cells.

Now, we discuss the dissociation and adsorption of O_2 on the Pd(100) surface. Above all, it is necessary to review the dissociation of the H1 state that O_2 uprightly adsorbs in the H site; therefore, we fix one O atom closing to the surface at the 4-fold site (H) and then change the angle of θ from 0 to 90° and the length of O−O bond from 1.0 to 3.0 Å. So, we can gain the potential energy surfaces (PES; see Figure 2) with the counter of 0.2 eV. It can be seen from Figure 2 that the O_2 perpendicularly adsorbing on the H site (H1) drops down and dissociates easily ($\varphi = 90°$), then, the two dissociated atoms

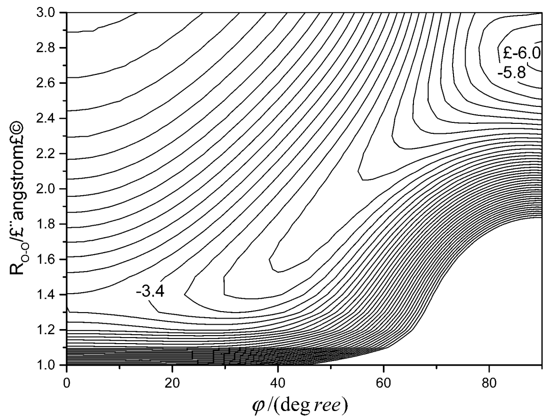

Figure 2. PES of O on Pd(100)(R - θ) (counter is 0.2 eV, $\varphi = 900$).

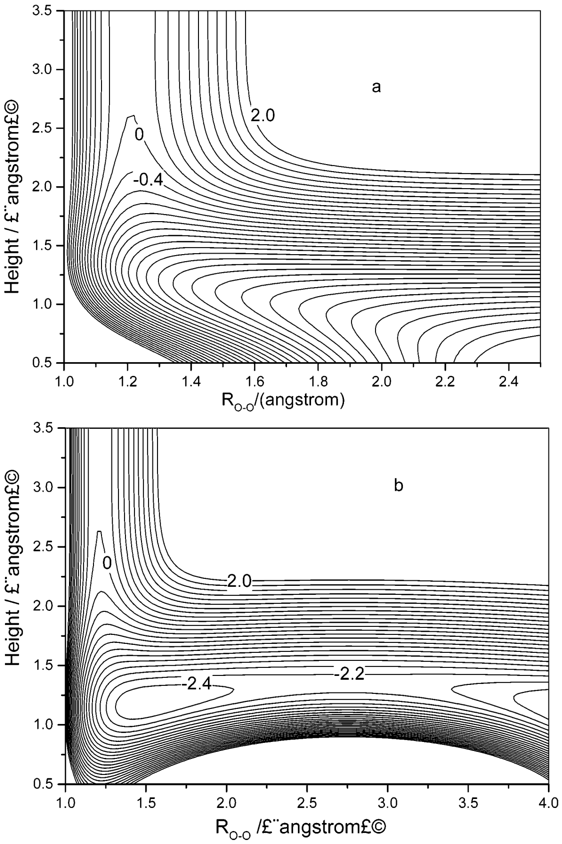

Figure 3. Dissociation of O_2 on Pd(100) (counter is 0.2 eV; a, B site; b, H site).

will locate in the nearest 4-fold hollow sites with the distance of O−O stretching to 2.6 Å. Evidently, at low coverage the H1 state exists as short-life. These phenomena suggest that only the bond of O_2 approximately paralleling the surface can dissociates easily; moreover, almost no active energy is needed for the change of O_2 from the perpendicular state to the parallel state. Furthermore, the dissociation channel of O_2 paralleling to the surface is searched, and two typical potential energy surfaces (PES; see Figure 3) are given with the counter of 0.2 eV. There are two marked typical molecular dissociation lines in Figure 1: one is named as bridge-site line (t) and the other one is hollow-site line (h). The analysis of many dissociation channels shows that the direct dissociation channel appears as the O_2 centroid closing to surface at the bridge-site line (t) and the precursor dissociation channel appears near the hollow-site line (h). Figure 3a describes the typical molecular dissociation channel where the O_2 axis is perpendicular with the bridge-site line and the O_2 centroid approaches the surface at the bridge site; Figure 3b describes the other typical precursor dissociation channel where the O_2 centroid is near the surface at the hollow site. Figure 3 also shows that the entrance of the direct dissociation channel (Figure 3a) needs a little active translation energy and the exit of the channel makes the two dissociated atoms locate at the hollow sites of the nearest unit cells, whereas the low potential barrier (0.185 eV) appears at the exit of the precursor dissociation channel (Figure 3b) which leads to the two dissociation atoms located at the hollow sites of the alternate unit cells. The two typical dissociation channels present the most probable ordinal distribution of the dissociation adatoms. Figure 3b gives the precursor state with $\lambda = 1$(H2) and the dissociation trans-state (HBH in Table 2) with $\lambda = 2$ (the negative engenvalue in x and r) which is the sectional maximum critical point. So, the precursor state (H2) only exists as instant life, and O_2 dissociates as shown in Figure 3b, or it diffuses to the bridge-site line (t) and dissociates as shown in Figure 3a.

The former analysis is the theoretical results at low coverage and still offers the full dynamical physical image for the dissociation and adsorption of O_2 on the Pd(100) surface. The observational molecular states cannot exist when the Pd(100) surface is exposed to oxygen at the beginning; the oxygen molecules can dissociate and the dissociation atoms locate at 4-fold hollow sites orderly or inorderly; with the increasing of the oxygen exposure, the interaction of the adatoms and the molecules make the trans-state (H1) changes into observational state. Furthermore, the side interaction makes the low binding energy H2 state change into the H1 state. This physical image accords well with the experimental information.[7−9]

3.2. Dissociation and Adsorption of O_2 on the Pd(110) Surface. The Pd(110) surface is more complex, which is a zigzag surface constituted by Pd(111) and Pd(11$\bar{1}$) microfaects. In one surface unit cell, there are double adsorption sites: the long-bridge site (LB) and the pseudo-3-fold hollow site (H_3; see in Figure 1). There is a little information about the adsorption and dissociation of O_2 on this surface in experiments; in this paper, we search the critical characteristics of molecular state with $\lambda \leq 1$(see in Table 2). Only one molecular adsorption state named H_3−H−H_3 is found with $\lambda = 0$. The adsorption geometry of the state is that the O−O axis is parallel to the surface and the centroid projects in the 4-fold hollow site with the two atoms locating at the nearest pseudo-3-fold hollow site (H_3) along the [1$\bar{1}$0] direction. In addition, there are two molecular construction trans-states with $\lambda = 1$ (the negative engenvalue in θ): one is named the LB state that the oxygen molecule perpendicularly locates at the long-bridge site and the other one is named the H_3 state that the oxygen molecule tilts ($\theta = 14°$, $\varphi = 0°$) in pseduo-3-fold site. Other critical characteristics are listed in Table 2.

To discuss the dissociation and adsorption of oxygen molecules on the Pd(110) surface, we review the dissociation and adsorption of the diatoms. We have studied the oxygen atom adsorbing and diffusing on the unit cells of Pd(110) surface[20] and found two atomic adsorption states that the atoms adsorbed in LB site and H_3 site, respectively. There are four adsorption sites and two pseduo-3-fold sites (H_3) in the unit cell, and the other two long-bridge sites (LB) used by the nearest unit cells. Can the nearest adsorption sites become adsorption states (with $\lambda = 0$) that the two atoms of O_2 can adsorb? This needs to be verified, for two oxygen atoms dissociated from one molecule must inhabit two adsorption sites. Our calculated results deny the twain adsorption sites of H_3−H_3 and H_3−LB in one unit cell; the former becomes the molecular adsorption state (H_3−

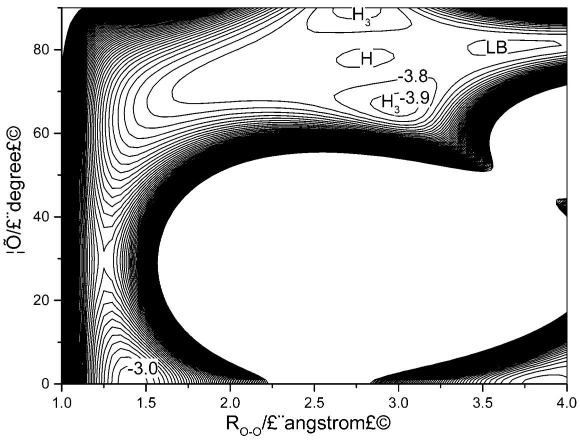

Figure 4. PES of O_2 on Pd(110) (R−φ) (counter is 0.2 eV).

H−H$_3$), whereas the latter cannot exist (discussion in the following). That is to say, only the atomic twain adsorption sites from the different unit cells (including the nearest unit cells) can offer adsorption sites ($\lambda = 0$) for the dissociated atoms.

We scan the molecular dissociation channels according to the parallel construction and draw the short-bridge line named s in Figure 1. There are two molecular dissociation channels: one is near the s line with the two dissociated atoms located at the LB site or H_3 site of the nearest unit cells and the alternation unit cells and the other one is near the hollow site along the [001] direction (the direction of the y axis in Figure 1) with the two dissociated atoms locating at the nearest LB sites. The characteristics of the dissociation channels are similar as shown in Figure 3a. O_2 drops down easily and then dissociate, and the dissociated atoms locate in the nearest H_3 sites and nearest LB sites, respectively. The characteristic of two trans-states is similar as shown in Figure 2, so the construction trans-states H_3 and LB only exist as twinkling life. In the end, we analyze the dissociation and adsorption of O_2 located at H_3−H−H_3. It is only along the [001] direction that there is a dissociation channel for the adsorption state listed in Table 2, and the molecular dissociated trans-states ($\lambda = 1$) H_3−LB1 and H_3−LB2 is also listed. From the characteristics, it can be seen that one oxygen atom locates in the H_3 site and the other one passes the near LB site along the [001] direction; finally, the molecule exist as the form of molecular dissociation states (the negative engenvalue in r), with the length of the O−O stretching to 2.38 and 2.53 Å and the potential barriers of being 0.27 and 0.26 eV, respectively. Obviously, the molecular adsorption state (H_3−H−H_3) is a sub-stable molecular dissociation precursor state, and the oxygen molecule cannot exist as observed life at low coverage. It is difficult to describe the dissociation process of the molecular adsorption state (H_3−H−H_3), because six freedom degrees all change in the process. However, the important mode is as follows: one oxygen atom adsorbs in the H_3 site, whereas the other oxygen atom turns to the [001] direction diffusing along the groove on the surface and passes the potential barrier of H_3-LB, then, adsorbs in H_3 of the nearest unit cell. To depict the process, we scan the potential energy surface (PES) (see in Figure 4). In the PES, one oxygen atom is fixed in the H_3 site as the axis center and the other atom stretches revolvably parallel to the surface; the degrees of φ and the length of the O−O bond are set as the x and y axes, respectively. The PES indicates clearly the wonderful process that the diffusing oxygen atom turns 65° and stretches to adsorb in H_3 site of the nearest unit cell. Above 60° in x axis, the PES displays the adsorption and diffusion of the oxygen atom on the (110) surface,[20] but the nearest LB site is not included, which shows that the twain adsorption sites (H_3−LB) in the same unit cell cannot become the adsorption sites ($\lambda = 0$) for the two dissociated atoms.

The foregoing theoretical results describe the physical prospect: at low coverage, the oxygen molecules on the (110) surface dissociate easily by the rich and colorful superficial channels and then the dissociated atoms adsorb in H_3 sites and LB sites, which are the β_1 state and β_2 state in the experiments;[13,14] only at high coverage can the adsorption state (H_3−H−H_3) exist as the observed life, which is the α state in experiments.[13,14]

3.3. O_2 Adsorption on Pd(111). In the low-index surfaces of the fcc metal, the (111) surface is the most compact one, and the adsorption and dissociation of O_2 on this surface is complex comparatively. So the interaction of O_2 and Pd(111) is always interested by all kinds of experimental and theoretical methods that have offered a great deal information about the molecular adsorption state and which is the emphasis in this paper.

At zero coverage, we get the critical points of O_2 on Pd-(111) surface with $\lambda \leq 1$ (see in Table 2). There is only one adsorption state named H−B−H with the O−O band paralleling the surface ($\lambda = 0$), the centroid of O_2 projects at bridge site (B), and the two atoms are located at the nearest 3-fold hollow sites; the stretching frequency of O−O is 565 cm^{-1} and the length of the O−O bond stretches to 1.67 Å. For the molecular side interaction, the two atoms do not dissociate, whereas they are present as the molecular adsorption state, which will be amplified in the following dissociation mechanism.

Two construction trans-states are found at $\lambda = 1$ (the negative engenvalue in θ) at H (fcc) site and H′ (hcp) site. The oxygen molecules are located at the H and H′ sites perpendicularly, which are named H and H′ states. The calculated results indicate that their characteristics are similar: the oxygen molecules located at the H and H′ sites are both apart from the surface of 1.74 Å and have stretching frequencies of 861 and 857 cm^{-1} and binding energies of 0.76 and 0.77 eV, respectively. It is difficult to distinguish the two states only from the frequency ect. in experiments, so they can be seen as identical states. In addition, there is a diffusing trans-state named the B state at the bridge site (B) with $\lambda = 1$ (the negative engenvalue in x or y).

In the experiments, the second peroxo-like state is identified with a vibrational frequency of 650[15] or 635[16] cm^{-1} at low coverage, here, which is regarded as the results of the side interaction among molecules. The two frequencies observed approximate that of the H−B−H state (565 cm^{-1}), whereas the ab initio[17] did not find it. With the coverage increasing, the trans-states that the O_2 located uprightly at the H and H′ sites become stable, which have the O−O stretching frequencies of 861 and 857 cm^{-1} that agree well with the experimental peroxo-like state of 850[15] or 805[16] cm^{-1} and the theoretical results of 855 and 876[17] cm^{-1}. At high coverage, O_2 locating at the B site forms the diffusing trans-state that has the O−O stretching frequency of 1067 cm^{-1} according to the experimental surperoxo-like state of 1035[16] cm^{-1} and the theoretical precursor state of 1026[17] cm^{-1}. Other characteristics of the critical points accord well with that of the experiments (in Table 3); the calculated results explain well three precursor states of the experiments.[15,16]

Why can so many molecular states be observed about the interactions of O_2 with the Pd(111) surface, and why is it so difficult to dissociate about the interaction of O_2 and the Pd-(111) surface? The concepts of the molecular dissociation limit and the surface dissociation distance are brought forward in the following, which are used to analyze the adsorption and

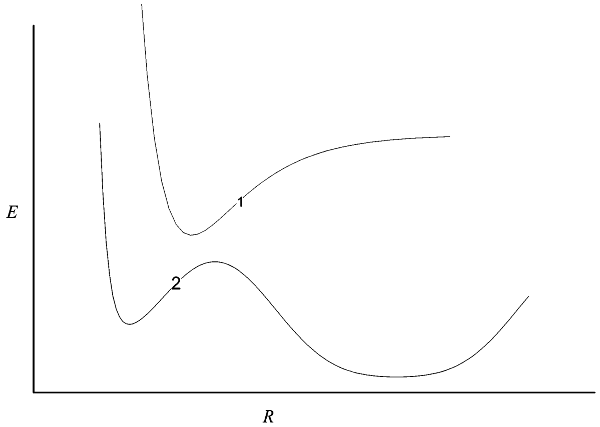

Figure 5. Sketch map for dissociation of the diatomic molecule (curve 1, the single potential well for gaseous diatomic molecule; curve 2, the double potential well for diatomic molecule on catalytic metal surface).

dissociation of O_2 on Pd(111) surface and offers the answer to the former questions at the same time.

3.4. Molecular Dissociation Limit and the Surface Dissociation Distance. The short-distance repulsion potential and the long-distance attraction potential appear in the dissociation process of the gaseous diatomic molecule commonly, which is called single potential well (see Figure 5 (curve 1)). There are many kinds of dynamical behaviors about the molecule dissociation and adsorptionon of the catalytic metal surfaces; in brief, they all can be described as double potential wells (Figure 5 (curve 2)), that is to say that the double repulsion potential appears in the dissociation of molecule on the surface. Figure 5 (curve 2) displays two familiar molecular dissociation channels with the signification as follows: (i) When the first potential well describes the adsorption state of two atoms, obviously, it is the direct molecular dissociation channel; the latter potential barrier and well displays the diffusing of the adatoms on the surface. (ii) When the first potential well describes the molecular adsorption state, without question, it is the precursor molecular dissociation channel; only the molecule passes the first potential barrier to the latter potential well, and it can dissociate to form an atomic adsorption state. Figure 5 (curve 2) also displays a simple physical prospect: when the diatom molecule dissociates at the first potential well, the length of two atoms (the molecular bond) stretches enough to counteract the atomic side interaction and form atomic adsorption states, which is the molecular direct dissociation channel induced by the first repulsion potential; or else, the length of two atoms (the molecular bond) is not enough to conquer the atomic side interaction and form the molecular adsorption state, which is the precursor molecular dissociation channel induced by the second repulsion potential. Evidently, the molecular bond is an important physical parameter for the molecular dissociation and adsorption. There is a threshold about the length of the molecular dissociation bond, which is called as the molecular dissociation limit. That is to say, only the length of the molecular bond passes the molecular dissociation limit and the molecule can dissociate.

Why do we especially emphasize the length of two atoms (molecular bond) about the molecular dissociation? Obviously, the molecular dissociation potential is the result of the interaction between the molecule and the catalytic metal surface, so it relates to the crystal lattice and the structure of the unit cell. Any positions on the catalytic metal surface may form the dissociation and adsorption channel of the incidence molecule, whereas the dissociated atoms cannot adsorb in any positions on the surface. So the atomic adsorption is decided by the adsorption geometry. The dissociated atoms often adsorb in the high symmetrical sites about the low-index surfaces of the fcc metal, such as the 4-fold hollow site on the (100) surface, the 3-fold hollow site on the (111) surface, the precursor-3-fold hollow site, and the long-bridge site (corresponding to the 4-fold hollow site) on the (110) surface. These sites have the higher sectional point cloud symmetry and the higher surface coordination, so they become the stable atomic adsorption sites. It is easy to assume that only the neighboring vacant adsorption sites (or the surface vacant twain sites) exist on the surfaces, and the diatomic molecule can dissociate. Evidently, the distance of the neighboring adsorption sites (the distance of the surface vacant sites) is the shortest distance of the molecular dissociation, which is called as the surface dissociation distance for the diatom molecule.

How do we judge two atoms that adsorb in the neighboring adsorption sites existing as the atomic adsorption states or the molecular adsorption state? It is easy to determine in theory. If two atoms inherit the dynamic critical characteristics of the atomic adsorption state, certainly, they are the atomic adsorption states that come from the molecular dissociation. Or else, two atoms have the side interaction and still exist as the molecular adsorption state. About the oxygen molecule, the side interaction represents the O−O stretching frequency of about 70−80 meV, which is bigger than that of the atomic vibration frequency.

Of course, the molecular dissociation needs the surface dissociation distance to exceed the molecular dissociation limit; however, the molecular dissociation limit restricts the surface dissociation distance. So, only if the surface dissociation distance is greater than the molecular dissociation limit can the molecule easily dissociate; otherwise, the molecular dissociation is difficult. But how long is the molecular dissociation limit? It is only estimated from the experience. The oxygen molecular dissociation limit is estimated to be about double the gaseous O−O bond. The surface dissociation distance can be obtained in quantification. In the following, we simply analyze the systems O_2−Pd(100) and (110) first, then, we review the adsorption and dissociation of O_2 on the Pd(111) surface.

About the Pd(100) surface, there is only the single atomic adsorption site and only one kind of surface vacant twain sites from the nearest unit cells. The surface dissociation distance is $(\sqrt{2}/2)a_0$, which is longer than the molecular dissociation limit. Obviously, the (100) surface offers the surface vacant twain sites for the incidence O_2. For the Pd(110) surface, there are the double adsorption sites, which offer many kinds of surface vacant twain sites. By analyzing the surface geometrical structure, it is easy to find that the distances of the surface vacant twain sites from the neighboring unit cells (the surface dissociation distance) are almost longer than the molecular dissociation limit; only the distance of the H_3−H_3 vacant twain sites from one unit cell is shorter than the molecular dissociation limit. Therefore, the H_3−H−H_3 state formed on the (110) surface and the short-life of the state have been searched. The two systems mainly present the dynamic characteristics of dissociation and adsorption.

We search the surface dissociation channels of the system O_2−Pd(111) and find that there is a direct dissociation channel near the bridge-site line (t). It is to say that only when the oxygen molecule closes to the surface at the top site and it can thoroughly dissociate do the dissociated atoms adsorb in the alternating 3-fold hollow sites. However, the dissociation channels mostly lead to the dissociated atoms adsorb in the neighbor 3-fold hollow sites and form the molecular adsorption

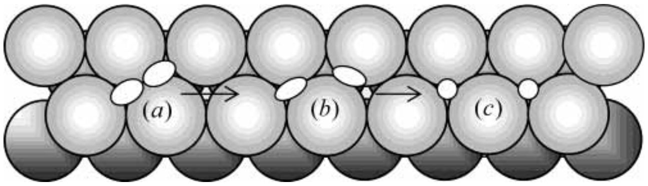

Figure 6. Mode for the dissociation of O_2 on Pd(111).

state (H−B−H). It is easy to see that the surface dissociation distance $[(\sqrt{6}/6)a_0]$ of the (111) surface is shorter than the molecular dissociation limit, so the molecular state exists naturally. For the molecular trans-states (H, H′, and B states), whether the molecules drop down directly or diffusely, finally, they exist as the form of molecular adsorption state (H−B−H) that is the dissociate precursor state. Just like the dissociation of O_2 at the H_3−H−H_3 site on the O_2−Pd(110), the dissociation of O_2 located at the H−B−H site needs to pass the top site along the molecular axis, and it will encounter the high potential barrier from the strong repulsion potential. So, it needs one atom of the diatom molecule to diffuse at the proper direction and dissociate through the lower potential barrier channel. The H−BB−H state (in Table 2) just acts the role of the dissociation trans-state (the negative engenvalue in *r*) that one atom adsorbs in 3-fold hollow site and the other one diffuses to the sub-neighbor bridge site (see in Figure 6b). In Figure 6, part b is deduced from the dissociation process of the molecular precursor state (H−B−H) denoted as (a). Figure 6 shows that the potential barrier of 0.48 eV will be needed if one atom of O_2 gets across the dissociation trans-state (b), dissociates, and adsorbs in the sub-neighbor 3-fold hollow site, and finally, the dissociated atoms exist as the atomic adsorption state (c).

About oxygen atom on the (111) surface, there is only the single adsorption site and one kind of surface vacant twain sites from the nearest unit cells, the surface dissociation distance is shorter than the molecular dissociation limit. The dissociation of the oxygen molecule depends on the dissociation channel of the precursor state (H−B−H), whereas the higher potential barrier is needed. So the precursor state (H−B−H) exists as the observed life (long-life). This answers well the former questions.

4. Conclusion

Based on the investigation of the atomic system of O−Pd,[20] in this paper, we make a further study of the molecular system of O_2−Pd and adopt the extended LEPS constructed by 5-MP. The results are as follows:

(1) For the O_2−Pd(100) system, at low coverage, the oxygen molecules mainly dissociate directly and hardly exist as the molecular adsorption state ($\lambda = 0$), and two trans-states (H1 and H2) are also found. With increasing oxygen exposure, the interaction between the adsorption atoms and the molecules makes the trans-state (H1) form the observed-life molecular state, whereas the side interaction leads to the trans-state (H2) can but transform into the trans-state (H1), which accords with the experimental information.[7−9] About the system of O_2−Pd-(110), at low coverage, the O_2 dissociates and the dissociated atoms adsorb in the H_3 and LB sites, which are the $\beta 1$ and $\beta 2$ states described in the experiments.[13,14] Only at high coverage can the molecular state H_3−H−H_3 be found, which is the α state in the experiments.[13,14] Oxygen molecules mainly exist as molecular adsorption states on Pd(111) surface. At low coverage, an oxygen molecule adsorbs in the H−B−H site, and with increasing coverage, the trans-states H and H′ become stable. At high coverage, the trans-state B also can exist stably. Our calculation results explain well the three states in the experiments.[15,16]

(2) We bring forward the conceptions of the molecular dissociation limit and the surface dissociation distance that are used to analyze the systems of O_2−Pd(100) and (110) and mostly analyze the adsorption and dissociation of the O_2 on the Pd(111) surface, which makes it clear for the question why it is more difficult to dissociate an oxygen molecule on the (111) surface than on the (100) and (110) surfaces. There are three main reasons: (1) Only one kind of surface dissociation distance of the oxygen atom on the Pd(111) surface is found, and it is obviously shorter than the molecular dissociation limit. (2) The single adsorption site is found about the oxygen atoms both on the Pd(100) suface and on the (111) surface, but only one dissociation channel is found on the (111) surface, the dissociation channel of the precursor state (H−B−H). (3) The dissociate potential barrier of the precursor state (H−B−H) is higher than that of ohers.

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