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Abstract. The adsorption of acetylene on Pd(111) and stepped Pd(111) surfaces as well as the influence and mechanism of a monatomic step have been investigated by theoretical calculations. On ideal Pd(111), the favourite acetylene adsorption site is the threefold hollow site. Our calculated geometry configuration and vibrational frequencies of adsorbed acetylene are consistent with previous studies. Generally speaking, steps have active effects, zero effects or inactive effects in the adsorption process. For acetylene on stepped Pd(111), a monatomic step as the active site makes the C–C bond of acetylene further weakened. Acetylene adsorption geometry in the second case (C–C bond axis tilts to the surface normal and the molecular plane is vertical to the step direction) is similar to that of the molecule on the Pd(110) surface because of the (110) structure of the step. Furthermore, the vibrational frequencies of acetylene are also in agreement with the results of HREELS studies of acetylene on Pd(110).

1. Introduction

Surface defects exist extensively on many metal and semiconductor surfaces. Surface defects such as steps, vacancies and kinks play a significant role in surface adsorption [1–6], epitaxial growth [7, 8] and surface diffusion [9, 10]. However, the study of surface defects is experimentally and theoretically difficult. Until now, the influence of surface defects is far from well understood. Therefore, the investigation of surface defects is of technological and theoretical importance.

Generally speaking, steps, the most typical defects, miscellaneously influence adsorbates on the surfaces. In some cases, steps are considered to behave as active sites, e.g. CO and O on $Pt(s)3(111) \times (001)$ [2]. On heating of the co-adlayer of CO and O on $Pt(s)3(111) \times (001)$, three CO_2 formation peaks appear in the range 200–400 K. The CO_2 desorption for each peak is sharply collimated along the terrace surface normal, indicating the occurrence of a combinative reaction on the declining terraces [2]. However, steps have little influence over adsorbates in other cases. Acetylene adsorption on stepped Cu(111) [3] is a case in point. The monatomically stepped Cu(111) strengthens the bonding between acetylene and the substrate but almost does not influence the activation of adsorbed acetylene. CO adsorption studies on a stepped Cu(111) surface by Bonicke *et al* [4] also indicate only that the step sites have a higher adsorption energy than the terrace sites, and no other change is observed. What is more, hydrogen adsorption on the $Ni(s)5(111) \times (\bar{1}01)$ surface [6] shows that the step sites are inactive in the dissociation of molecular hydrogen.

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In our recent study of acetylene adsorption on stepped Cu(111) [3], acetylene on the stepped surface is changed little compared with that on the ideal Cu(111) surface. On the other hand, acetylene adsorption geometry on Pd(111) is different from that on Cu(111) owing to different vibrational spectroscopy [11]. Acetylene on Pd(111) is considered to be on a threefold hollow site [12–17]. Thus, we expect that there is different behaviour of acetylene on stepped Pd(111) from that on stepped Cu(111).

In this paper, we give much information about the configuration and mechanism of acetylene on stepped Pd(111). We have tried to make clear the function of surface steps in the adsorption process. Like the study of acetylene adsorption on stepped Cu(111), we used the atom superposition and electron delocalization molecular orbital (ASED-MO) and discrete variational Xα (DV-Xα) methods in the process of the theoretical study.

2. Models and methods

In this paper, two model clusters of Pd_{24}–C_2H_2 and Pd_{33}–C_2H_2 are adopted to simulate the C_2H_2 adsorption on Pd(111) (figure 1(*a*)) and stepped Pd(111) (figure 1(*b*)), respectively.

The ASED-MO theory is used in our total energy (TE) calculations and has been applied to many systems [18–21]. This fast method seems appropriate especially for calculating the bond geometry and force constants of complex systems. The atomic parameters used in our calculations are listed in table 1 [22–24]. Using these parameters, the C–H and C–C bond lengths of the free C_2H_2 molecular are overestimated by 0.11 Å and 0.09 Å, respectively, while the C–H stretching and C–C stretching frequencies are 3299 cm^{-1} and 1945 cm^{-1}, respectively, in good agreement with the experimental results of 3374 cm^{-1} and 1974 cm^{-1} (relative errors are only 2.22% and 1.47%, respectively).

Table 1. Atomic parameters employed in the calculations: n, the principal quantum number; I_p, the ionization potential; ζ, the Slater orbital exponent.

	s orbital			p orbital			d orbital				
Atom	n	I_p (eV)	ζ (au)	n	I_p (eV)	ζ (au)	n	I_p (eV)	ζ_1 (au)	ζ_2 (au)	c_1	c_2
H	1	12.30	1.20									
C	2	15.29	1.658	2	9.96	1.618						
Pd	5	8.777	2.074	5	5.337	1.783	4	11.54	2.478	5.387	0.5538	0.6440

In order to determine the equilibrium geometry, we used a modified conjugate gradient algorithm [25] in our ASED-MO TE calculations, where energy gradients are calculated according to the scheme in [26]. This modified conjugate gradient scheme has the advantage of possessing a single local minimum that is also the global minimum [25].

Our experiences show that it is efficient using the ASED-MO method to determine the geometry configuration but that it is not suitable for calculating energy levels and the density of states. As in our previous study, the DV-Xα method is employed to develop a deeper insight into the bonding mechanism and electronic properties. The molecular wavefunctions and eigenvalues were determined using the self-consistent charge (SCC) approximation to the potential. In the present procedure, the C 1s and the Pd 1s–4p core orbitals have not been varied, that is to say the 'frozen-core' approximation has been used. More details of this method have been given in [27].
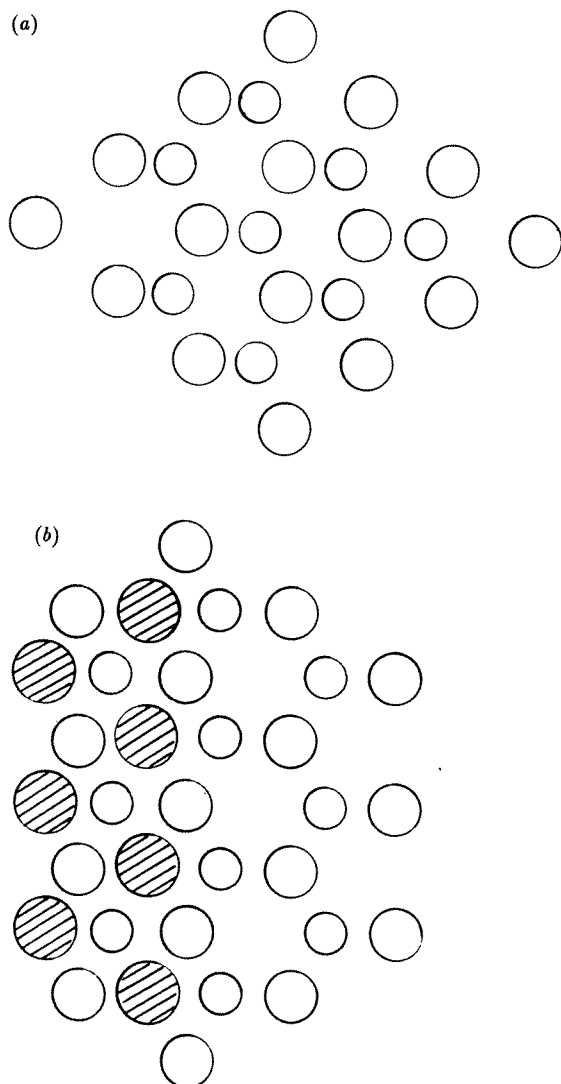
Figure 1. (*a*) Model cluster Pd$_{24}$ applied to simulate the flat Pd(111) surface: ○ , the first-layer Pd atom; ○, the second-layer Pd atom. (*b*) Model cluster Pd$_{33}$ applied to simulate the stepped Pd(111) ○ , the first-layer Pd atoms; ○, the second-layer Pd atoms; hatched circles, the step-layer Pd atoms.

3. Results and discussion

3.1. Acetylene on ideal Pd(111)

First, we must study the adsorption of acetylene on ideal Pd(111) using the ASED-MO method so that we can develop insight into the adsorption of acetylene on stepped Pd(111). We calculated the binding energies of acetylene on atop, bridge and threefold hollow sites. In our calculations, we optimized 12 coordinates of the four atoms of acetylene on those possible adsorption sites. Our results show that the favourite adsorption site is the threefold

hollow site. The results of the optimized geometry are shown in table 2. It turns out that the adsorbed acetylene molecule has an elongated C–C bond, 1.470 Å, compared with the calculated C–C bond length in the gas-phase molecule, 1.290 Å, and a strongly distorted C–C–H angle of 130.7°. The molecular plane is slightly tilted at 14.4° from the surface normal. These data are in good agreement with the results of recent calculations [17]. The results in [17] indicated that the molecular plane tilted angle from the surface normal would increase and the C–C–H angle would decrease with increase in acetylene coverage on Pd(111). So our calculated results have a slight discrepancy with those of the near-edge x-ray absorption fine-structure and x-ray photoelectron spectroscopy data on the same system [16], which may be considered as the case of high C_2H_2 coverage.

Table 2. Optimal geometrical parameters of acetylene adsorbed on Pd(111) and stepped Pd(111).

	C–C distance (Å)	C–H distance (Å)	C–C–H angle (deg)	Tilt angle (deg)	Binding energy (eV)
C_2H_2–Pd(111), threefold hollow	1.470	1.160	130.7	14.4	2.274
[17]	1.344	1.085	130	14	1.91
C_2H_2–Pd(s)(111), first case	1.528	1.176	140.1	14.9	2.325
C_2H_2–Pd(s)(111), second case	1.528	1.193	131.3	—	2.172
		1.149	112.6		

Furthermore, we calculated the vibrational frequencies of C–H and C–C bonds to compare with the electron energy loss spectroscopy (EELS) study. We used a Morse-type expression to simulate the TE curve versus the bond length near the equilibrium position [21]:

$$E(x) = E_0 + [a + b(x - x_0) + c(x - x_0)^2][1 - \exp(-\alpha(x - x_0))]^2$$

where $E(x)$ is the TE at position x, x is the bond length, and x_0, E_0, a, b, c and α are the parameters to be found. Using the least-squares method for the data of our calculated TE near the equilibrium position x_0, we can obtain the equilibrium position x_0, minimum total energy E_0 and force constants $k = (d^2E/dx^2)|_{x=x_0} = 2a\alpha^2$.

We obtained C–H and C–C bond-stretching frequencies of 3123 cm^{-1} and 1381 cm^{-1}, respectively, in excellent agreement with the results of the EELS study, 2990 cm^{-1} and 1400 cm^{-1} [28] (table 3). The C–H bond length stretches by only 0.02 Å, and the C–H stretching frequency decreases a little, which indicates that the C–H bond is only slightly weakened. On the other hand, the C–C bond length stretches considerably by 0.18 Å, to a value between those of the double and single bonds indicating a drastic weakening of the C–C triple bond. The large decrease in the C–C bond-stretching vibrational frequency to values between those of the double (1600 cm^{-1}) and single (1000 cm^{-1}) [29] bonds also shows significant weakening of the C–C bond. In addition, we calculated C–C and C–H bond orders which are listed in table 4. The C–C bond order decreases from that of gas-phase acetylene, 1.83, to 1.07 while the C–H bond order decreases only slightly.

To study the dependence of the results on the size of Pd cluster, we also have calculated the TEs of C_2H_2 adsorbed on the Pd(111) surface using the cluster Pd_{30}–C_2H_2. We found that the results of adsorption geometry and the bond orders are not varied. The binding energy of 2.439 eV, compared with that using Pd_{24}–C_2H_2, 2.274 eV, also changes little. These results show that there is no essential difference in the C_2H_2 adsorption on the Pd(111) surface when the size of the cluster is varied.

Furthermore, we employed the DV-Xα method to calculate the same system in order to

Table 3. Calculated and experimental vibrational frequencies (in parentheses) of C–C and C–H stretching modes.

	Vibrational frequency (cm^{-1})	
	C–C	C–H
C_2H_2 (free)	1945 (1974)	3299 (3374)
C_2H_2–Pd(111)	1381 (1400)	3123 (2990)
C_2H_2–Pd(s)(111) first case	1264	3043
C_2H_2–Pd(s)(111) second case	1224	3188
		2847
C_2H_2–Pd(110) (experimental)	1230	2985
		2820

Table 4. The bond orders of C–H and C–C of C_2H_2 adsorbed on the ideal Pd(111) and the stepped Pd(111) surface.

	Bond order	
	C–H	C–C
C_2H_2 (free)	0.81	1.83
On ideal Pd(111)	0.79	1.07
On stepped Pd(111), first case	0.72	0.92
On stepped Pd(111), second case	0.80	0.90
	0.66	

study the electronic structures of acetylene on Pd(111). We adopted the coordinates of the equilibrium structure determined above. The electronic occupation numbers of acetylene molecular orbitals are calculated, and the results are shown in table 5. It turns out that adsorbed acetylene π orbital donates to the surface about $0.98e$ and the surface back-donates to the π^* orbital about $1.29e$, which accounts for the drastic weakening of the C–C triple bond.

Table 5. Molecular orbital occupation numbers of C_2H_2 adsorbed on the ideal Pd(111) and the stepped Pd(111) surfaces.

	σ_s	σ_s^*	σ_p	π	π^*
C_2H_2 (free)	2.00	2.00	2.00	4.00	0.00
C_2H_2 (on ideal Pd)	2.00	2.00	2.00	3.02	1.29
On stepped Pd, first case	2.00	2.00	2.00	2.90	1.73
On stepped Pd, second case	2.00	2.00	2.00	2.95	1.61

The calculated total density of states (TDOS) for the cluster of favourable structure is shown in figure 2(a), where the Fermi energy is considered as zero and the broken curve shows the TDOS of the clean Pd surface. Figure 2(b) is the differential spectrum between the clusters of acetylene on the Pd(111) surface and the clean surface. The peaks 13.74 eV, 9.66 eV and 7.21 eV below the Fermi energy in the TDOS are from σ_s, σ_s^* and σ_p acetylene molecular orbitals, respectively.
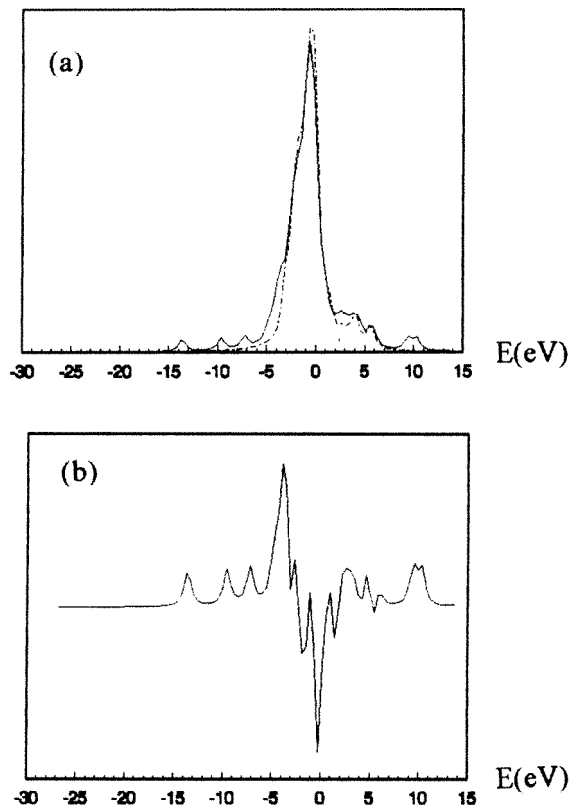
Figure 2. DOS curves of C_2H_2 on ideal Pd(111): (*a*) TDOS curve together with the TDOS of clean Pd (– – –); (*b*) the differential spectrum.

3.2. Acetylene on stepped Pd(111)

In order to simulate the step, we adopted a cluster of Pd_{33}–C_2H_2 (see figure 1(*b*)). In our ASED-MO TE calculations, two kinds of adsorption site on stepped Pd(111) are considered: one is the site where the acetylene molecular plane is parallel to the step direction (the first case); the other is the site where the acetylene C–C bond axis tilts to the surface normal and its molecular plane is vertical to the step direction (the second case).

The results of geometrical optimization of the two kinds of case are shown in figure 3 (only part of the cluster is drawn) and summarized in table 2. In the first case, adsorbed acetylene has a slightly elongated C–C bond length, 1.528 Å (compared with acetylene on ideal Pd(111)), a C–H bond length of 1.176 Å and a distorted C–C–H angle of 140.1°. The molecular plane, like acetylene on ideal Pd(111), is slightly tilted at about 14.9° from the surface normal (see figures 3(*a*) and 3(*b*)). In the second case, a more complicated local structure is obtained and is shown in figures 3(*c*) and 3(*d*), which show that the C–C bond length is also larger than that of acetylene on the ideal Pd(111) plane, and the C–C bond axis is inclined to the surface plane. The binding energy in the first case is slightly larger than in the second case (see table 2).

In order to study the electronic properties of acetylene adsorbed on the stepped surface, we have also calculated the vibrational frequencies of C–C and C–H bonds (see table 3),
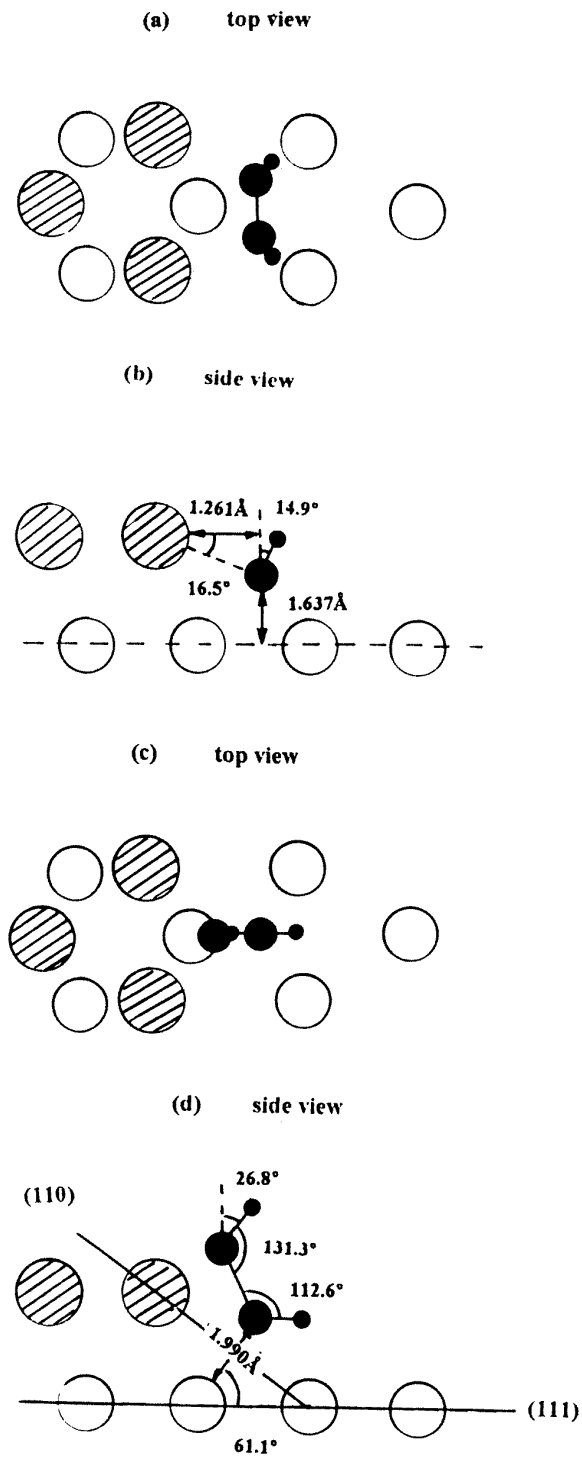
(a)   **top view**

(b)   **side view**

(c)   **top view**

(d)   **side view**

Figure 3. Schematic adsorption geometry for C_2H_2 on stepped Pd(111) (*a*), (*b*) for the first case and (*c*), (*d*) for the second case: ⬤ , C atom; •, H atom. Only part of the cluster is drawn.
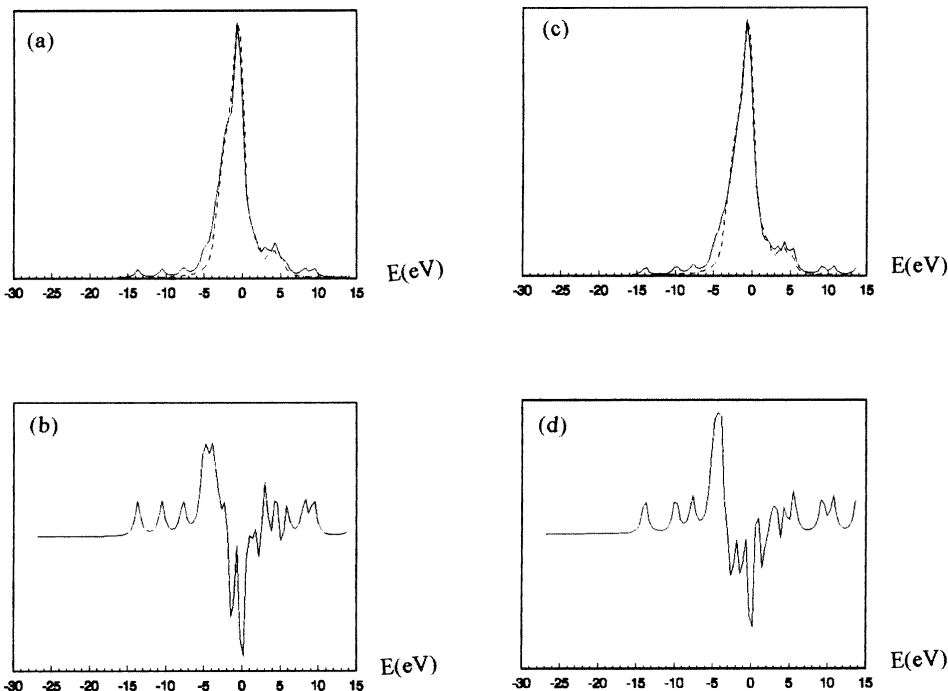
Figure 4. TDOS curves of C_2H_2 on stepped Pd(111): (*a*) TDOS of the first case, together with the TDOS of clean Pd (– – –); (*b*) the differential spectrum of the first case. (*c*) TDOS of the second case, together with the TDOS of clean Pd (- - - -); (*d*) the differential spectrum of the second case.

the bond orders of those bonds (see table 4), and the electronic occupation numbers of the molecular orbitals (see table 5). In comparison with ideal Pd(111), we found that, in the first case, the C–C stretching frequency decreases from 1381 to 1264 cm^{-1}, and the C–C bond order also decreases from 1.07 to 0.92. These results indicate that the C–C bond is further weakened when acetylene is adsorbed on the stepped plane. This is clearer from the data in table 5. When acetylene is adsorbed on the stepped surface, the π bonding orbital further transfers electrons to the surface, and the π^* antibonding orbital obtains more electrons from the surface. Thus, the C–C bond is further weakened.

As mentioned above, steps have active effects, zero effects or inactive effects in adsorption process. In the paper, for acetylene on stepped Pd(111), steps as active sites make the acetylene further weakened according to our above analyses.

In addition, an investigation of the cluster shown in figure 1(*b*) will reveal that the step under investigation has a (110) structure. The (111) and (110) planes are indicated as lines in figure 3(*d*). In comparison with acetylene on Pd(110) [30], acetylene in the second case has a similar adsorption geometry, e.g. a tilt angle of C–C bond axis to the (110) plane. Our calculated C–C stretching frequency is 1224 cm^{-1}, in excellent agreement with the result of HREELS studies of about 1230 cm^{-1} [30]. We have also calculated two C–H stretching modes listed in table 3. One of the C–H stretching modes is obviously softened because the H atom is closer to the surface Pd atoms [31]. Overall, our calculated vibrational frequencies are consistent with the experimental values, which confirm the suggestion of the HREELS studies.

Finally, like the case of ideal Pd(111), the TDOS of acetylene on the stepped surface is given in figure 4, where the Fermi energy is considered as zero and the broken curve is the TDOS of the clean Pd surface. Figures 4(*b*) and 4(*d*) show the differential spectra between the cluster of acetylene on the stepped Pd(111) surface and the clean surface. The peak for σ_s does not change, but the peaks for σ_s^* and σ_p move to 10.48 eV and 7.62 eV below the Fermi energy in the first case, and they appear at 10.07 eV and 7.62 eV below the Fermi energy in the second case.

4. Summary

The adsorption of acetylene on the Pd(111) and stepped Pd(111) surfaces as well as the influence and mechanism of a monatomic step have been investigated by theoretical calculations. A summary of the important results is as follows.

(1) On the ideal Pd(111), the favourite acetylene adsorption site is the threefold hollow site. Our calculated geometry configuration and vibrational frequencies of adsorbed acetylene are consistent with previous studies.

(2) Our calculated results of vibrational frequencies, bond orders and electronic occupation numbers of molecular orbitals show that the monatomic step on stepped Pd(111) is the active site, which further weakens the adsorbed acetylene.

(3) Acetylene adsorption geometry in the second case is similar to that of the molecule on the Pd(110) surface because of the (110) structure of the step. Furthermore, the vibrational frequencies of acetylene are also in agreement with the results of HREELS studies of acetylene on Pd(110).

Acknowledgment

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