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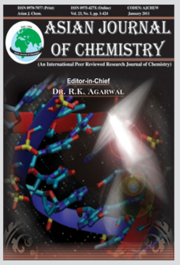

Adsorption and Vibration for S Atom on Rh Three Low-Index Surfaces

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All critical characteristics between S atom and Rh surfaces have been systematically studied by 5-parameter Morse potential. The calculated results show that S atom locates in the fourfold hollow site of the (100) surface. Different from the atoms in the first and second period, S atom tend to occupy the fourfold hollow site of (110) surface. For S-Rh(111) adsorption system, S atom adsorbs in the fcc and hcp threefold hollow sites and the two adsorption sites are found to be approximately equivalent. In accordence with the conclusion of S-Ni and Cl-Ag adsorption system, the surface binding energy of S atom is also found to be relevant to the coarse degree of cluster surface with the binding energy ordered as (111) < (100) < (110) in this paper.

Key Words: S-Rh system, 5-Parameter Morse potential, Surface adsorption, Surface vibration.

INTRODUCTION

The dynamics of the interaction between the atoms, molecules and solid surfaces has been paid more and more attention during the past decades with the rapid development of the chemical industry and the surface adsorption as the key of the heterogeneous catalysis has taken on the more and more expansive prospect. Recently, the interests are paid on the adsorption and diffusion of sulfur on well-defined metal surfaces. On the one hand, the pollution of the sulfur and sulfur compounds in air have awaken people's attention, on the other hand, the adsorption of sulfur atom on the metal surfaces can make the catalyst poisoning, inhibit catalytic reaction and affect the recycle use of catalyst. Therefore, the study on the interaction of sulfur with metal surfaces will have a far-reaching significance.

For S-Rh system, a number of studies focus on the interaction of S atom with three low-index surfaces of rhodium. Liu *et al.*[1] had studied S adsorption on Rh(100) by low energy electron diffraction (LEED) and detected the formation of c(2 × 2) and p(2 × 2) phases. Both the two phases were found that S atom located in the fourfold hollow site. In addition, Liu *et al*. obtained the adsorption height of 0.130 nm and the bond length of 0.231 nm for S-Rh(100)-c(2 × 2) phase and the adsorption height of 0.136 nm and the bond length of 0.230 nm for S-Rh(100)-p(2 × 2) phase. Prior to Liu *et al.*[1], Zeng *et al.*[2] and Bahr *et al.*[3] obtained the same bond length of 0.226 nm by using LEED and an angle resolved photoemission extended structure (ARPEFS), respectively. The high resolution electron energy loss spectroscopy (HREELS) performed by Dubois[4] to detcect atomic sulfur resided in four-fold hollow sites and the stretching frequency of 313 cm^{-1}.

About S-Rh(110)system, Hengrasmee *et al.*[5] found that sulfur atom located on the fourfold hollow site and predicted the adsorption height of 0.077 nm as well as the bond lengths of 0.212(1) and 0.245(4) nm.

Few studies are done for S-Rh(111) adsorption system. And so far, it is also lacking of theoretical investigation on the S-Rh system. Therefore, the entirely study on the characteristics of all critical points should be carried out so as to thoroughly understand the interaction of the S-Rh surface system. In order to achieve the purpose, it is difficult only relying on the traditional experiments while the semi-experience theoretical method is possible. The five-parameter Morse potential (5-MP) method is applied that included five adjustable parameters: D, β, R_0, Q_1, Q_2. The method has been performed on S-Ni[6], Cl-Ag[7], O-Rh[8], H-Pt[9], CO-Pt[10], NO-Pd[11] and CO-Rh[12] surface systems recently and the results are in excellent agreement with experiments data. In this paper, the further S adsorption on the low-index surface of Rh is studied using the the five-parameter Morse potential (5-MP) method and obtained the characteristics of all the critical points.

COMPUTATIONAL METHOD

As described in the recent works[6-12], we constructed 5-MP first for S-Rh interaction systems in this paper. Our calculation carried out in the approximation of frozen surface.

The total potential function $V(\vec{R})$ of the interaction between the adsorbed atom, which coordinate is specified by $\vec{R}$ and the whole surface cluster constructed by n metal atoms can be expressed as following:

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

In eqn. 1, R_i is the distance between adsorbed atom and the ith surface atom (denoted as $\vec{r}_i$), namely, $R_i = |\vec{R} - \vec{r}_i|$; h_i is the vertical distance between the adatom and the surface where the ith metal atom is in; D is a simulating energy parameter and Q_1 and Q_2 are two simulating parameters; β and R_0 are the parameters for vibration and equilibrium distance, respectively. The potential function $V(\vec{R})$ comprises five adjustable parameters: D, β, R_0, Q_1 and Q_2. So we call $V(\vec{R})$ as the 5-parameter Morse potential between an adatom and the metal surface cluster and D, β, R_0, Q_1, Q_2 are adjustable parameters.

We use the number of negative eigenvalues from Hessian matrix which is denoted as λ to characterize the nature of critical points. The Hessian matrix of 3 × 3 dimensionality is gained by the second derivative of $V(\vec{R})$. The critical point of $\lambda = 0$ is the minimum point which corresponds to atomic surface adsorption state. The one of $\lambda = 1$ is the saddle point which corresponds to surface diffusion transitional state. The one of $\lambda = 2$ and $\lambda = 3$ is the maximum point and the one of $\lambda = 2$ corresponds to surface diffusion maximum point (the case of $\lambda = 3$ doesn't exist on the cluster surface).

We employed the experimental data of three low index silver surfaces (100), (111) and (110) to adjust the five parameters at the same time. The kinetic characteristics of adsorption such as the adsorption sites, adsorption geometry, binding energy and eigenvalue for vibration etc. for the adatom on a metal surface can be gained through our theoretical method. In this way, the potential function constructed by the optimum seeking parameters is applicable to deal with the atom adsorption system on the three low index rhodium surfaces (100), (111) and (110) synchronously.

Model of surface clusters: Metal rhodium belongs to fcc lattice with the lattice constant $a_0 = 0.3796$ nm. Considering both the local geometrical symmetry in a point group and the whole surface lattice displacement, we simulate the Rh plane by rhodium clusters with at least 5 layers of cell atoms and every layer contains at least 6(length) × 6(wide) atoms, which contains about 300-rhodium atoms. The size of the cluster is defined by the principle that there is no boundary effect in our calculation.

The adsorption sites of S on Rh planes are defined as in Fig. 1. They are the hollow site (H), bridge site (B) and top site (T) of Rh (100) plane, the fcc hollow site (H) and hcp hollow site (H') of Rh (111) plane and the pseudo-3-fold hollow site (H3), long-bridge (LB) site, short-bridge (SB) site as well as the transitional state (S) between long-bridge site and pseudo-3-fold hollow site of Rh (110) plane, respectively.

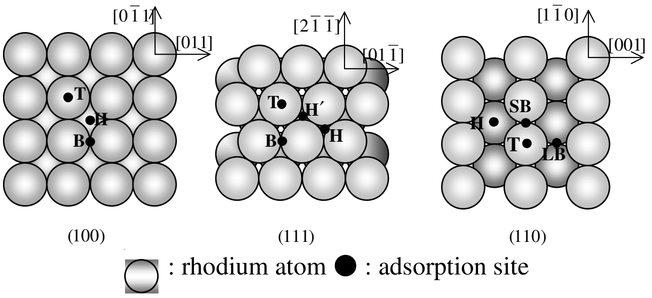

Fig. 1. Surface sites are illustrated on Rh (100), Rh (111), Rh (110)

RESULTS AND DISCUSSION

In S-Rh surface interaction systems, the five optimum parameters are listed in Table-1. Using 5-MP, we investigated S-Rh (100), (111), (110) systems and obtained the whole critical characteristics, the corresponding results are summarized in Table-2. For the S-Rh surface system, we have gained binding energies (E_b), bond length between S adsorbed atom and its nearest neighbor Rh atoms ($R_{S\text{-}Rh}$), the vibrational frequencies (f) and the distance of O atom above the surface ($Z_{S\text{-}Rh}$) for S adsorption on all the sites. In Table-3, we make a comparison between present results and the results from literatures on S-Rh(100), (110), (111) systems.

TABLE-1
FIVE PARAMETERS FOR S-Rh SYSTEM

System	D (eV)	β (nm^{-1})	R_0 (nm)	Q_1 (nm)	Q_2 (nm)
S-Rh	0.65	21.0	0.234	0.1210	0.010

S-Rh(100) system: The calculated results about the S-Rh (100) surface system in Table-2 show that the top site T ($\lambda = 2$) is the surface diffusion maximum point, the bridge site B ($\lambda = 1$) is the surface diffusion transition state and the four-fold hollow site H ($\lambda = 0$) is the surface adsorption state that has a C_{4V} local geometrical symmetry. From Table-2, it can be seen that the bond length and adsorption height (0.131 and 0.230 nm) in this paper coincide with the experimental results obtained by Liu *et al.*[1], Zeng *et al.*[2] and Bahr *et al.*[3]. Besides, Zeng *et al.*[13] and Hengrasmee *et al.*[14] calculated the bond length of S-Rh (100) and obtained the theoretical values of 0.230 nm and 0.227 nm, respectively, which is consistent with present result. Table-3 shows that the perpendicular vibration of 313 cm^{-1} agrees well with 313 cm^{-1} of the HREELS spectrum[4].

S-Rh(111) system: The Rh (111) surface is the most compact surface among the three single crystal surfaces. Calculations show that there are four different non-equivalent critical points on (111) surface. H' and H three-fold hollow sites are surface adsorption states with $\lambda = 0$ in a C_{3v} local geometrical symmetry. B is surface diffusion transitional state. T is the diffusion peak. Considering the structure of the Rh (111) surface H' and H are non-equivalent adsorption sites, but analysis from the results listed in Table-2, we can see that the difference between their characteristic critical points is very little, the same RS-Rh , Z S-Rh and Eb as well as a considerably low discrepancy of 1 cm^{-1} in in parallel vibraional frequencies, so they can be considered approximately equivalent.

The perpendicular vibration model of 388 cm^{-1} and parallel vibraional model 242 cm^{-1} obtained for three-fold adsorption

TABLE-2
CRITICAL CHARACTERISTICS OF S-Rh (100), (110), (111) PLANE SURFACE SYSTEM

S-Rh	Adsorption site	N	λ	E_b (eV)	F (cm^{-1}) //	F (cm^{-1}) ⊥	$R_{S\text{-}Rh}$ (nm)	Z (nm)
(100)	H	4	0	4.24	340 × 2	313	0.230 × 4	0.131
	B	2	1	2.77	273	373	0.229 × 2	0.185
	T	1	2	1.82	–	373	0.226	0.226
(110)	H	5	0	4.40	172, 112	416	0.215, 0.250 × 4	0.086
	LB	4	1	3.44	540	243	0.217 × 2 0.345 × 2	0.099
	SB	2	1	2.49	264	361	0.230 × 2	0.187
	T	1	2	1.60	–	356	0.228	0.228
(111)	H	3	0	3.61	242 × 2	388	0.220 × 3	0.169
	H´	3	0	3.61	241 × 2	388	0.220 × 3	0.169
	B	2	1	3.19	296	394	0.217 × 3	0.176
	T	1	2	2.01	–	388	0.216	0.216

TABLE-3
COMPARISONS BETWEEN PRESENT RESULTS AND LITERATURE

S-Rh	System	Experimental data	Theoretical values	This work
R (nm)	(100)H	0.231[1] 0.230[1] 0.230[14]	0.227[13]	0.230 × 4
	(110)H	0.211, 0.245[5]	0.211, 0.245[13]	0.215 × 1, 0.250 × 4
	(111)H	0.218[15]	0.216[16]	0.220 × 3
Z (nm)	(100)H	0.130[1]. 136[1]	–	0.131
	(110)H	0.077[5]	–	0.081
f (cm^{-1})	(100)H	⊥313[4]	–	313

state in this paper. The bond length 0.220 nm enjoyed good agreement with the experimental result of 0.218 nm obtained by Wrong *et al.*[15] and the theoretical value of 0.216 nm obtainen by Mitchell[16]. In addition, the adsorption height of 0.169 nm and binding energy of 3.61 eV are predicted in this paper. We expect more experimental and theoretical information to verify present results.

S-Rh(110) system: The Rh (110) surface is the most rough among the low-index surfaces. From Table-2, it can be seen that there are four kinds of non-equivalent critical points on this surface. Among them, fourfold-hollow site (H) are surface adsorption stable state with λ = 0. Long-bridge site and short bridge is the surface diffusion transitional state, of which short bridge is the surface diffusion transitional state between two H sites along the [001] direction and long-bridge site is the surface diffusion transitional state between two H sites along the $[1\bar{1}0]$ direction. T are surface diffusion maximum point. Differenting from the adatoms in the first and second period that adsorb in the pseudo-threefold hollow site and long-bridge site on the (110) surface, S atom tend to occupy fourfold hollow site on the Rh(110) surface. The pseudo-threefold site is annihilated thoroughly during the adsorption and long-bridge site becomes the surface diffusion transitional state for S-Rh (110) adsorption system. From the elements periodic table, we find that the effective atomic radius of S is 0.270 nm, which is larger than that of those atoms in the first and second period. It suggest that the sulfur atom only adsorbs in the surface site with lower electron density. Our conclusion is consistent with that of S-Ni system[6] and Cl-Ag[7] described in the previous works and get the support of the experimental result of Hengrasmee *et al.*[5].

Thorough analysis of present results about the S-Rh(110) surface system, we display the PES contour figure of adsorption and diffusion of S atom on Rh (110) surface crystal cell at the height of 0.150 nm above the surface as shown in Fig. 2. The surface positions and characteristics of three non-equivalent critical points are clearly labeled on it. From the PES, one can clearly see that S atom adsorbs in the fourfold hollow site. From Table-2, it can be seen that the perpendicular vibration model of 416 cm^{-1} and parallel vibrational model 112 and 172 cm^{-1} obtained for four-fold adsorption state, of which the former is the vibrational model along the [001] direction and the latter is the vibrational model along the $[1\bar{1}0]$ direction. The adsorption height of 0.086 nm obtained in this paper is very close to the results of Hengrasmee *et al.*[5].

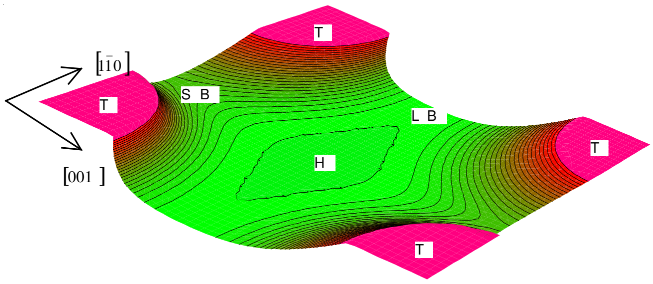

Fig. 2. PES contour of S atom on Rh (110) crystal cell

In addition, it can be clearly seen from Table-2 that the binding energy for S-Rh(100), S-Rh(110) and S-Rh(111) is 4.24, 4.40 and 3.61 eV, respectively. They are ordered as (111) < (100) < (110), agreeing with the order of the coarse degree for cluster surface. Thus, the binding energy of S atom is relevant to the coarse degree of cluster surface. The same conclusion is also obtained for S-Ni and Cl-Ag systems. It suggests that the binding energy for those atoms in third period is relevant to the coarse degree of cluster surface, generally speaking, the more rough metal surface is, the larger the binding energy is.

Conclusion

In this paper, the five-parameter Morse potential (5-MP) method is applied to examine the characteristics of S-Rh(100), (110) and (111) plane surface systems. The results agree well with the experiments. In relevant conclusions:

(i) For S-Rh(100) system, the calculated results show that S atom adsorbs in the fourfold hollow site. The bond length, adsorption height as well as the perpendicular vibration obtained in this paper agree well with experimental results.

(ii) Although quasi-3-fold site and long-bridge site is the stable asorption site on metal(110) surface for the first and second period atoms, the fourfold hollow site becomes the most stable adsorption site for S on Rh(110) and S atom tends to occupy 3-fold site on Rh(111) surface. In addition, we also predict the perpendicular and paralle vibration for S-Rh(110) and S-Rh(111) systems, which is looked forward to be vertified by experimental methods.

(iii) On the S-Rh(111) surface system, we find that fcc(H) and hcp(H') can be considered equivalent approximately in (111) surface.

(iv) The theoretical results show that the surface binding energy of S atom is relevant to the coarse degree of cluster surface with the binding energy ordered as (111) < (100) < (110), which is consistent with the conclusion about S-Ni and Cl-Ag adsorption system.

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