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Hydrogen catalyzed adsorption of alkenes on the diamond (001) surface

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We present first-principles density-functional calculations for the [2+2] cycloaddition reaction of ethylene on the (001) surface of diamond. For comparison we also study the same reaction of ethylene on the Si(001) surface as well as that of two ethylene molecules. Similar to the latter case, a concerted reaction on top of the C dimer is symmetry forbidden due to the symmetric dimer configuration of C(001). However, in both cases the symmetry-forbidden reaction can be avoided by allowing a rotation of the C—C bond of ethylene. This asymmetric reaction path yields an energy barrier of 2.29 and 0.90 eV for the cases of two ethylene molecules and C_2H_4/C(001), respectively. In contrast, the reaction of ethylene on Si(001) takes place via an intermediate state, caused by the asymmetric Si dimer structure. The reaction energy barrier of C_2H_4 on C(001) is too high to attain direct adsorption. Here we propose that the [2+2] reaction path is catalyzed by a few hydrogen impurities.

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I. INTRODUCTION

The [2+2] cycloaddition reaction is of fundamental importance in the synthesis of organic molecules.[1] A simple example of such reaction is the formation of cyclobutane from two ethylene molecules (see Fig. 1). According to the symmetry conservation rule of Woodward and Hoffmann,[1] a face-to-face concerted reaction of two ethylene molecules is symmetry forbidden because orbital symmetry characteristics of the reactants and the product differ from each other. As shown in Fig. 2, the symmetries of frontier orbitals, i.e., the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) cross between two ethylene molecules and cyclobutane, resulting in a very large symmetry-imposed barrier. This symmetry-imposed barrier can be avoided when one of the electrons is promoted to the LUMO state of two ethylene molecules by photochemical excitation.[1]

Recently the [2+2] cycloaddition reaction has been extended to the hybridization of organic molecules with the (001) surface of Si and diamond.[2–5] Here, the hybridizing organic molecules, such as acetylene,[6] ethylene,[7] cyclopentene,[8] cyclohexadiene,[9] and cyclooctadiene[10] have the π bond of unsaturated hydrocarbons and the two (001) surfaces exhibit a surface reconstruction in which pairs of surface atoms bond to each other, forming dimers. As a result of the [2+2] cycloaddition reaction, the π bond of unsaturated hydrocarbons and the π bond of a dimer interact to produce two new σ bonds. The adsorption of the above organic molecules on Si(001) is facile at room temperature with a sticking coefficient of nearly unity.[7–10] Theoretically, the reaction pathway for the [2+2] product predicts little or no barrier[6,11–13] through a low-symmetry intermediate state because of the asymmetric Si dimer structure. On the other hand, a very low sticking coefficient ($\sim$0.001) was reported for cyclopentene on C(001).[14] Hovis *et al.*[14] pointed out that this may be caused by a high reaction barrier due to the symmetric dimer configuration of C(001) including a larger π-π^* surface-state band gap and a stronger π bond compared to those of Si(001). However, Carbone[15] argued that the adsorption of cyclopentene could take place on defects rather than on C dimers, analogous to oxygen on Si(001).[16,17] Thus, it is controversial whether C dimers are reactive with unsaturated hydrocarbons or not. Note that our previous theoretical study for adsorbed cyclopentene on C(001) only considers the binding energy and structure of the [2+2] product.[18] For this reason a detailed theoretical study for the kinetics of the [2+2] cycloaddition reaction of unsaturated hydrocarbons on C(001) is required.

In this paper we study the kinetics of the [2+2] cycloaddition reaction of C_2H_4 on C(001), and, for comparison, those of two C_2H_4 molecules and C_2H_4/Si(001). Here we chose C_2H_4 as a representative of all the alkenes. In the following section our computational method is described. In the third section we obtain estimates of the energy barriers, concluding that the sticking coefficient of C_2H_4 on a perfectly clean C(001) surface is much less than 10^{-15} at room temperature. In the fourth section we propose that less than 1% of H impurities on the surface could catalyze the reaction and account for the experimentally observed rate of adsorption and in the fifth section our conclusions are given.

II. CALCULATIONAL METHOD

We performed the total-energy and force calculations by using density-functional theory[19] within the generalized-gradient approximation (GGA). We used the exchange-correlation functional of Perdew, Burke, and Ernzerhof[20] for the GGA. The C (Si and H) atom is described by ultrasoft[21]

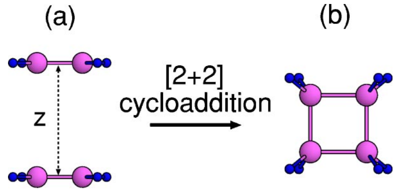

FIG. 1. (Color online) [2+2] cycloaddition reaction of two C_2H_4 molecules: (a) two separated C_2H_4 molecules and (b) cyclobutane. *z* represents the distance between two C_2H_4 molecules.

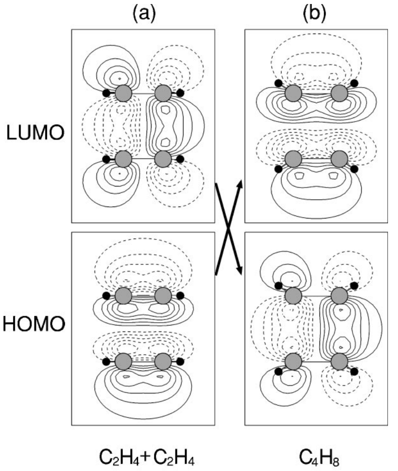

FIG. 2. (Color online) Calculated wave functions of the HOMO and the LUMO for (a) two C_2H_4 molecules and (b) a C_4H_8 molecule. The plots at the separation at which two (C_2H_4) molecules and C_4H_8 have approximately equal total energies, $\Delta z = 0.65$ Å, are displayed. The first solid (dashed) line is at a positive (negative) 0.03 $(e/\mathrm{bohr}^3)^{1/2}$ with spacings of a positive (negative) 0.03 $(e/\mathrm{bohr}^3)^{1/2}$. The large and small circles represent C and H atoms, respectively. Another H atoms lies directly below each H atom visible in this figure.

(norm-conserving[22]) pseudopotentials. The C_2H_4/C(001) and C_2H_4/Si(001) systems are modeled by a periodic slab geometry. Each slab contains five C (Si) atomic layers and the bottom C (Si) layer is passivated by two H atoms per C (Si) atom. The thickness of the vacuum region between these slabs is about 14 Å, and C_2H_4 molecules are adsorbed on the unpassivated side of the slab. We carried out most of the slab calculations using a (4×2) unit cell where two dimer rows are included, but a (4×3) unit cell was employed for the calculations of the H-mediated $[2+2]$ cycloaddition reaction. The calculations for the reaction of two C_2H_4 molecules were performed using $10\times12\times18$ Å^3 supercell with one **k** point. A plane-wave basis set was used with 25 Ry cutoff, and the **k** space integration was done with two and one points in the (4×2) and (4×3) surface Brillouin zones, respectively. Relaxation of the atoms was done using the calculated Hellmann-Feynman forces until the residual force components were less than 1 mRy/bohr.

III. CLEAN SURFACES

Our purpose here is not to obtain an exact value for the sticking probability of C_2H_4 on C(001), but only to show that it is completely negligible. In order to determine the accuracy of our estimates we initially study the dimerization of ethylene to cyclobutane whose activation energy is known[23] to be 2.71 eV. We first study a face-to-face concerted reaction of two C_2H_4 molecules. In our calculations this reaction is simulated by varying the distance z between two C_2H_4 molecules [see Fig. 1(a)]. Here the positions of H atoms as well as the length of the C—C bond are optimized at each separation. In Fig. 3(a) the calculated energy and C—C bond length ($d_{\mathrm{C—C}}$) are given as a function of $\Delta z = z - z_0$, where z_0 is the equilibrium distance (1.56 Å) of cyclobutane. We find that there are two states characterized by $d_{\mathrm{C—C}}$. One state which exists above $\Delta z = 0.55$ Å has a shorter C—C bond length of $d_{\mathrm{C—C}} \approx 1.34$ Å compared to that ($d_{\mathrm{C—C}} \approx 1.55$ Å) of the other state which exists below $\Delta z = 0.81$ Å, indicating that the former (latter) has double (single) bond character. Note that the single- and double-bond states coexist between $\Delta z = 0.55$ Å and 0.81 Å and their energies are close to each other at $\Delta z = 0.65$ Å. In order

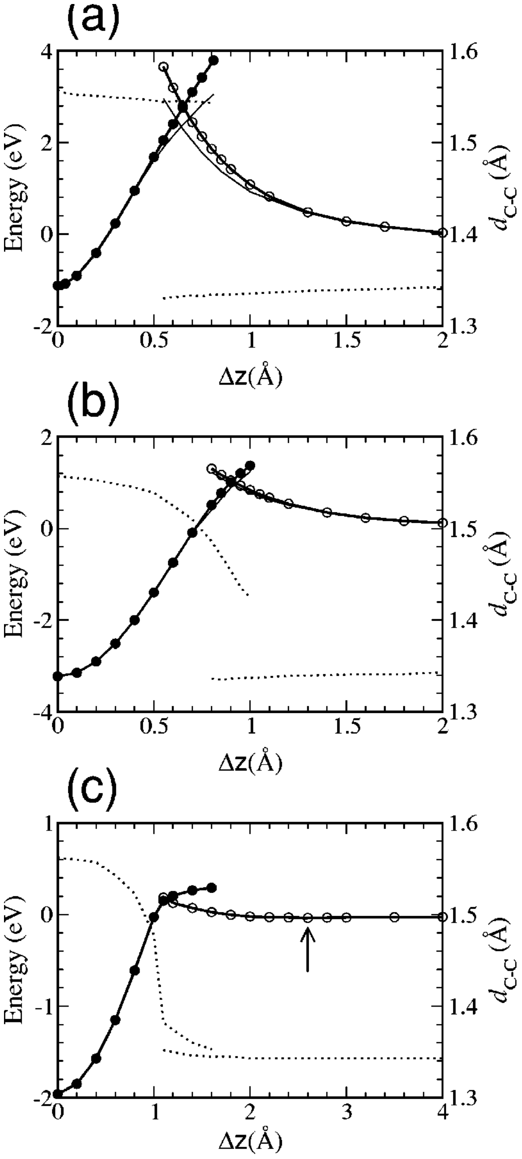

FIG. 3. (Color online) Calculated energy and C—C bond length along the $[2+2]$ cycloaddition reaction path: (a) two C_2H_4 molecules, (b) C_2H_4 on C(001), and (c) C_2H_4 on Si(001). The solid (open) circles represent the energies of the single (double)-bond state in which the two C atoms of C_2H_4 have an identical Δz. Δz for each case is defined in the text. The thin solid lines in (a) and (b) represent the energy curve obtained by allowing the rotation of the C—C bond of C_2H_4. The arrow in (c) indicates a local minimum. The energy in each case is referenced from the total energy of its separated limit. The dotted lines represent the C—C bond length of C_2H_4, corresponding to the single-bond and the double-bond states.

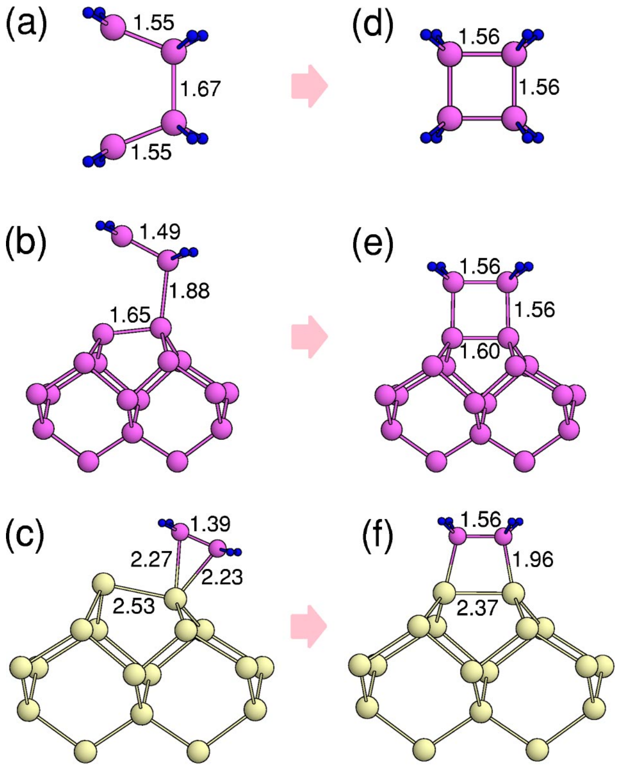

FIG. 4. (Color online) Atomic geometries of the intermediate and final states: (a) the buckled structure of two C_2H_4 at $\Delta z = 0.65$ Å, (b) the buckled structure of $C_2H_4/C(001)$ at $\Delta z = 0.9$ Å, (c) the three-atom intermediate structure of $C_2H_4/Si(001)$, (d) the $[2+2]$ product of two C_2H_4, (e) the $[2+2]$ product of $C_2H_4/C(001)$, (f) the $[2+2]$ product of $C_2H_4/Si(001)$. The numbers denote the bond lengths in Å.

to examine the symmetry of the two states, we plot the wave functions of the HOMO and LUMO, calculated at $\Delta z = 0.65$ Å. As shown in Fig. 2, the symmetry of the two (C_2H_4) HOMO (LUMO), i.e., the double-bond state, is the same as that of the C_4H_8 LUMO (HOMO), i.e., the single-bond state. Therefore, the orbital symmetry between the reactants and the product is not conserved, demonstrating that the face-to-face concerted reaction is symmetry forbidden.[1] The barrier height is 2.76 eV, close to the experimental activation energy. A lower bound to the barrier height may be obtained by allowing additional relaxation of the C atoms while keeping z between the centers of the two C—C bonds fixed. In the double-bond state the rotation of the C—C bond of one C_2H_4, relative to the other C_2H_4, about the z axis is more favorable than the parallel structure [Fig. 1(a)], leading to a minimum in energy at a rotation angle of $\theta = 90°$. On the other hand, in the single-bond state, i.e., C_4H_8, such a rotated structure is not favored over the parallel structure, but rather a buckled structure is favored [Fig. 4(a)] in which the two facing C atoms on one side are attracted to each other. This is not the actual reaction pathway since the incoming double bonded molecule must somehow become single bonded and at some point get on the minimum-energy single bonded pathway. However the crossing energy of these two minimum-energy curves does represent a lower bound for the energy barrier. The thin solid lines in Fig. 3(a) represent the calculated energies of the rotated and buckled structures as a function of Δz. We obtain an energy barrier of 2.29 eV, which is lower by 0.47 eV compared to the energy height (2.76 eV) at the crossing point of the single- and the double-bond states along the face-to-face reaction path. It is interesting to note that the latter value is almost a half of the energy difference (5.61 eV) between the π and π^* levels of C_2H_4 [see Fig. 5(a)]. Because the reaction can proceed when one of the molecules is photoexcited to the π^* state, one would expect the energy barrier to depend on the π-π^* gap although there is no reason to expect any particular value for the calculated barrier to gap ratio, especially since GGA energy gaps do not represent excitation energies. A smooth reaction pathway does not appear along an energy valley and over a saddle point with the $\pi \rightarrow \pi^*$ transition occurring adiabatically as the molecules traverse the pathway. Rather, the actual reaction pathway[23] seems to require the molecules to approach one another in unstable excited states.

The C dimer bond of C(001) is composed of a σ bond and a π bond, similar to the double bond of alkenes. The calculated dimer-bond length at a clean C(001) surface is 1.39 Å, which is somewhat longer than the $C{=}C$ bond length (1.34 Å) of an isolated C_2H_4 molecule. This implies that the π bond of the C dimer should be weaker than that of C_2H_4. Since the bonding character of the C dimer is similar to that of C_2H_4, the $[2+2]$ cycloaddition reaction of C_2H_4 with C(001) is expected to be analogous to that of two C_2H_4 molecules. We therefore study a concerted reaction of C_2H_4 on top of the C dimer. Here the position of C_2H_4 is displaced upward from the equilibrium structure [Fig. 4(e)] of the $[2+2]$ product: this displacement is denoted by Δz. For a given Δz all the atoms are fully relaxed within the (4×2) unit cell, except the bottom C layer atoms and the two C atoms of C_2H_4 (but the $C{=}C$ bond length is optimized). The results of the energy and d_{C-C} are displayed in Fig. 3(b) as

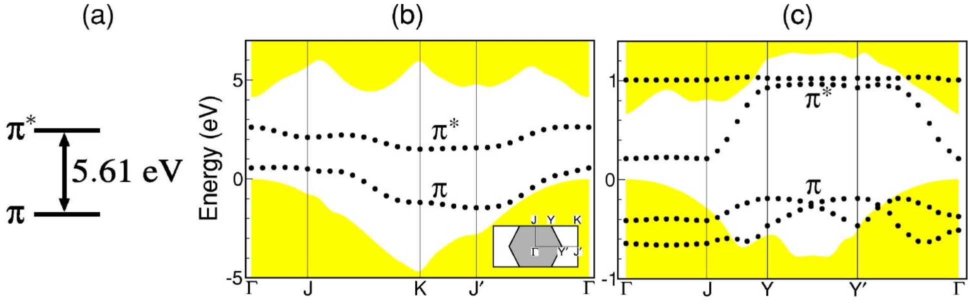

FIG. 5. (Color online) Occupied π and unoccupied π^* states for (a) a C_2H_4 molecule, (b) a clean C(001)-(2×1) surface, and (c) a clean Si(001)-$c(4\times2)$ surface. The inset in (b) shows the surface Brillouin zone for the (2×1) and $c(4\times2)$ unit cells. Shaded areas in (b) and (c) are the projected bulk-band structure.

a function of Δz. We find that the single (double)-bond state exists below (above) $\Delta z = 1.0(0.8)$ Å, and the energy curves of both states cross at about $\Delta z = 0.9$ Å. The general feature of the existence of the single- and double-bond states and their energy curve crossing is similar to the case of two C_2H_4 molecules. However, in $C_2H_4/C(001)$ the decrease of $d_{C—C}$ ($\Delta d_{C—C} \sim 0.13$ Å) in the single-bond state is rather steeper with increasing Δz compared to the two C_2H_4 case where $\Delta d_{C—C}$ is less than 0.02 Å. Note that the energy height at the crossing point of the single- and the double-bond states is ~ 1.01 eV, which is almost a half of the calculated energy difference (2.06 eV at Γ point) between the π and π^* surface states of C(001) [see Fig. 5(b)].

As in the case of two C_2H_4 molecules, we further relax the C atoms of C_2H_4 from the parallel structure. In the double-bond state the 90° rotation of the C—C bond of C_2H_4, relative to the C dimer, about the z axis is more favorable than the parallel structure, whereas in the single-bond state a buckled structure [Fig. 4(b)] is favored. The thin solid lines in Fig. 3(b) represent the calculated energies of the rotated and buckled structures. Here we obtain an energy barrier of 0.90 eV. Note that because of the different bond lengths and rotation angles, the atomic nuclei do not overlap so there is no possibility of a transition between the two structures and the 0.90 eV barrier merely represents a lower bound to the actual barrier. If we assume that the actual barrier lies between the face-to-face barrier and the lower bound, as was the case for ethylene to cyclobutane, we estimate the actual barrier to be ~ 0.97 eV. If we assume that every molecule with enough energy to get over the barrier does, and sticks to the surface, the sticking coefficient is given by $e^{-E_b/kT}$. This yields (at room temperature) an estimated sticking coefficient of 5.4×10^{-17} and an upper bound of 8.1×10^{-16}. On the other hand, Hovis *et al.*[14] observed the adsorption of cyclopentene on C(001) with a sticking coefficient of ~ 0.001. This disagreement for the sticking coefficient of alkenes between our prediction and experiment may be reconciled by considering the so-called ‘‘stepwise’’ reaction which involves intermediate states. As a matter of fact, it has been proposed that on Si(001) the initial reaction stage of unsaturated hydrocarbons (e.g., acetylene,[6] ethylene,[7] cyclopentene,[8] 1,4-cyclohexadiene,[24] and 1,5-cyclooctadiene[10]) involves the three-atom intermediate state which is composed of a three-membered ring with the two C atoms and the down atom of the Si dimer shown in Fig. 4(c). However, on C(001) we cannot find such an intermediate state. Thus, it is likely that the adsorption of alkenes on a clean C(001) surface is not feasible by a direct reaction.

Although our concern here is only with diamond, it is of some interest to see how diamond differs from Si. Since the energy barrier for the concerted reaction of C_2H_4 on C(001) is correlated with the energy difference between the π and π^* surface states of C(001), we calculate the surface band structure of Si(001) for comparison with the energy barrier in the $C_2H_4/Si(001)$ case. Figure 5(c) shows the surface-state energy bands of the Si(001)-$c(4\times2)$ surface employed in our $p(4\times2)$ unit-cell calculations for the reaction of C_2H_4 on top of the Si dimer. There are the two occupied π and two unoccupied π^* states due to the four dangling bonds in each $c(4\times2)$ unit cell. At the Γ point the energy difference π-π^* and valence maximum- π^* band gap are 0.62 and 0.21 eV, respectively. On the other hand, our calculated energy profile [Fig. 3(c)] for the reaction path of C_2H_4 on top of the Si dimer shows an energy barrier of ~ 0.15 eV, close to the above obtained band gap and below a half of π-π^*. Here, the two C atoms of C_2H_4 are constrained to have an identical height for a given Δz, but the C—C bond length is optimized. At the crossing point ($\Delta z_c \approx 1.1$ Å) of the single- and the double-bond states the $d_{C—C}$ values of both states are close to each other and the double-bond state no longer exists below Δz_c. Unlike $C_2H_4/C(001)$ where the energy of the double-bond state monotonically increases as Δz decreases, the double-bond state in $C_2H_4/Si(001)$ shows a local minimum at $\Delta z = 2.6$ Å, where the energy is a negative 0.04 eV relative to the energy sum of a clean Si(001) surface and an isolated C_2H_4 molecule. This result indicates the existence of a weakly bound intermediate state along the reaction path on top of the Si dimer, possibly caused by the asymmetric Si dimer structure. It is notable that the above mentioned three-atom intermediate state in $C_2H_4/Si(001)$ is attributed to the energetically favored hybridization between the π bonding state of C_2H_4 and the empty dangling-bond state of the down Si atom. In the present work we find the three-atom intermediate state [Fig. 4(c)] with an adsorption energy of 0.49 eV, therefore more strongly binding than the intermediate state obtained along the on-top reaction path.[25] We find that when we increase the height of the C_2H_4 from its bound state, relaxing the condition that both atoms are at the same height (i.e., only the height of the center of the C—C bond is fixed), the molecule follows the reaction pathway from the three-atom intermediate state to the [2+2] product, but in the reversed direction, attaining the same optimized structure along each point. We[26] have found an energy barrier of 0.03 eV between the three-atom intermediate state and the bound state with the electronic transition occurring adiabatically along the reaction pathway. Therefore $C_2H_4/C(001)$ bears no relation to $C_2H_4/Si(001)$.

IV. HYDROGEN MEDIATED ADSORPTION

Contrary to our present prediction and Carbone's argument[15] that alkenes such as ethylene and cyclopentene would not be reactive with the C dimers on C(001), the Fourier-transform infrared (FTIR) spectroscopy data of Hovis *et al.*[14] showed that the spectrum of cyclopentene on C(001) is very similar to that obtained on Si(001) for which STM images clearly show reaction with the Si dimers. In order to explain the evidence of adsorbed cyclopentene on C(001), we propose an H-mediated [2+2] cycloaddition reaction of alkenes on C(001). Since Hovis *et al.* prepared a clean C(001) surface from a hydrogen-capped C(001) surface by heating to 1375 K, we speculate that the C(001) surface might not be perfectly H-free. When a H atom is attached to one C atom of the C dimer, a dangling bond is created on the other C atom as a consequence of breaking the π bond of the C dimer. Similar to the formation of the three-atom intermediate state in $C_2H_4/Si(001)$, this dangling bond can easily react with the π bond of C_2H_4, producing an

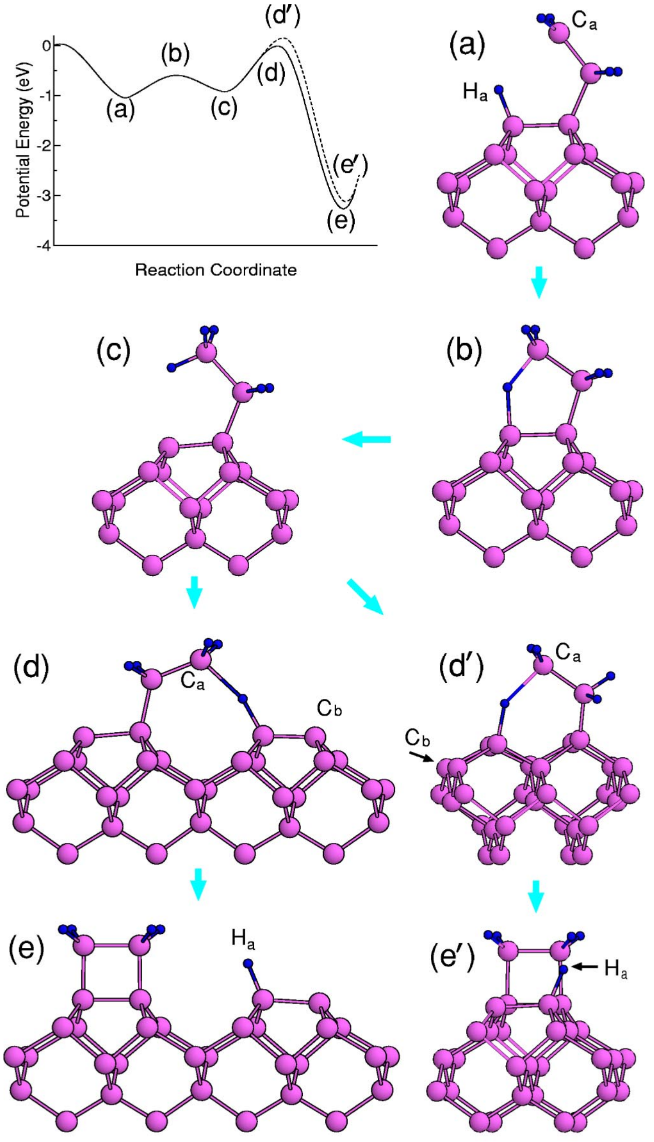

FIG. 6. (Color online) Calculated energy profile for the H-mediated $[2+2]$ reaction path for C_2H_4 on C(001) and the atomic geometries at several representative points. Energy [in eV/(4×3) surface unit cell] is referenced from the total energy of the separated limit consisting of a free C_2H_4 molecule and one H attached C(001)-(4×3) surface. Explanation for each state is given in the text. For the H-donation process the reaction path I (II) is displayed by the solid (dashed) line.

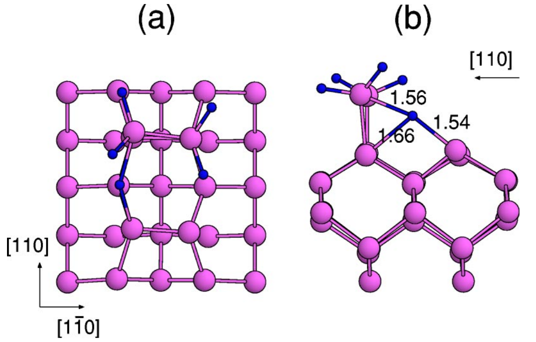

FIG. 7. (Color online) Transfer of H_a [in Fig. 6(a)] to the neighboring dimer. The position of H_a is constrained within a (110) plane near the center region between the two adjacent dimers. Top and side views of the optimized structure are displayed in (a) and (b), respectively. The numbers in (b) denote the interatomic distances (in Angstroms).

intermediate state [Fig. 6(a)] with an adsorption energy of 1.05 eV. Thus the π bond of C_2H_4 opens to form one C—C bond and one C radical. For the next step we performed a preliminary study for the transfer of H_a [in Fig. 6(a)] to the neighboring C atom along the dimer row, accompanying formation of the $[2+2]$ product. When the H_a atom is placed near the center region between two adjacent dimers, the energy of the optimized structure (Fig. 7) is 0.61 eV above the zero of potential in Fig. 6. Thus, we did not further consider such a reaction path. As another $[2+2]$ reaction path, the created C radical in Fig. 6(a) can be stabilized by H abstraction from the bonding C dimer. To examine the energy profile for this H-abstraction process, we consider the most probable abstraction pathway by decreasing the distance between the abstracted hydrogen H_a and the C_a atom [see Fig. 6(a)]. We optimize the structure for each constrained value of $d_{H_a—C_a}$ (but not the angle of that bond) using the gradient-projection method.[27] The calculated energy profile is displayed in Fig. 6, together with the atomic geometries of the transition state [Fig. 6(b)] and the H-abstracted state [Fig. 6(c)]. We obtain an energy barrier of 0.45 eV for H abstraction. In the H-abstracted state the attached C_2H_5 can easily rotate around the axis of the diamond-ethylene bond because of its single-bond character. As a result, the abstracted H atom can be transferred to neighboring C dimers. For this H-donation process we consider the two reaction paths where the structure is again optimized for constrained values of $d_{H—C_a}$. One path (I) is H donation to the nearest C atom in the adjacent dimer row and the other path (II) is that to a neighboring C atom in the same dimer row. After H donation, the C_a atom becomes the C radical again, thereby easily reacting with the remaining dangling bond of the bonding C dimer. The optimized atomic geometries of the transition and final states for the reaction path I (II) are given in Fig. 6(d) [6(d′)] and Fig. 6(e) [6(e′)], respectively. We obtain an energy barrier of 0.91 (1.03) eV for the reaction path I (II) and an adsorption energy of 3.26 (3.11) eV for the final $[2+2]$ product. As a result of the H-donation process, another dangling bond is created on the H-attached C dimer, setting off a consecutive H-mediated $[2+2]$ reaction for incoming C_2H_4.

Based on our calculated energy profile in Fig. 6, we consider thermal activation for the H-mediated $[2+2]$ cycloaddition reaction. Using an Arrhenius-type activation process with the usual attempt frequency of $\sim 10^{14}$ Hz,[28] we estimate the reaction rate for H abstraction as $\sim 3\times 10^{6}\ \mathrm{s}^{-1}$ at room temperature, indicating an easy thermal activation. On the other hand, the reaction rate for the H donation along the path I is $\sim 5.51\times 10^{-2}\ \mathrm{s}^{-1}$ at room temperature, corresponding to a half-life time of about 13 s, whereas the H-donation process along the path II yields a relatively small reaction rate ($\sim 5.36\times 10^{-4}\ \mathrm{s}^{-1}$) and large half-life time (1293 s).

According to the FTIR spectroscopy data of cyclopentene on C(001),[14] a uniform increase in infrared absorption intensity was observed up to exposures of ~ 5000 langmuir (1×10^{-5} Torr for 500 s). Assuming that the reaction rates of alkenes are similar to one another (and assuming that the 13 s half-life from reaction path I were correct), the number of H-mediated $[2+2]$ reactions per H in the cyclopentene/C(001) system amounts to ~ 40 during a saturation exposure time of 500 s. Noting that cyclopentene can only bond to somewhat less than half of the C dimers,[18] we find that the clean C(001) surface used in the experiments of Hovis *et al.*[14] would require H atoms on less than 1.5% of the surface dimers. We suspect that our Arrhenius prefactor is too large by three or more orders of magnitude because only a small fraction of the attempts to transfer a hydrogen will be made in the direction of the neighboring dimer. We find if the Arrhenius prefactor is reduced by five orders of magnitude to 10^9 Hz, but we assume 4% of the energy of adsorption into the precursor state remains undissipated, resulting in an effective temperature in the Arrhenius formula, that the half-life becomes 1.8 s. Thus only about 0.2% of the dimers would need a H atom to account for the observed time required to saturate C(001) with cyclopentene. When 10% (40%) of the energy remains the half-life becomes 4×10^{-6} (6×10^{-9}) s. Thus the hydrogen may be abstracted very quickly and only 0.1% of the dimers need to be occupied by H impurities to account for the 0.001 sticking coefficient.

V. CONCLUSIONS

We have studied the $[2+2]$ cycloaddition reaction of C_2H_4 on the C(001) surface using first-principles density-functional calculations. Unlike C_2H_4/Si(001) which involves an adsorption intermediate, the C_2H_4/C(001) system does not exhibit such precursor-mediated adsorption. Moreover, a concerted reaction on top of the C dimer is symmetry forbidden due to the symmetric dimer configuration of C(001). Even though this symmetry-imposed barrier can be avoided by a low-symmetry approach of C_2H_4, the adsorption is kinetically prohibited because of a high activation barrier whose lower bound (within the GGA) is 0.90 eV and whose sticking probability is much less than 10^{-15} (compared with the experimental 10^{-3}). We then showed that C_2H_4 could easily be adsorbed on a C(001) dimer which had a hydrogen impurity and how that H atom could be transferred to a neighboring dimer to repeat the process. The only important uncertainty involves the rate at which the adsorption energy into the precursor state is dissipated. The facts are as fellows. Alkenes adsorb on perfect C(001) surfaces with essentially zero probability. Cyclopentene adsorbs on a clean C(001) surface. Most experimentalists would consider a surface with less than 1% H impurities to be clean. Although we do not claim to have proved our process is the correct one, it is the only one thus far suggested which can account for all the facts.

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