

Articles

Adsorption and Vibration of Carbon on Low Index and Defect Nickel Surface

ZHANG, Wen-Xia(张文霞) QIAO, Qing-An(乔青安) CHEN, Shou-Gang(陈守刚)
CAI, Mei-Chao(蔡梅超) WANG, Ze-Xin*(王泽新)

Chemistry Department, Shandong Normal University, Jinan, Shandong 250014, China

The 5-parameter Morse potential of interaction between carbon and the nickel surface was constructed. We studied the adsorption and vibration of carbon atom on Ni(100), Ni(110) and Ni(111) single crystal low index surfaces and obtained the data of adsorption sites, adsorption geometry, binding energy and eigenvibration *etc.*, which were in good agreement with the experimental results. Meanwhile, the influence of step defect on Ni(100) surfaces for carbon adsorption was also investigated.

Keywords C-Ni surface system, adsorption and vibration on surface, surface step defect

Introduction

Chemisorbed carbon plays an important role as intermediate in many of the catalytic reactions involving the production or reaction of hydrocarbons. Meanwhile, carbon deposits on surfaces can poison the catalyst in some reactions. Thus, the investigations of interaction between carbon and catalyst are of great value. Since the 1970s, to the accompaniment of the development on surface technique, most experiments have been performed on this kind of system, such as LEED,¹⁻³ EELS,⁴⁻⁶ AES,⁶ SEXAFS,^{7,8} PED⁹ and other techniques,¹⁰⁻¹³ and obtained a lot of useful data. On the other hand, many theoretical treatments were also done, such as EMT,^{14,15} ASED,^{16,17} DFT,^{18,19} *ab initio*,²⁰ BEBO,²¹⁻²³ and others.²⁴ All the researches above have deepened our understanding of chemisorption of carbon and its role in the catalytic formation of hydrocarbons.

By using LEED¹⁻³ and AES⁶ two different types of carbon adsorbates on Ni(100) and Ni(111) surfaces can be identified: carbidic and graphitic carbon. The carbidic carbon consists of nearly non-interacting carbon atoms while graphitic carbon resembles carbon in graphite. Ibach *et al.*⁴ and Lenard, *et al.*⁵ obtained the eigenvibration data through EELS technique. Furthermore, Takatoh, *et al.*⁶ measured carbon K-edge adsorption on Ni surfaces by electron energy loss fine spectroscopy (EELFS). Their results indicate that both carbidic and graphitic carbon can be formed on Ni(100) and Ni(111), and the nearest neighbor distance for C—C and C—Ni were obtained respectively. The experimental and theoretical studies by Blakely and co-workers^{2,12,13,21} also examined carbon adsorption on nickel. They found that for Ni(100) the carbon coverage was directly related to the temperature and was well described by a Langmuir model. The variation of the total binding energy of a carbon atom to the Ni(100) surface in a coverage range of 0.3—0.68 was less than 2%. In contrast to the Ni(100) results, sharp changes in carbon coverage versus temperature were observed for Ni(111), indicating the presence of a distinct carbon phase. Upon cooling to temperatures below approximately 1080 K, the carbon phase was identified as a monolayer of graphite with a binding energy of 7.55 eV. Although an isolated carbon adatom was not observed at lower temperature, an estimated binding energy of ≤ 6.93 eV was reported. Onuferko, *et al.*,¹ Bader, *et al.*,⁷ Arivaanitis, *et al.*⁸ and Kilocoyoe, *et al.*⁹ also investigated C-Ni(100) sys-

* E-mail: qqawzx@263.net3

Received July 28, 2000; revised and accepted December 18, 2000.

Project supported by the Natural Science Foundation of Shandong Province.

tem by means of LEED, SEXAFS and PED respectively. Data for binding energy, height of carbon adatom above nickel surface, the nearest neighbor C—Ni distance and surface reconstruction were obtained. One of them⁷ took account into the distributions of the second layer nickel atoms which had the nearest neighbor distance of 0.196 nm with the carbon adatom and could not be resolved experimentally. But the results from Jacobsen, *et al.*¹⁴ and Darling, *et al.*¹⁵ by EMT method showed that binding energy, the nearest neighbor C—Ni distance and the eigenvibration were varied with the hybridization strength between carbon adatom and metal d-band. They also found that in a $p(1 \times 1)$ surface structure, carbon-carbon interactions were weak, and a coverage of two carbon atoms per surface metal atom was necessary to observe strong interactions. Meanwhile, Burghraef, *et al.*¹⁶ and van Langeveld, *et al.*¹⁷ examined the characteristic quality of C-Ni (111) system by ASED-MO method. But there was great discrepancy between their results. The DFT method was also employed on this system by de Koster, *et al.*¹⁸ and Klinke II, *et al.*,¹⁹ and their results indicated that the fcc hollow site is the most energetically favorable position for carbon chemisorption on Ni(111) at all coverages. The relative stability is described as follows: fcc hollow \approx hcp hollow \gg bridge \gg top-on site. The barrier for carbon adatom migrating to form graphitic carbon was ≥ 163.176 kJ/mol. Both the C—C bond formation barrier and the C—Ni bond strength were dependent on the valence-electron occupation. Isett, *et al.*²¹ obtained the binding energy for C-Ni (100) and C-Ni (111) system as well through BEBO method. This method was also applied by Weiberg, *et al.*,^{22, 23} who got the energy data for C adsorbed at fcc hollow site and hcp hollow site on Ni(111) surface. The model of PCV was used by Frese Jr.²⁴ to calculate the binding energies at zero coverage for H, O and C atoms adsorbed on single crystal and polycrystalline metals, including Si, Fe, Ni, Pt, Pd *etc.* He got the binding energy for carbon-single crystal of nickel for 6.47 eV.

The analysis above shows that the nature of the interactions between C and Ni surface needs a further investigation and examination both experimentally and theoretically. Furthermore, the discrepancy among various theoretical methods makes it very necessary for a deepened research.

In order to make a fine understanding of the mechanism of carbon atom adsorption on metal surfaces, it is

necessary for us to get the specific characteristic of all the critical points. The 5-parameter Morse potential of interactions between an atom and metal surface was performed on H-Ni surface system in our previous studies,²⁵ and the results were in good agreement with experimental data. Its advantages lie on the independence between the parameters and the metal surface structure. That is to say we can deal with different metal surfaces with the same parameters. So this method can be used to deal with metal surfaces with defect. In this paper we made a further study of C-Ni surface system, and obtained the specific characteristic of all the critical points. At the same time we also examined the influence of step defect on Ni surfaces for carbon adsorption. All the work will get ready for a further study of hydrocarbons or other polyatomic molecular adsorption on metal surface.

Theoretical model and calculation method

If the interaction potential $U(R)$ between adsorbed atom and solid surface is regarded as the sum of the interaction potential $V_i(R)$ between the adsorbed atoms and surface atoms, then

$$U(R) = \sum_i V_i(R) \quad (1)$$

where i is valid to the whole cluster, $V_i(R)$ can be expressed by Morse potential as follows:

$$V_i(R) = D_i \{ \exp[-2\beta(R_i - R_0)] - 2 \exp[-\beta(R_i - R_0)] \} \quad (2)$$

where $D_i = D \cos \zeta_i$, D is binding energy, R_i is the distance between adsorbed atom and surface atom, ζ_i is the correcting angle between the adsorbed atom and the normal line of the nickel surface and can be described as follows: $\zeta_i = \cos^{-1} \left(\frac{h_i + Q_1}{R_i + Q_2} \right)$, where h_i is the vertical distance between the adatom and the metal surface, Q_1 and Q_2 are simulating parameters. β and R_0 are the parameters for equilibrium distance of vibration.

Metal nickel belongs to fcc lattice with the lattice constant $a_0 = 0.352$ nm. Considering both the local geometrical symmetry in point group and the whole surface lattice displacement, we simulate the metal surface by a nickel cluster with $12(1) \times 9(w) \times 5(h)$ layers of cell

atoms, which have 540-nickel atoms. Through the optimum seeking of the simulating parameters (see Table 1), we obtained the characteristics (see Table 2) of carbon atom adsorbed in fcc hollow site (H), hcp hollow site (H'), bridge site (B) and top-on site (T) (see Fig. 1) on Ni(100), Ni(110) and Ni(111) surfaces respectively, which are in good agreement with the experimental results. For C-Ni(110) system, LB denotes long-bridge site and SB the short-bridge site. H₃ is the

pseudo-3-folded hollow site and S is the transitional state between LB and H₃ site. The influence of step surface of C-Ni{*n*(100) × (111)-[011̄]} (see Fig. 2) system for carbon adsorption is also gathered in Table 2.

Table 1 Simulating parameters

<i>D</i> (eV)	β (nm ⁻¹)	<i>R</i> ₀ (nm)	<i>Q</i> ₁ (nm)	<i>Q</i> ₂ (nm)
1.54	20.0	0.188	0.182	0.091

Table 2 Critical characteristics of C-Ni surface system

System	Site	<i>N</i>	λ	<i>E</i> _b (eV)	<i>z</i> (nm)	<i>F</i> (meV)		
						//	⊥	<i>R</i> (C-Ni) (nm)
C-Ni(100)	H	5	0	7.69	0.020	104.07 × 2	46.55	0.177 × 4, 0.197
	B	2	1	4.96	0.132	78.05	80.90	0.182 × 2
	T	1	2	3.36	0.179		92.09	0.179
C-Ni(111)	H	3	0	6.23	0.116	66.56, 66.60	77.34	0.185 × 3
	H'	3	0	6.24	0.115	67.08 × 2	77.25	0.184 × 3
	B	2	1	5.58	0.131	82.52	84.29	0.181 × 2
	T	1	2	3.68	0.178		95.28	0.178
C-Ni(110)	H	1	2	6.47	0.056		95.24	0.180
	H ₃	3	0	6.55	0.054	38.75, 33.56	88.86	0.195 × 2, 0.182
	S	2	1	6.51	0.054	37.20	92.14	0.195, 0.181
	LB	4	0	7.18	0.018	105.77, 52.98	66.74	0.177 × 2, 0.189 × 2
	SB	2	1	4.51	0.133	77.07	79.07	0.182 × 2
	T	1	2	2.97	0.180		88.38	0.180
C-Ni { <i>n</i> (100) × (111)-[011̄]}	H ₁	5	0	9.22	0.018	114.26, 116.06	48.98	0.176 × 2, 0.179 × 2, 0.194
	H ₂	5	0	7.76	0.020	104.48, 104.82	47.36	0.177 × 2, 0.178 × 2, 0.196
	H ₃	5	0	6.47	0.179	58.93, 50.83	86.85	0.145, 0.178, 0.180, 0.191 × 2

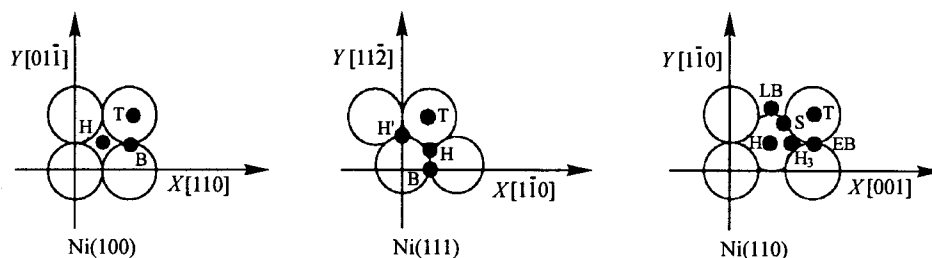


Fig. 1 Model for Ni(100), Ni(111) and Ni(110) surface (○: Ni atom; ●: adsorption site).

Results and discussion

Carbon adsorption on flat nickel surfaces

We list our calculations in Table 2, where *N* de-

notes the number of the nearest neighbor Ni atoms around C adatom ($R_{C-Ni} \leq 0.20$ nm), *E*_b the binding energy, *z* the distance of C above the surface and *f* the eigenvibration. In Table 3 we compare our results with data from literatures either experimentally or theoretically.

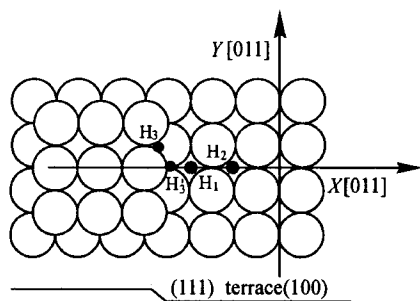


Fig. 2 Model for C-Ni $\{n(100) \times (111) - [01\bar{1}]\}$ system
(\circ : Ni atom; \bullet : adsorption site).

A carbon atom has three freedom degrees when it moves on nickel surface, the interaction potential $U(R)$ constitutes a four-dimension potential energy hypersurface $U(x, y, z)$, which has four kinds of critical states. The characteristic of these states can be described by the number λ of negative eigenvalues from Hessian matrix. The state with $\lambda = 0$ is the critical point of minimum energy and $\lambda = 1$ the saddle point, while the points with $\lambda = 2$ or $\lambda = 3$ have the maximum energy either locally or wholly. When C adsorbed on Ni surface, the system has no negative eigenvalue towards Z axis, so there are only three kinds of critical points in the sys-

Table 3 Comparison with literature

System			EMT ¹⁴	ASED-MO	CFSSO-BEBE ²¹	DFT	Experimental	This paper
E_b (eV)	(100)	H	6.50, 8.10		7.43		7.35 ² , 7.37 ¹⁰ 7.55 ¹³	7.69
	(111)	H	6.40, 8.25	8.59 ¹⁶ 3.82 ¹⁷	6.63	6.17 ¹⁸ 6.68 ¹⁹	6.8 ¹⁹ , < 6.95 ¹⁰	6.23 6.24
		H'		8.74 ¹⁶ 3.94 ¹⁷		5.97 ¹⁹		
Z (nm)	(100)	H					0.03 \pm 0.012 ¹ 0.02 \pm 0.02 ⁷ 0.025 \pm 0.005 ⁹	0.020
R_{C-Ni} (nm)	(100)	H	0.191, 0.185				0.180 \pm 0.0015 ¹ 0.182 \pm 0.005 ⁷ 0.189 \pm 0.005 ⁸ 0.185 \pm 0.006 ⁹	0.177 \times 4 0.197
							(111)	H
		H'						
F (meV)	(100)	H	\perp 45, \perp 40				\perp 48.4 ⁴	\perp 46.5 ⁵
	(111)	H	\perp 85, \perp 75				\perp 64.5 ⁴	\perp 77.3 ⁴
		H					\perp 67 ⁵	\perp 77.2 ⁵

tem. The stable adsorption state is denoted by $\lambda = 0$, the diffusing transitional state by $\lambda = 1$ and the diffusing peak by $\lambda = 2$.

In C-Ni(100) system, the surface lattice has a C_{4v} local geometrical symmetry in point group. It can be seen from our results that there are three different kinds of critical points for the C-Ni(100) system corresponding to three types of non-equivalent adsorption states. The top-on site is the peak point for carbon diffusing on surface while the hollow site is the most stable adsorption site energetically, and the transitional state between

them is the bridge site. The hollow site in Ni(100) surface has a local geometrical symmetry in group point of C_{4v} . The eigenvibrations parallel to the surface of C adatom are 104 meV corresponding to the irreducible representation E in C_{4v} point group and the one perpendicular to the surface is 46.55 meV which belongs to the full-symmetrical A1 representation in C_{4v} . The datum of 48.4 meV from EELS⁴ experiment is corresponding to A1 expression. The binding energy of C adsorption on Ni hollow site is 7.687 eV and the carbon adatom has four nearest neighbor Ni atoms conjugated with $R_{C-Ni} =$

0.177 nm. All the results from our calculations are in fine agreement with EELS, LEED and PED experimental data.^{1,2,4,5,7-10} It can be seen that at low coverage carbon atom is inclined to diffuse from top-on site or bridge site to hollow site. Namely, the favorable adsorption site for C atom is the site of the highest geometrical symmetry, which agrees with the literature as well.

Ni(111) surface is the most compact surface of the three, which has C_{3v} local geometrical symmetry in point group. As for C-Ni(111) system, there are also three different kinds of critical points corresponding to three types of non-equivalent adsorption states respectively. The characteristics for top-on site (T) and bridge site (B) are the same as mentioned above. Considering the structure of Ni(111) surface, although H' and H are different types of adsorption sites, the difference between their characteristics of critical points is very little from our calculations. The discrepancy for binding energy is 0.013 eV, for eigenvibration less than 1 meV and for R_{C-Ni} 0.001 nm. All the discrepancies are too little to distinguish by experiments, so H' and H sites can be considered equivalent approximately, which is consistent with the DFT results.^{18,19} On the other hand H' and H sites were proved to coexist in the Ni(111)-(1 × 1) structure by LEED experiment.³ The adsorption state in H site has C_{3v} local geometrical symmetry in point group. The adsorbed C atom has three nearest neighbor Ni atoms with $R_{C-Ni} = 0.185$ nm and the bonding energy is 6.23 eV. These data are consistent with the experimental results very well.^{6,7,9,10} Moreover, the eigenvibrations parallel to the surface of C adatom are 66.6 meV, corresponding to the irreducible representation E in C_{3v} point group. And the one perpendicular to the surface is 77.3 meV which belongs to the full-symmetrical A_1 representation in C_{3v} .

Ni(110) surface, the structure of which is relatively a little complex, is a zigzag surface constituted by Ni(111) and Ni(11 $\bar{1}$) surfaces. So it is inevitable for the similarity of the characteristics between Ni(110) and Ni(111) surface. The Ni(110) system has C_{2v} local geometrical symmetry in point group. Our calculations indicate that there are six different kinds of critical points for the C-Ni(110) system corresponding to six types of non-equivalent adsorption states (see Table 1). The characteristics of top-on site (T) and shot-bridge site (SB) are similar to the T and B sites mentioned above

while H is the peak point for carbon diffusing on the surface. Both H₃ and LB are stable sites for adsorption. The binding energy for H₃ is 6.548 eV which is close to that of fcc hollow site of C-Ni(111) system, and there are three nearest neighbor Ni atoms which are nearly equivalent conjugated C atom with $R_{C-Ni} = 0.195$ nm (two) and 0.182 nm (one) respectively. Since the geometrical symmetry of H₃ is like the slightly distortional C_{3v} , the vibrations which should belong to the equivalent irreducible representation E now split into two one-dimension irreducible representations Γ 38.75 meV and 33.56 meV respectively. But the variance between them is too small to distinguish experimentally. From Table 2, it shows that LB site has the lowest binding energy, while the binding energy of H, S and H₃ sites is very similar to each other, so it is very easy for carbon to migrate among them.

Carbon adsorption on Ni{ $n(100) \times (111)$ }-[011 $\bar{1}$]} step surface

The real surfaces of catalyst always have some defect sites that are considered as the active centers in many reactions. So it is necessary to examine the characters of such system. In this section, we have investigated the C-Ni { $n(100) \times (111)$ }-[011 $\bar{1}$]} adsorption system (Fig. 2). From Table 2, we can see that due to the existence of surface step defect, the geometrical symmetry of the surface is destroyed and the four-folded hollow sites in the Ni(100) terrace, H₁ and H₂, are also disturbed. The degree of distortion for H₁, which is much closer to the step, is greater than that of H₂ site. The binding energy for H₁ is 1.53 eV higher when compared with the H site in Ni(100) plane and the variation of eigenvibration parallel to the surface of C adatom is much larger than that of the perpendicular one. All these indicate that H₁ is the most stable adsorption site of the three. Meanwhile, there is relative little change of H₂ site both for the binding energy and eigenvibrations. Whether the carbon atom is adsorbed at H₁ or H₂ site, the influence from the step causes it to depart from the center of equilibrium place. As for H₃, which is the most unstable site of the three, the binding energy is slightly higher than that of fcc hollow site of Ni(111) plane, and we did not get the stable adsorption state at H₃' site. In order to get a more direct viewing, we have plotted the

potential energy surface (PES) for carbon adsorption on Ni $\{n(100) \times (111)-[01\bar{1}]\}$ step surface, describing the status of a carbon atom diffusing along X axis (in a_0

unit) with the height varying from 0—0.2 (nm). From Fig. 3, we can see that the diffusing barrier for $H_1 \rightarrow H_2$ is about 4 eV which is more than twice of the diffusing barrier for $H \rightarrow H$ at Ni(100) plane. All

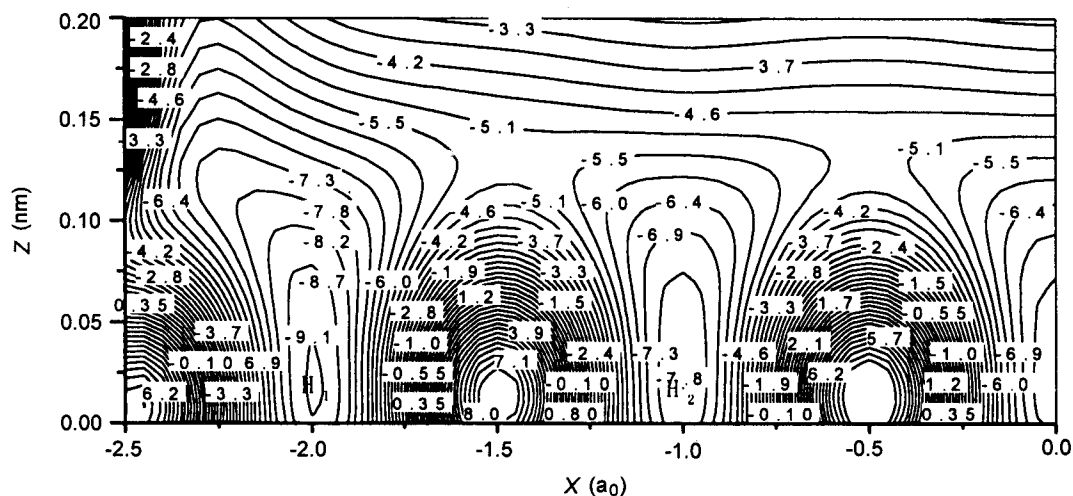


Fig. 3 PES for C adsorption on Ni $\{n(100) \times (111)-[01\bar{1}]\}$ step surface (Energy unit in eV).

the analyses above show that the adsorbed carbon atom prefers to migrate from H_2 or H_3 site to H_1 site. Namely, the probability for C adatom located at H_1 site is much greater than that of other sites. This case is quite different from Ni(100) plane, where the possibility for every four-folded hollow site for carbon diffusion is equal. So we suppose that adsorption places near the step like H_1 may be the active centers in chemical reactions and the adsorption of carbon may block them. Maybe this causes the catalyst to be poisoned and impedes the process of the whole reactions. Nevertheless, the influences of the interaction between carbon atoms, the surface relaxation and surface reconstruction or other factors may give a more comprehensive explanation for carbon adsorption on metal surface at low coverage, so that further studies are necessary both theoretically and experimentally.

As a result, all the achievements above confirm the feasibility of our method again, that is, we can employ one set of optimum parameters to deal with different metal surfaces of low index. This is not occasional since we have already got satisfying results in our previous investigations for H-Ni surface system.²⁵ Both the results indicate that our method approaches the intrinsic nature of interaction for carbon-metal system very well.

References

- 1 Onuferko, J. K.; Woodruff, D. P.; Holland, B. W. *Surf. Sci.* **1979**, *87*, 357.
- 2 Isset, L. C.; Blakely, J. M. *Surf. Sci.* **1975**, *47*, 645.
- 3 Gamo, Y.; Nagashima, A.; Wakabayashi, M.; Terai, M.; Oshima, C. *Surf. Sci.* **1997**, *374*, 61.
- 4 Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*, Academic Press, New York, **1982**, p.277.
- 5 Lenard, S.; Ibach, H. *Surf. Sci.* **1979**, *89*, 425.
- 6 Takatoh, S.; Arai, K.; Hayashi, T.; Enokijima, T.; Yikegaki, T.; Tsukajima, J.; Fujikawa, T.; Usami, S. *Phys. B.* **1995**, *208&209*, 245.
- 7 Bader, M.; Ocal, C.; Hillert, B.; Haase, J.; Bradshaw, A. M. *Phys. Rev. B.* **1987**, *35*, 5900.
- 8 Arivaanitis, D.; Baberschke, K.; Wenzel, L. *Phys. Rev. B.* **1988**, *37*, 7143.
- 9 Kilocoyoe, A. L. D.; Woodruff, D. P.; Robison, A. W.; Linder, T.; Somers, J. S., Bradshaw, A. M. *Surf. Sci.* **1991**, *253*, 107.
- 10 Gadzuk, J. W., in "Surface Physics of Materials", Ed. Blakely, J. M., Academic Press, **1975**.
- 11 Terborg, R.; Hoeft, J. T.; Polcik, M.; Lindsay, R.; Schaff, O.; Bradshaw, A. M.; Toomes, R. L.; Booth, N. A.; Woodruff, D. P.; Rotenberg, E.; Denlinger, J. *Surf. Sci.* **2000**, *446*, 301.

- 12 Shelton, J.; Patil, H.; Blackly, J. *Surf. Sci.* **1974**, *43*, 493.
- 13 Eizenberg, M.; Blackly, J. *Surf. Sci.* **1979**, *82*, 228.
- 14 Jacobsen, K. W.; Norskov, J. K. *Surf. Sci.* **1986**, *166*, 539.
- 15 Darling, G. R.; Penday, J. B.; Joyner, R. W. *Surf. Sci.* **1989**, *221*, 69.
- 16 Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *Surf. Sci.* **1995**, *324*, 345.
- 17 van Langeveld, A. D.; de Koster, A.; van Santen, R. A. *Surf. Sci.* **1990**, *225*, 143.
- 18 de Koster, A.; van Santen, R. A. *J. Catal.* **1991**, *127*, 141.
- 19 Klinke II, D. J.; Wilke, S.; Broadbelt, L. J. *J. Catal.* **1998**, *178*, 540.
- 20 Wutting, M.; Ibach, H. *Phys. Rev. Lett.* **1986**, *56*, 1583.
- 21 Issett, L. C.; Blakely, J. M. *Surf. Sci.* **1976**, *58*, 397.
- 22 Weiberg, W.; Merrill, R. *Surf. Sci.* **1972**, *33*, 493.
- 23 Weiberg, W.; Merrill, R. *Surf. Sci.* **1973**, *39*, 206.
- 24 Frese, K. W. Jr. *Surf. Sci.* **1987**, *182*, 85.
- 25 Wang, Z. X.; Hao, C.; Zhang, J. S.; Han, E. S.; Chen, Z. Q. *Acta Chem. Sin.* **1993**, *51*, 417 (in Chinese).

(E200007149 JIANG, X.H.; DONG, L.J.)