DFT-GGA Calculation of C_2H_4 and C_2H on Pd(110)

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Our recent first principles calculations of ethylene (C_2H_4) and ethynyl (C_2H) adsorbed on Pd(110) surface are reviewed. Adsorption site of C_2H_4 at high coverage, intermolecular interaction of C_2H_4 at low coverage, and bright and dark spots observed in STM image of C_2H are discussed.

Introduction

The catalytic reactions of organic molecules on transition-metal surface have been of great interest due to their important applications to the chemical industry. In particular, ethylene (C_2H_4) and its related molecules have been actively studied to understand the mechanism of the catalytic reactions because they have simple structures and industrial importance.

Ethylene molecules adsorb on most transition-metal surfaces by forming sigma-bonds between each carbon atom and the surface and losing the double bond nature of the C-C bond. On Pd surfaces, however, ethylene molecules adsorb on atop sites by forming a pi-bond. By raising the temperature above 280 K, the molecule dehydrogenates to adsorbed ethynyl (C_2H).[1]

In this article we report a series of DFT-GGA calculations of ethylene and ethynyl adsorbed on Pd(110) and examine them by comparing with experimental results.

C_2H_4 (high coverage, $\theta = 0.5$ ML)

Recent HREELS, NEXAFS, and STM experiments [2–4] have shown that, after annealing, ethylene molecules adsorb on atop sites of Pd(110) with their C-C axes along [1–10] at both high and low coverages. At a high coverage of 0.5 ML, they form the $c(2 \times 2)$ structure (Fig. 1a).

To understand this result, we calculated [5] the binding energy of eight adsorption modes, i.e., four adsorption sites (atop, short bridge, long bridge, and atop hollow) and two molecular orientations for each adsorption site (C-C axis oriented along [1–10] and [001] directions). The binding energy was calculated by

$$\Delta E_b = E_{Pd/et} - (E_{Pd} + E_{et}),$$

where $E_{Pd/et}$, E_{Pd}, and E_{et} are the total energies of the Pd(110)–$c(2\times2)$-ethylene adsorption system, the bare Pd slab and the free ethylene molecule, respectively. The supercell for the calculation had dimensions of $a = b = 4.780$ Å, $c = 19.319$ Å, $\alpha = \beta = 90°$, and $\gamma = 70.53°$, and consisted of seven layers of Pd atoms and a vacuum region with a thickness of approximately, 11 Å. The lattice constant (3.903 Å) was determined by relaxing the bulk Pd model, and it is close to the experimental value of 3.8903 Å.[6] The top four Pd layers were relaxed during geometry optimization, while the bottom three layers were fixed at their bulk configuration. The force on the atom was relaxed to less than 0.1 eV/Å and no space symmetry constraints were used. The Brillouin zone was sampled with a $7 \times 7 \times 1$ Monkhorst-Pack (MP) mesh. This MP k-point set yielded a converged value of the binding energy (Fig. 2). All the calculations were performed by using a first principles molecular dynamics program CASTEP4.2 with the gradient-corrected exchange-correlation functional of Perdew and Wang (GGA-PW91),[8] the Vanderbilt-type ultrasoft pseudopotentials,[9] and the plane-wave cut-off energy of 340 eV.

Four out of the eight configurations were found to be stable (Fig. 1a–d). The most preferred configuration is the C_2H_4 directed to [1–10] at the short bridge site ($E_b = 967$ meV), the second is one directed to [1–10] at the atop site ($E_b = 771$ meV) and the remaining two are those at the atop site ($E_b = 660$ meV) and the long bridge site both directed to
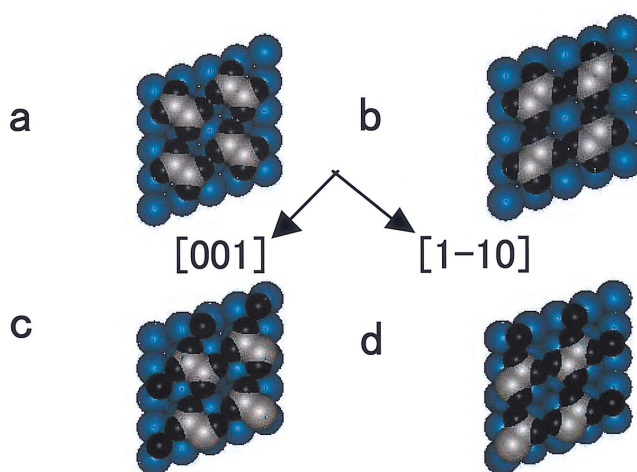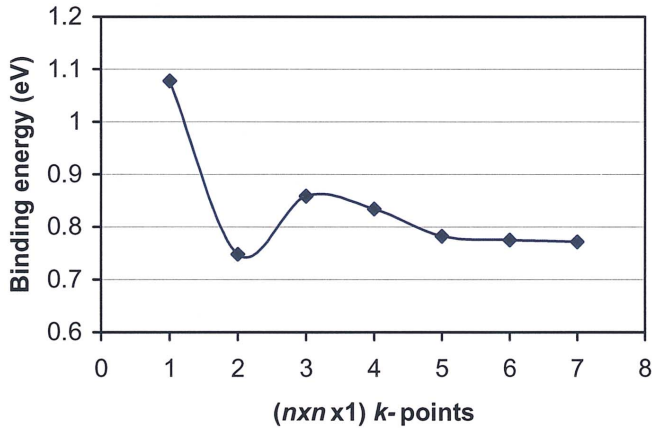

Fig. 1. Stable adsorption states of $c(2\times2)$-C_2H_4 on Pd(110): (a) atop [1–10], (b) atop [001], (c) short bridge [1–10], and (d) long bridge [001].

Fig. 2. Convergence behavior[5] of the binding energy for atop [1–10] mode as a function of the $(n \times n \times 1)$ k-point grid, with $n = 1$–7.

Table 1. Normal mode frequencies.

Frequency (meV)				
Gas		adsorbed on Pd(110)		
Exp.	DFT	Exp.	DFT	
			atop	bridge
388	396	376	397	389
388	392	369	393	385
378	384	361	384	374
374	383	353	380	369
203	202	178	193	202
180	178	172	189	177
168	167	150	167	161
155	148	137	149	137
118	134	112	138	135
119	118	105	116	110
103	119	64	103	99
	101	46	91	88
		39	60	52
			48	45
			21	33
E0			1415	1378
F			−145	−146

[001].

This result is in contradiction to the experimental results described at the beginning of this section.[2,3] Interestingly, Feibelman *et al.* also reported the error of approximately 0.2 eV in the short bridge/atop site preference for the CO/Pt(111) system.[10]

To identify the origin of this inconsistency between the DFT-GGA calculation and the experimental observation, we have checked our calculation from several viewpoints.

We tried the GGA-RPBE[11] functional in place of GGA-PW91 since it is known to improve adsorption energies of molecules on metal surfaces. The result gave, however, the same order of adsorption preference as that of GGA-PW91, namely, the short bridge site was preferred by 175 meV than the atop site. We also tried a hybrid-DFT method[12] with a localized basis set. However, the results of single-point B3PYL calculations for the structures optimized by CASTEP with GGA-PW91 have shown no improvement thus far.

The difference in the zero point energy of molecular vibration at each site affects the site preference in some cases. Tabulated in Table 1 are the experimental and DFT-GGA calculated normal mode frequencies of gaseous and adsorbed ethylene. The frozen substrate approximation was adopted. The difference in the total zero point energy is approximately 0.04 eV in favor of the bridge site. Therefore, the effect of zero point energy cannot solve the problem within this approximation.

The entropy difference between atop and short bridge sites was estimated by calculating potential energy surface[5] since the results of lowest frequencies in Table 1 were not reliable due to numerical errors. The estimated difference is of the order of a few tens of millielectron volts in favor of the atop site. It is therefore difficult to conclude that this effect is important.

The thermal equilibrium of the system was assumed to be good because the $c(2 \times 2)$ structure was formed by annealing from 260 K, where the hopping of ethylene molecules was observed by STM. The calculated barrier[5] of 80 meV along
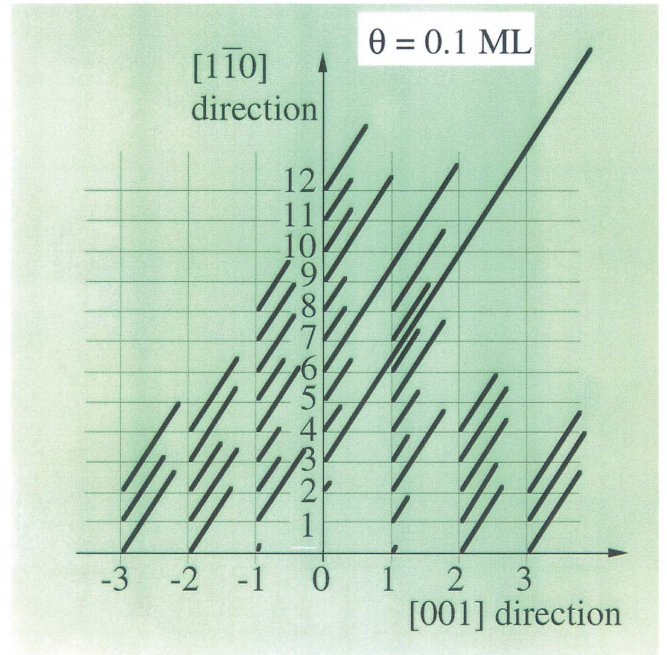

Fig. 3. Experimental radial distribution[4] of ethylene molecules on Pd(110) at $\theta = 0.1$ ML.

the straight line between top and bridge sites suggests that molecules are passing the other way.

C_2H_4 (low coverage, $\theta = 0.1$ ML)

At a low coverage of 0.1 ML, recent STM and HREELS experiments have shown that ethylene molecules adsorb on the atop sites of Pd(110) with their C-C axes along [1–10] and form a one-dimensional (3×1) structure (see Fig. 3 for the radial distribution),[4] suggesting attractive interaction between

the ethylene molecules at three lattice sites along the [1–10] direction.

To study the intermolecular interaction, we calculated the total energy of models with two ethylene molecules oriented along the [1–10] direction and were adsorbed on atop sites separated by n surface lattice vectors ($n = 2$, 3, and 4) on a

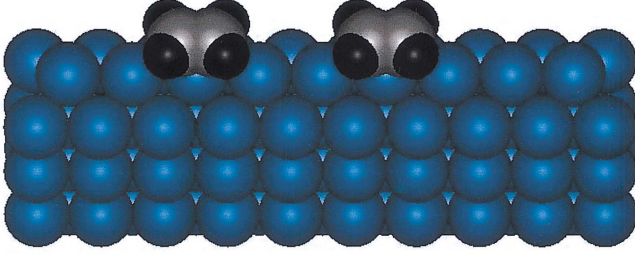
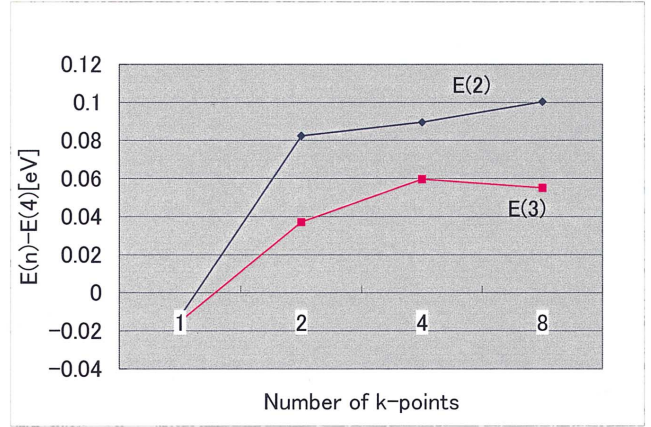Fig. 4. Model for ethylene molecules separated by three lattice vectors along the [1–10] direction.

Fig. 5. Intermolecular interaction $E(n) - E(4)$, where $E(n)$ is the total energy of the slab model with two ethylene molecules separated by n lattices.
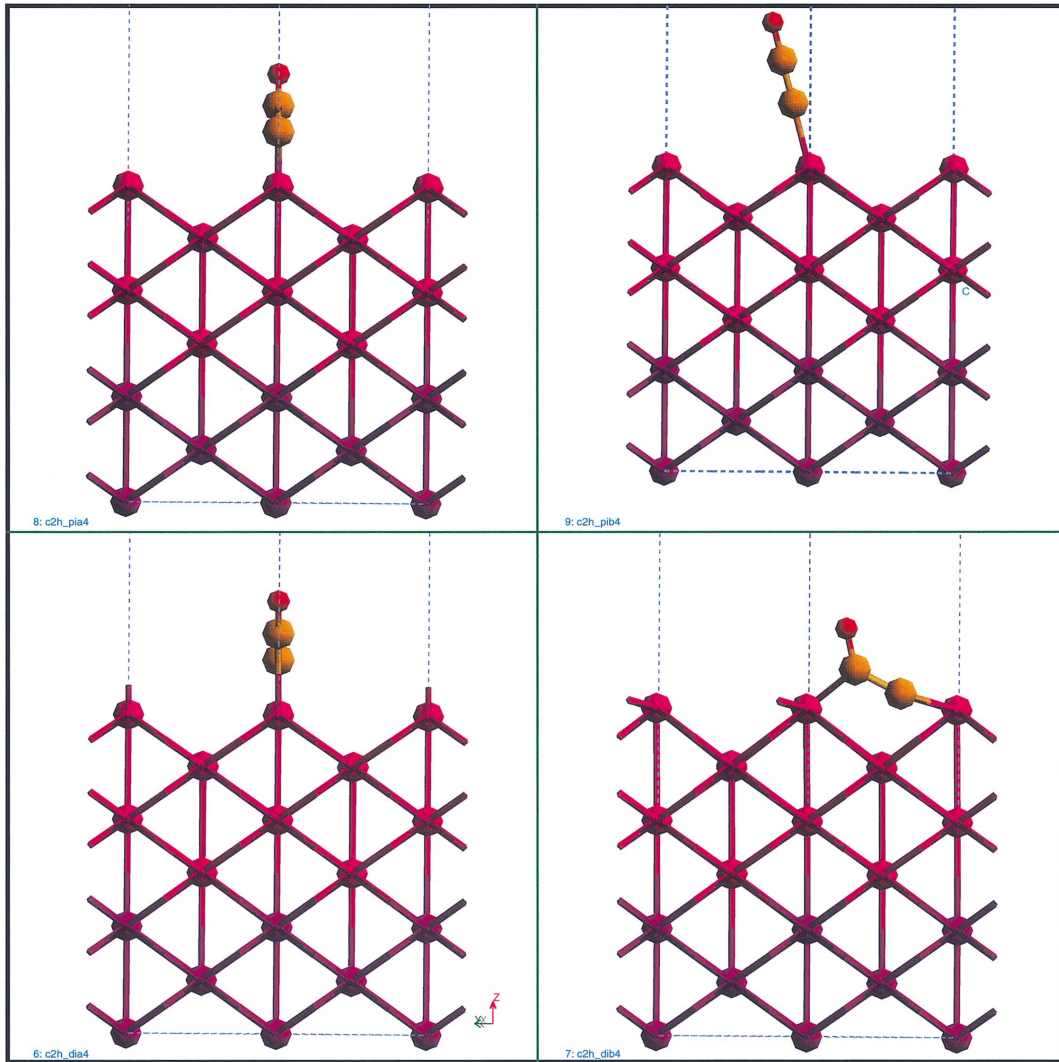

Fig. 6. Optimized structure of ethynyl on Pd(110) viewed from [1–10]. Top left is Model A, top right is Model B, bottom left is Model C, and bottom right is Model D.

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9×1 slab model of seven layers (Fig. 4).

Figure 5 shows the calculated intermolecular interaction as a function of the number of k-points. They converge well with eight-k-point calculation. From this, we found that the intermolecular interaction is a monotonic function of distance n, i.e., $E(2) > E(3) > E(4)$, and there is no energy minimum at $n = 3$. Therefore, our present DFT calculation could not explain the one-dimensional 3×1 structure observed in the experiments, which has been also interpreted by a very naïve model.[13]

We also calculated the site preference of C_2H_4 at low coverage. The adsorption energy of C_2H_4 calculated with one molecule on the 9×1 slab is again 0.2 eV in favor of the bridge site.

C_2H

Recent STM and NEXAFS experiments [14] have revealed that the orientation of ethynyl adsorbed on Pd(110) is the [001] direction and the inferable adsorption site is the μ-bridge site.

We also carried out DFT calculations for this system. The initial models were constructed by removing three hydrogen atoms from the four stable C_2H_4/Pd(110) structures in section 2, that is, A) atop [1–10], B) atop [001] C) short bridge [1–10] and D) long bridge [001]. Then, these models were optimized with the same parameters as those in the calculations of the C_2H_4-$c(2 \times 2)$ structure. The total groundstate energies of these models were found to be 1.38 eV, 2.07 eV, 1.38 eV, and 0 eV, respectively, where the total energy of Model D was set to zero.

The optimized structures are shown in Fig. 6. Model A and Model C converge to the same structure directed to [1–10] and positioned between atop and short bridge sites, in accordance with their identical total energies. Model B converges to the structure of a straight line almost normal to the surface at the atop site. Model D converges to the molecular structure directed to [001] and positioned at the top hollow site, which has the lowest total energy. This structure may be assigned to the experimentally observed structure.

Ogasawara et al.[14] discussed the origin of the pre-edge structure in NEXAFS and the bright and dark spots in STM measurement in terms of the change of local DOS near the Fermi level due to the ethynyl-Pd interaction.

We discuss here the results of NEXAFS and STM separately. Figure 7 shows the calculated local DOS (LDOS) of hydrogen and carbon atoms, where C1 indicates the acetylene-like carbon atom bonding with a hydrogen atom H1 and located 0.7 Å away from the surface compared to the carbide-like carbon atom C2, which is strongly interacting with the Pd surface.

The LDOS of both C1 and C2 atoms above the Fermi level is enhanced due to the interaction with surface, although C2 is somewhat more enhanced between 1 and 5 eV. This is considered to be the origin of the pre-edge structure [14] in NEXAFS spectra.

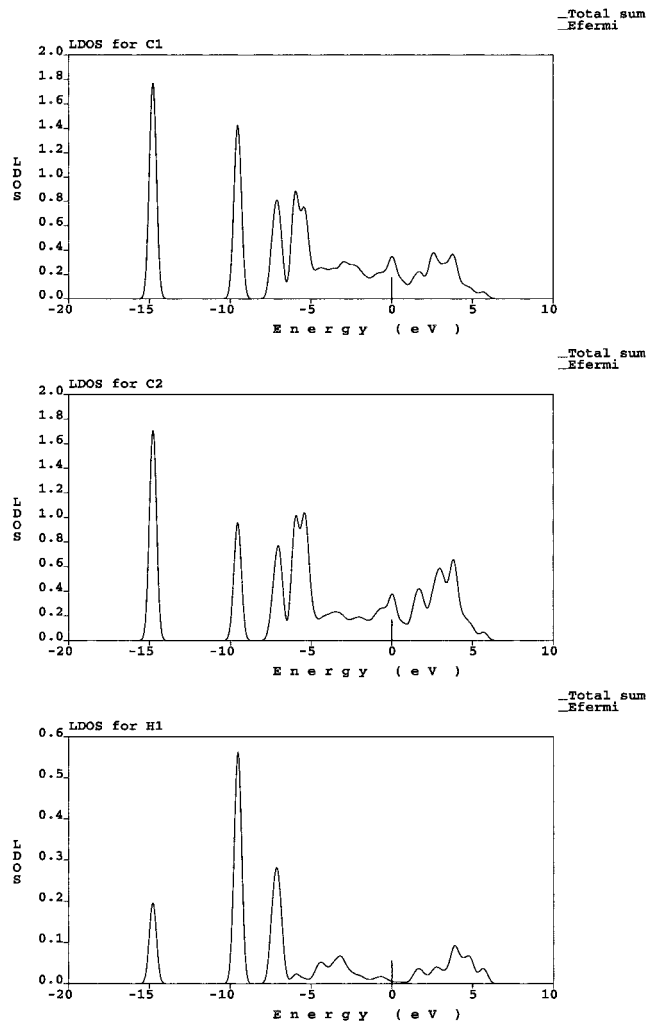The LDOS very near the Fermi level is, however, almost the

Fig. 7. LDOS of ethynyl for atoms C1, C2, and H1.

same for the two carbon atoms. Considering the bias voltage of 0.02 V, the contrast in STM spots may be due to not the LDOS effect but the geometrical effect that C1 is 0.7 Å closer to the STM tip than C2 (Fig. 8). In this case, the bright spot is assigned to the C1 atom, which is in contrast to the bright C2 atom predicted by the model based on the change of LDOS.

Summary

In this article, we reviewed our recent studies of ethylene and ethynyl adsorption on Pd(110) surface.

In section 2, we discussed the $c(2 \times 2)$ structure of C_2H_4 on Pd(110), and found that GGA calculation prefers the short bridge site than the atop site with a energy difference of 0.2 eV, which is not small compared to the typical errors in DFT-GGA calculation. This result does not agree with recent HREELS, NEXAFS, and STM experiments [2–4] that suggest the atop adsorption site. Although we have checked several possibilities of the origin of this contradiction, the problem is still remains unsolved.

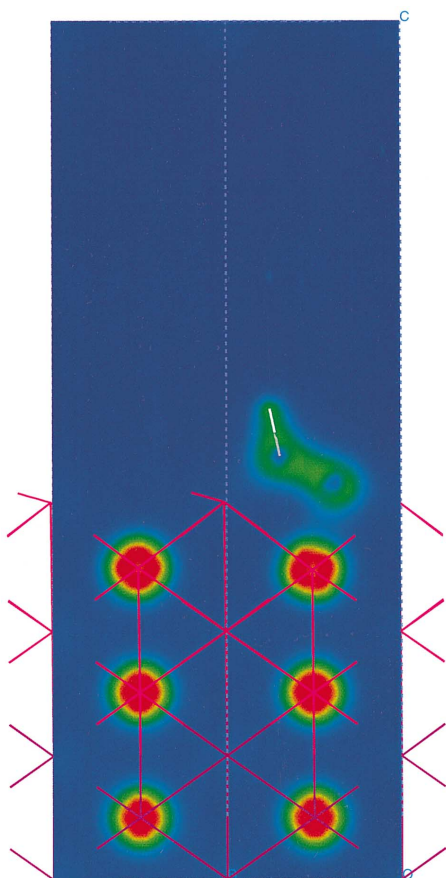In section 3, we attempted to calculate the interaction be-

Fig. 8. Charge density distribution on the slice plane normal to [1−10] and including the C-C axis.

tween ethylene molecules of low coverage on Pd(110). We found that the interaction does not have a potential minimum at the distance of three lattice vectors, and we could not explain the one-dimensional 3×1 structure theoretically. However, this disagreement is not as surprising as in the case of the site preference, because the estimated interaction is small, i.e., approximately $0.03\,\mathrm{eV}$, which is the order of usual GGA errors.

In section 4, we discussed the bright and dark spots in the STM measurement of ethynyl on Pd(110) in terms of local DOS of carbon atoms.

The combination of DFT calculation and experimental techniques such as STM, HREELS, and NEXAFS can serve as a very powerful tool for understanding surface phenomena microscopically. Since the goal of our study is to understand and control the process of chemical reactions of organic molecules on transition-metal surfaces, the discrepancy between experiment and theory should be identified and solved.

References

1) M. Nishijima, J. Yoshinobu, T. Sekitani, and M. Onchi: J. Chem. Phys. **90**, 5114 (1989).
2) H. Okuyama, H. Kato, M. Kawai, and J. Yoshinobu: J. Chem. Phys. **113**, 2866 (2000).
3) H. Okuyama, S. Ichihara, H. Ogasawara, H. Kato, T. Komeda, M. Kawai, and J. Yoshinobu: J. Chem. Phys. **112**, 5948 (2000).
4) S. Ichihara, J. Yoshinobu, H. Ogasawara, M. Nantoh, M. Kawai, and K. Domen: J. Electron. Spectrosc. Relat. Phenom. **88/91**, 1003 (1998).
5) F. Pichierri, T. Iitaka, T. Ebisuzaki, M. Kawai, and D. M. Bird: J. Phys. Chem. B, in press.
6) D. R. Lide: *CRC Handbook of Chemistry and Physics*, 80th Ed., 1999–2000, (CRC Press, Boca Raton. 1999).
7) M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos: Rev. Mod. Phys. **64**, 1045 (1992); CASTEP 4.2 academic version, licensed under the UKCP-MSI Agreement, 1999.
8) J. P. Perdew and Y. Wang: Phys. Rev. B **46**, 6671 (1992).
9) D. Vanderbilt: Phys. Rev. B **41**, 7892 (1990).
10) P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic: J. Phys. Chem. B **105**, 4018 (2001).
11) B. Hammer, L. B. Hansen, and J. K. Norskov: Phys. Rev. B **59**, 7413 (1999).
12) V. R. Saunders, R. Dovesi, C. Roetti, M. Causa, N. M. Harrison, R. Orlando, and C. M. Zicovich-Wilson: CRYSTAL98 User's Manual (1999).
13) T. Iitaka, F. Pichierri, M. Kawai, D. M. Brid, and T. Ebisuzaki: Proc. 3rd Japan-Korea Joint, Workshop on First-Principles Electronic Structure Calculations, Tsukuba, 2001-10∼11, p. 293 (2001).
14) H. Ogasawara, S. Ichihara, H. Okuyama, K. Domen, and M. Kawai, J. Electron. Spectrosc. Relat. Phenom. **114/116**, 339 (2001).