Adsorption of O Atom on Cr (100), (110), (111), and (211) Surfaces: An 5-Parameter Morse Potential Method Study

Ling-Li Han[†] and Tao Liu[†,‡,*]

[†]*Department of Chemistry and Chemical Engineering, Jining University, Qufu 273155, Shandong, China*
[‡]*School of Chemistry and Chemical Engineering, Shandong University, Jinan 250010, Shandong, China*
[*]*E-mail: liutao3569@gmail.com*

The 5-parameter Morse potential (5-MP) method for the interaction between O atom and Cr surfaces is constructed in the present work. The adsorption of O on Cr (100), (110), (111), and (211) surfaces are studied with 5-MP in detail. The fourfold hollow site of the Cr (100) surface is favored for O atom. On Cr (110), quasi-threefold site is favored with the parallel frequencies (the frequencies of O atom paralleling the metal surface) of 342 and 538 cm^{-1}, and perpendicular frequency (the frequency of O atom perpendicular to the metal surface) at 526 cm^{-1}. On Cr (111), the most favored mode for O atom is found to be the quasi-threefold site with the perpendicular frequency at 553 cm^{-1} and the parallel frequencies at 253 and 399 cm^{-1}. According to our calculation results, we speculate the most preferred mode for O adsorption on Cr (211) surface is the quasi-threefold site with the perpendicular frequency at 583 cm^{-1} and the parallel frequencies at 449 and 185 cm^{-1}.

Introduction

The mechanism of transition metal oxidation continues to be an active research area due to its impact upon corrosion, deactivation of catalysts, and metal oxide interface physics.[1] It is well known that the oxidation of chromium metal plays a major role in the corrosion resistance, and a number of studies have been carried out.[2,3]

On Cr (110) surface,[1,4-9] experimental scientists have made plenty of investigations to ascertain the adsorption states of O atoms. However, chemists do not determine whether quasi-threefold or long bridge sites were occupied. Shinn *et al.*[1,4] found the adsorption pattern of oxygen atom was of two-fold symmetry. However, Baca's groups[9] reported that the oxygen atoms adsorption sites were both at long bridge and threefold patterns, and the corresponding stretching frequencies were about 560 and 420 cm^{-1}, respectively. Meanwhile, they also found two frequencies at 440 and 580 cm^{-1} on Cr (111) surface. Therefore, they proposed that there were similar adsorption sites for oxygen on the two surfaces. The same phenomenon can be found in O-Mo (110)[10-12] and O-W (110)[13-15] systems.

There also were many studies on O-Cr (100) system.[2,9,16-18] At EELS experiment, Baca and co-workers[2] observed the Cr-O stretching frequencies between 495 cm^{-1} and 545 cm^{-1}, but they did not demonstrate the adsorption sites. In their further study,[9] oxygen atoms were indicated to be adsorbed at four-fold hollow sites. The Cr-O stretching frequency at 520 cm^{-1} was consistent with a four-fold hollow site at low coverage of oxygen on Cr (100).

In several decades, scientists have studied the adsorption of oxygen atom on the body-centered cubic (BCC) surfaces. However, some important features still need to be claried. In particular, the favored sites for oxygen atoms on the (110) surface, the adsorption height, and the adsorption bond length are still little to be known. Therefore, we revisited the Cr system again, which is the iso-group element of Mo and W, after O-Mo[19] and O-W[20] systems. To gain the complicated surface geometries, theoretical methods is more helpful than traditional experiments. In this work, we investigated the low-index Cr (100), (110), (111) surfaces and the stepped Cr (211) surface using the five-parameter Morse potential (5-MP) method. The 5-MP method adopted in this paper has been successfully used in the studies of S-Ni,[21] H-Ni,[22] Cl-Ag,[23] H-Fe[24] low index surfaces systems and H-Fe (211),[24] H-Pd (311),[25] O-Cu (211), (410),[26] O/N-Ni (311)[27] stepped surface systems.

Theoretical Calculation Methods and Surface Cluster Models. In previous work,[19-27] the 5-MP method was utilized successfully to study the interactions between atoms and surfaces, so it is presented in brief. An assumption called "surface frozen approximation" is adopted in this method. In other words, the surface cluster of metal atoms is fixed. The total potential energy $V(\vec{R})$ between the adsorbed atom and the whole surface cluster can be expressed as follows:

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

In the Eq. (1), R_i is the distance between the adsorbed atom and the ith surface atom ($R_i = |\vec{R} - \vec{r_i}|$); $\vec{R}$ and $\vec{r_i}$ specifies the coordinate of adsorbed atom and the ith metal surface atom, respectively; h_i is the vertical distance between the adsorbed atom and the surface where the i-th metal atom lies; β and R_0 are the parameters for vibration and equi-

librium distance, respectively; D is a simulating energy parameter; Q_1 and Q_2 are two simulating equipartition of energy parameters. We employ such a method to deal with the adsorption system in order to take account of the orientation affect of transition metal d electrons. We distinguish different adsorbed atom using the atomic weight M and distinguish different metallic system using lattice constant a_0. The total potential energy $V(\vec{R})$ we have constructed consists of only five parameters: D, β, R_0, Q_1, and Q_2. Apparently, $V(\vec{R})$ embodied by R relates to the surface structure.

Oxygen atom possesses three degrees of freedom when it moves on the cluster surface. In the Eq. (1), the potential energy $V(\vec{R})$ gives a potential hypersurface of four-dimensionality. The second derivative of $V(\vec{R})$ with respect to R in the critical point composes a Hessian matrix of 3×3 dimensionality. Then there are four kinds of critical points for the potential hypersurface. We apply the number of negative eigenvalues from Hessian matrix which is denoted as λ to characterize the nature of critical points. The critical point of λ = 0 is the minimum point which corresponds to the atomic surface adsorption state. The one of λ = 1 is the saddle point which corresponds to surface diffusion transitional state. The ones of λ = 2 and λ = 3 are the maximum point, and the one of λ = 2 corresponds to surface diffusion maximum point (the case of λ = 3 does not exist on the cluster surface). That is to say, our calculation can directly give the adsorption state, transitional state, *etc.*, for the adatom on the cluster surface by λ of critical points. Moreover, eigenvalues from Hessian matrix are relevant to the vibration frequency for the adatom on the cluster surface. The adsorption geometry is also determined by the information of adsorption state. In our calculation, different parameters can derive different results. If a set of parameters can gain the result that is consistent with the information from experiments, we then believe they are the optimum one. The characteristic that experimental scientists have not provided for the limit of experiment or the time or any other inexplicable reasons can be obtained by our calculation. On this point, we have confidence that our calculation can provide helpful information for experiments in reverse.

Therefore, in the whole work of the calculation, the key step is how to adjust the parameters. We employ the experimental data (for example: Cr-O stretching frequency, adsorption site, O-Cr bond length, *etc.*) of three low-index Cr surfaces (100), (110), and (111) to adjust the five parameters at the same time. The kinetic characteristics of adsorption such as the adsorption site, adsorption geometry, binding energy, and eigenvalue for vibration, *etc.*, for the adatom on a metal surface can be gained through our theoretical method. When our calculation results agree well with the experimental data, the 5 optimum parameters are determined. In this way, the potential energy $V(\vec{R})$ constructed by the optimum seeking parameters is applicable to deal with the atom adsorption system on low index Cr surfaces (100), (110), and (111) synchronously. $V(\vec{R})$ is also applicable to the adsorption system on the stepped surfaces
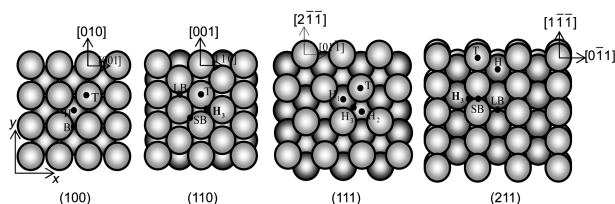

Figure 1. Cluster models and adsorption sites of Cr (100), (110), (111) and (211) surfaces. Shaded circle: Cr atom. ●: adsorption site.

that are constructed of low index surfaces mentioned above. That is to say, $V(\vec{R})$ is independent of the surface structure now after the five parameters have been fitted and fixed.

Metal chromium belongs to BCC lattice with the lattice constant $a_0 = 0.2884$ nm. Figure 1 shows the cluster models and the adsorption sites of Cr (100), (110), (111), and (211). From Figure 1, we can find the hollow site (H), bridge site (B), and top site (T) for Cr (100), the quasi-threefold hollow site (H_3), long-bridge site (LB), short-bridge site (SB) for Cr (110) surface, the second layer hollow site (H_1), coordinated by three Cr atoms of the row and one Cr atom of the next layer, the third layer hollow site (H_2), coordinated by three Cr atoms of the row and one Cr atom of the third layer, and quasi-threefold hollow site (H_3) for Cr (111) surface, and long-bridge site (LB), hollow site (H) and quasi-threefold hollow site (H_3) for Cr (211), respectively. Considering the local geometrical symmetry in a point group, the displacement symmetry for a surface crystal cell and the boundary effect of adsorbed atoms, we simulate the Cr surfaces by a chromium cluster with at least 5 layers of cell atoms. Every layer contain at least 6 (length) × 6 (width) atoms, which contains about 300 chromium atoms.

However, due to the relatively low local geometrical symmetry of Cr (211) surface, a chromium cluster with 8-layer cell atoms is used, and each layer contains at least 10 (length) × 10 (width) atoms.

Results and Discussion

For O-Cr system, 5 optimum parameters have been determined according to experiment data. The results are listed in Table 1. Systematical investigations are conducted using 5-MP method for O-Cr (100), (110), (111), and (211) systems, and all the critical characteristics are obtained. We list the results of our calculation in Table 2. There, λ denotes the number of the negative eigenvalues of Hessian matrix and can be used to represent the critical characteristic of potential energy surface; N denotes the number of Cr atoms near O atom; E_b is binding energy; f is eigenvibration frequencies ($f_{//}$ and $f_\perp$ denote parallel and perpendicular vibration frequency, respectively); $R_{O\text{-}Cr}$ is bond length; Z is the vertical distance between O atom and the cluster surface. The

Table 1. 5 parameters for O-Cr system

System	D/eV	β/nm^{-1}	R_0/nm	Q_1/nm	Q_2/nm
O-Cr	0.9	21.6	0.2	0.182	0.02

Table 2. Critical characteristics of O-Cr surface systems (All of the data are obtained from our calculation)

O-Cr	Site	N	λ	E_b/eV	f/cm^{-1} //	f/cm^{-1} $\perp$	$R_{\text{O-Cr}}$/nm	Z/nm
(100)	H	5	0	5.55	329 × 2	586	0.21 × 4, 0.197	0.053
	B	2	1	3.38	572	487	0.194 × 2	0.13
	T	1	2	2.02		581	0.195	0.195
(110)	H$_3$	3	0	4.55	342, 538	526	0.201, 0.196 × 2	0.124
	LB	4	1	4.37	626	532	0.24 × 2, 0.192 × 2	0.127
	SB	2	1	3.73	496	587	0.195 × 2	0.15
	T	1	2	2.42		621	0.193	0.193
(111)	H$_3$	4	0	5.11	253, 399	553	0.212 × 2, 0.2, 0.198	0.021
	S	2	1	3.49	392	593	0.2, 0.195	0.1
	M	4	1	4.81	333	616	0.2, 0.244 × 2, 0.194	0.024
	H$_1$	4	2	3.12		648	0.26 × 3, 0.192	0.108
	H$_2$	4	2	4.7		634	0.237 × 3, 0.194	0.027
	T	1	2	1.8		565	0.196	0.196
(211)	H$_3$	3	0	4.55	449, 185	583	0.196, 0.207, 0.195	0.0613
	LB	4	0	5.16	269, 434	554	0.21 × 2, 0.199 × 2	0.037

Table 3. The comparisons between the results in this work and the literatures

O-Cr	System	Experimental results	This paper
	(100) H	495-545[2]	586
	(110) H$_3$	420-440 [9]	526
$f_\perp$/cm^{-1}	(110) LB	605-615[1], 565-605[4] 555-585[9]	532
	(111) H$_3$	407-439 [9]	553
	(111) LB	520-580 [9]	616

comparison between our results and the data reported in the literatures are listed in Table 3.

For the O-Cr (110) system, H$_3$ site is the surface adsorption state with $\lambda = 0$, LB, and SB are the surface diffusion transitional states with $\lambda = 1$, and T is the surface diffusion maximum point with $\lambda = 2$, respectively (as shown in Table 2). The potential energy surface (PES) contour figure of adsorption and diffusion of an oxygen atom on Cr (110) at a height of 0.15 nm above the surface is scanned at the range (0, 1.0) along the [1$\bar{1}$0] direction and at (−0.5, 1.0) along the [001] direction, respectively (see Figure 2). The lowest energy contour is −5.0 eV and the contour energy interval is 0.1 eV in Figure 2. We can find from the Figure 2 that the oxygen atom can diffuse on the Cr (110) surface through H$_3$-LB-H$_3$ and H$_3$-SB-H$_3$. A potential energy barrier of 0.82 eV is found on the H$_3$-SB-H$_3$ diffusion channel, which gives an obvious clue that the diffusion on H$_3$-SB-H$_3$ channel on (110) surface is quite difficult to take place. Otherwise, on the H$_3$-LB-H$_3$ channel, the potential energy barrier is 0.18 eV, which indicates that the diffusion between the two stable adsorption states (H$_3$) in the same cell is very easy. The possible reason, we think, can owe to the close distance between the H$_3$ site and LB site on (110) surface and the similar adsorption height for O atom on them. Our calculation results predict a low-energy surface diffusion channel
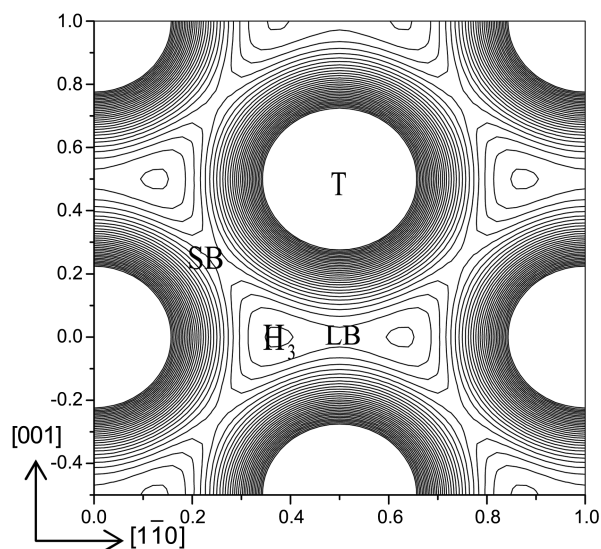
Figure 2. PES contour of O atom on Cr (110) at a height of 0.15 nm above the surface, the lowest energy contour is −5 eV and the contour energy interval is 0.1 eV.

for the O atom on the Cr (110) surface.

The geometrical symmetry of H$_3$ is the C$_S$ point group. The frequency of 526 cm^{-1} we obtained is the eigenvibration mode perpendicular to the surface. The vibration mode of 342 cm^{-1} is the one parallel to the surface for O atom along [1$\bar{1}$0] direction and that of 538 cm^{-1} is the one parallel to the surface along [001] direction. The adsorption height of O atom is 0.124 nm.

Baca groups[9] found two frequencies at their experiment, and reported the three-fold site for the 420 cm^{-1} peak and the long bridge site for the 560 cm^{-1} peak. Dinardo and his co-workers[28] reported analogous assignments using EELS for O/W (110), where the vibration frequencies at 380 and 580 cm^{-1} were observed. We compare Baca's experiment graph

with Dinardo's, and find their graphs are very similar. Recently, Elbe and his co-workers[14] did Dinardo's experiment again and found that O atoms sit on three-fold sites on W (110) surface. The parallel frequency (the frequency of O atom paralleling the metal surface) was at 380 cm^{-1} and the perpendicular frequency (the frequency of O atom perpendicular to the metal surface) was at 580 cm^{-1} for the three-fold sites. Queeney and his co-workers[11] reported that O atoms on Mo (110) surface preferred three-fold sites with parallel frequency at 398 cm^{-1} and perpendicular frequency at 605 cm^{-1}. Cr, Mo, and W are in the same group in the periodical table with similar characters, so O atoms adsorption on the three metal surfaces should be similar. According to our results and studies on Mo and W,[11,14,15,19,20,29] we speculate that the 420 cm^{-1} and 560 cm^{-1} peaks in Baca's experiment are parallel frequency and perpendicular frequency, respectively, for the three-fold site.

The unit cell of Cr (111) surface is larger than other low-index surfaces, so it is more difficult to analyze the surface configuration by experiment accurately and the studies of O-Cr (111) system are few. From Table 2, we can find that the quasi-threefold site (H$_3$) is the surface adsorption state, M is the surface diffusion transitional state between the two H$_3$ sites in the same cell, S is the one between the two H$_3$ sites in the adjacent cells, and H$_1$, H$_2$, and T are all the surface diffusion maximum points, respectively. To depict the PES contour figure of adsorbing and diffusing of O atoms on Cr (111) more distinctly, we scan it at $z = 0.05$ nm (see Figure 3).

On Cr (111) surface, a potential energy barrier of 0.30 eV exists on the diffusion channel H$_3$-M-H$_3$, and a potential energy barrier of 1.62 eV exists on the H$_3$-S-H$_3$ channel, which are much higher than those on Cr (110) surface. Therefore, we speculate that O atom can diffuse between the two H$_3$ sites in the same cell, but can not diffuse between the two H$_3$ sites in the adjacent cells easily.
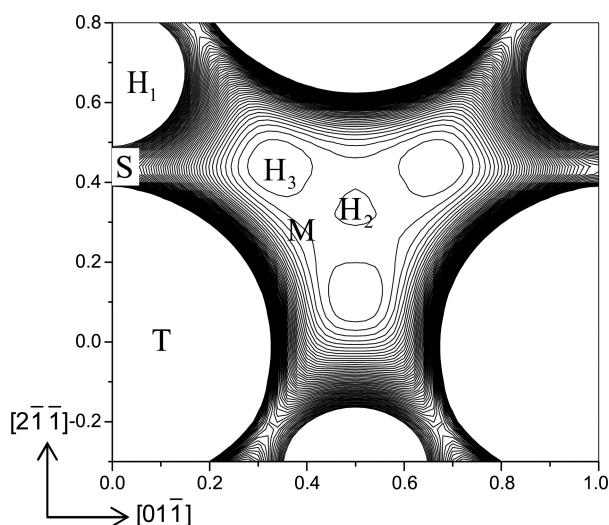

Figure 3. PES contour of O atom on Cr (111) at a height of 0.05 nm above the surface, the lowest energy contour is −6 eV and the contour energy interval is 0.2 eV.

The eigenvibration mode of 553 cm^{-1} perpendicular to the surface in our calculations corresponds to A$_1$ irreducible representation. The parallel vibrations belonging to the equivalent irreducible representation E now split into two one-dimension irreducible representations $\Gamma = 253$ and 399 cm^{-1}, respectively, which is attributed to the slightly distortion of the geometrical symmetry of H$_3$.

Baca and his co-workers[9] reported that O atoms were adsorbed on the threefold sites and long bridge sites (between first and third layer atoms), and the Cr-O stretching frequencies were 440 and 580 cm^{-1}, respectively. However, as reported in the previous studies,[19,20,30] O atoms only sat quasi-threefold sites with parallel frequency of 450 cm^{-1} and perpendicular frequency of 600 cm^{-1} for O-Mo (111) and O-W (111) systems. Our calculations show that the perpendicular frequency of the quasi-threefold site is 553 cm^{-1}, and one of the parallel frequencies is 399 cm^{-1}, which is agree very well with the Baca's experimental results (440 cm^{-1} and 580 cm^{-1}).[9] Therefore, we conclude that the frequencies reported by Baca groups should be the perpendicular and parallel frequencies of the quasi-threefold site.

As shown in Table 2, there are three kinds of possible sites on Cr (100) surface: T is the surface diffusion maximum point, B is the surface diffusion transitional state, and H is the surface adsorption state. These data support Baca's experimental results definitely.[2,9] The potential energy barrier is 2.17 eV on the diffusion channel H-B-H, so the diffusion of O atom on Cr (100) surface is very difficult.

The fourfold hollow site has a C_{4V} local geometrical symmetry. The 586 cm^{-1} eigenvibration (perpendicular to the surface) are determined to be the full-symmetrical A$_1$ irreducible representation. The 329 cm^{-1} eigenvibration (parallel to the surface) corresponds to the two-dimension degenerate irreducible representation E. Baca and his co-workers[2,9] observed vibrational frequencies between 495 and 545 cm^{-1} for fourfold hollow site, and the bond of O-Cr to the second layer Cr atom were 0.01-0.02 nm shorter than other bonds. Our calculation results ($f_\perp = 586$ cm^{-1}, $R_{O\text{-}Cr1} = 0.21$ nm, $R_{O\text{-}Cr2} = 0.197$ nm) agree well with their experimental results.

The step of BCC (211) surface is shorter than other step surfaces, so it is named as high index surface. The local geometrical symmetry of the Cr (211) surface is C_1. There are seven kind possible sites, similar to Mo (211) and W (211). To depict the potential energy surface contour figure of adsorbing and diffusing of O atoms on Cr (211) more distinctly, we scan it at $z = 0.072$ nm (see Figure 4). Among them, H$_3$ and LB are the surface adsorption states, SB is the surface diffusion transitional state between the two adjacent H$_3$ sites, S1 and S2 are the surface diffusion transitional state between the H$_3$ and LB sites, and T is the surface diffusion maximum points. We have discussed the character of all critical points for O-Mo[19] system in details, so we only list the surface adsorption states in Table 2 and will not discuss them in this paper anymore.

As there are many adsorption sites on Cr (211), to determine the particular adsorption geometry of O atoms on
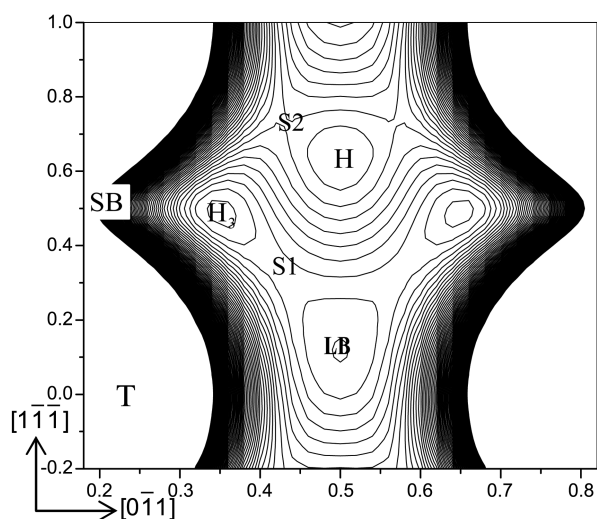
Figure 4. PES contour of O atom on Cr (211) at a height of 0.072 nm above the surface, the lowest energy contour is −6 eV and the contour energy interval is 0.1 eV.

Cr (211) is very difficult. As far as we know, there is no report on adsorption characteristic of O atoms on this surface. The calculation using our model can predict the information that has not been detected by experiments yet. Our calculation results show that the frequency at 583 cm^{-1} is the perpendicular vibration mode of H$_3$ state, 449 cm^{-1} is the parallel vibration mode for oxygen atoms along the $[0\bar{1}1]$ direction, 185 cm^{-1} is the parallel vibration mode along the $[1\bar{1}\bar{1}]$ direction, the vibration mode of 554 cm^{-1} corresponds to perpendicular frequency of LB state, and 269 and 434 cm^{-1} correspond to parallel frequencies, respectively. The vibration frequencies of adsorption states we calculated are similar to the experimental and theoretical results of O-Mo[19,31] and O-W[20,32] systems, which gives us confidence to assume that our calculation can predict the experimental results accurately. Comparing with LB site in cell, H$_3$ site is closer to the surface, the density is larger, and the space masking effect is smaller. By analogizing the results with Mo and W system, we predict that O atoms prefer H$_3$ sites in factual adsorption and LB sites will disappear. We would expect that the accurate calculation results for the model systems will be useful for the experimental researchers working in this field.

Conclusion

In this work, we have described the interactions between O atoms and Cr surfaces, and total critical characteristics of O-Cr system by the 5-MP method. These results suggest:

(1) At low coverage, O atoms are adsorbed on fourfold hollow sites of Cr (100) surface. The frequency at 586 cm^{-1} is the perpendicular vibration mode, which agrees well with experimental results (495-545 cm^{-1}).[2,9]

(2) On Cr (110), (111), and (211) surfaces, oxygen atoms all sit on quasi-threefold sites, similar to O-Mo and O-W systems.[13,16,18,19,29,30,31] The perpendicular frequency is 526

cm^{-1} on (110) surface and 553 cm^{-1} on (111) surface. On (211) surface, the O-Cr stretching frequency at 583 cm^{-1} and the parallel frequencies at 449 and 185 cm^{-1} are predicted.

(3) The order of the binding energy of an O atom adsorbed on the three low index metal surfaces is (100) > (111) > (110). The diffusional barrier for O atom on Cr (110) is 0.18 eV, which indicates that the diffusion for O atom on Cr (110) is easy. On the other hand, the diffusion on Cr (100) is very difficult owing to the high diffusional barrier of 2.17 eV.

Our work in this paper is the key basis for the further study. In the future, we will study the adsorption and dissociation of the molecular (O$_2$ or CO) on the Cr surfaces using the extended LEPS constructed by 5-MP.

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