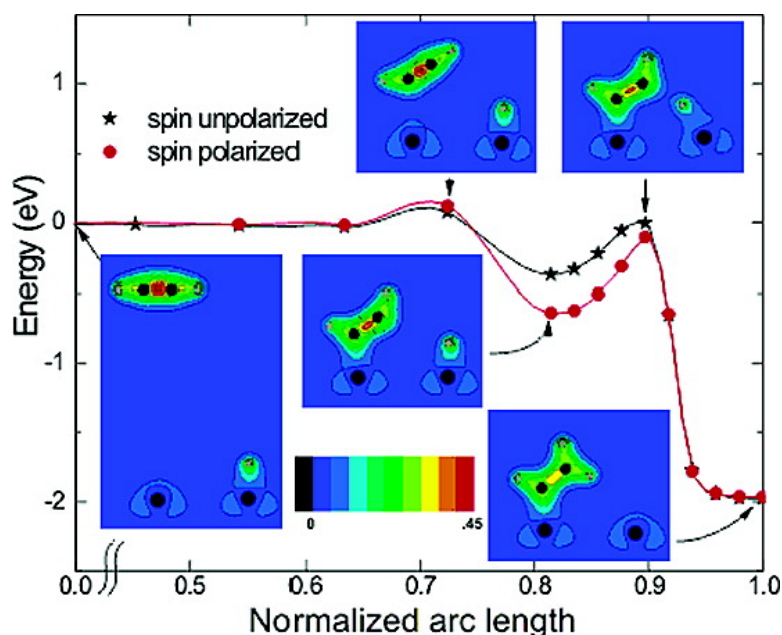


Surface Reaction of Alkynes and Alkenes with H-Si(111): A Density Functional Theory Study

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J. Am. Chem. Soc., **2004**, 126 (48), 15890-15896 • DOI: 10.1021/ja046702w • Publication Date (Web): 12 November 2004

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Surface Reaction of Alkynes and Alkenes with H-Si(111): A Density Functional Theory Study

Noboru Takeuchi, Yosuke Kanai, and Annabella Selloni*

Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey 08540

Received June 4, 2004; E-mail: takeuchi@princeton.edu; ykanai@princeton.edu; aselloni@princeton.edu

Abstract: Recent experiments on the addition of alkene and alkyne molecules to H-terminated silicon surfaces have provided evidence for a surface chain reaction initiated at isolated Si dangling bonds and involving an intermediate carbon radical state, which, after abstraction of a hydrogen atom from a neighboring Si-H unit, transforms into a stable adsorbed species plus a new Si dangling bond. Using periodic density functional theory (DFT) calculations, together with an efficient method for determining reaction pathways, we have studied the initial steps of this chain reaction for a few different terminal alkynes and alkenes interacting with an isolated Si dangling bond on an otherwise H-saturated Si(111) surface. Calculated minimum energy pathways (MEPs) indicate that the chain mechanism is viable in the case of C₂H₂, whereas for C₂H₄ the stabilization of the intermediate state is so small and the barrier for H-abstraction so (relatively) large that the molecule is more likely to desorb than to form a stable adsorbed species. For phenylacetylene and styrene, stabilization of the intermediate state and decrease of the H-abstraction barrier take place. While a stable adsorbed species exists in both cases, the overall heat of adsorption is larger for the alkyne molecules.

Introduction

The modification of silicon surfaces by the attachment of unsaturated organic molecules has been a topic of increasing interest over the last 10 years.^{1–6} The idea that combining organic chemistry with semiconductor technology could bring new advances and/or applications⁶ has been an important motivation for the activity in this field. The ability of organic molecules to absorb and emit light at certain frequencies, to sense molecules, or to recognize biological samples are examples of some applications that could be translated to silicon technology.⁷ Methods for preparing films of organic molecules on different silicon surfaces have been developed, involving both wet chemical and ultrahigh-vacuum (UHV) approaches.^{2,3} Among these, a particularly promising approach is a radical-initiated reaction of terminally unsaturated molecules with hydrogen-terminated Si surfaces. Slightly different versions of this basic reaction have been reported for the Si(111)^{8–10} and (001)^{1,11} surfaces and for porous silicon.³ Here we shall focus

on the prototype case of H-Si(111), where, depending on the experimental conditions, the reaction with terminal alkynes and alkenes has been shown to lead to the formation of densely packed monolayers^{8,9} or islands¹⁰ of molecules attached through C–Si bonds.

On the bulk-terminated Si(111) surface, each surface atom carries one dangling bond (db) containing one electron with energy approximately halfway between the bulk valence and conduction band edges. Dangling bonds are highly reactive, and therefore the surface rearranges (“reconstructs”) in such a way as to reduce their number. This is the main mechanism behind the well-known (2 × 1) and (7 × 7) reconstructions which are observed under UHV conditions; in both structures, the atomic positions at the surface are quite different from those of the bulk-terminated surface. Hydrogen adsorption strongly modifies the energetic balance. A monolayer of hydrogen saturates the dangling bonds of the bulk-terminated Si(111) surface, thus suppressing the driving force of surface reconstruction. This gives rise to a practically “ideal” surface in which Si atoms are very close to the regular bulk positions.^{2,12} Since all dangling bonds are saturated, the surface has a wide energy gap and is very unreactive. However, if a H vacancy on an otherwise hydrogen-saturated Si(111) surface is present, a dangling bond with a single spin-unpaired electron is formed, which can readily react with an incoming molecule.

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It is now widely accepted that the interaction between the alkene/alkyne molecule and the surface initiates at such an isolated Si dangling bond of the otherwise H-terminated Si(111) surface.¹⁰ Here the molecule binds to the surface through a Si–C bond and gives rise to a surface-bound organic group with a carbon-centered radical. It has been further inferred that the highly reactive carbon radical abstracts a hydrogen atom from a neighboring Si–H group to produce a new silicon dangling bond,^{9,10} which can act as attachment site for another alkyne or alkene molecule, thus leading to a surface chain reaction. However, various aspects of this mechanism, particularly the structures and energies of the (meta)stable and transition states along the reaction pathway, are not well understood yet.² For instance, recent STM measurements under UHV conditions have found that styrene on H-Si(111) forms small islands nucleated at each Si dangling bond site.¹⁰ The authors attributed these islands to self-limited surface chain reactions, but also mentioned the possibility of an alternative explanation based on styrene polymerization, which would lead to oligostyrene molecules attached to the surface by a single Si–C bond. For a fully unambiguous assignment of the observed structures, a detailed knowledge of the pathway would be clearly desirable.

On the theoretical side, besides a few force field calculations of the structure of full alkyl monolayers,¹³ work on the reactions of unsaturated hydrocarbons with hydrogenated silicon surfaces is still rather limited. A light-activated hydrosilylation reaction on a Si₂₉H₂₄ quantum dot has been recently studied;¹⁴ however this reaction is directly related to quantum confinement effects and has no counterpart in the chemistry of bulk Si surfaces. A number of DFT calculations have been carried out for the reactions of a few different alkene molecules with H-Si(100)^{1,11,15–17} and H-Si(111),^{10,18} using either slab¹⁷ or, more frequently, cluster^{1,10,11,15,16,18} models. However, very few studies examined the full reaction pathways,^{15,16a,17,18} and, to our best knowledge, no such investigation has been performed for alkyne molecules on hydrogenated silicon surfaces. Moreover, the agreement between the available calculations, as well as between calculations and experiments, is not fully satisfactory. For instance, H-abstraction barriers much higher than desorption barriers have been sometimes predicted¹⁷ for molecules for which stable adsorbed species are experimentally observed.

In this paper, we present a first-principles DFT investigation of the reaction of alkyne and alkene molecules with the hydrogenated Si(111) surface. Given the established role of isolated surface dangling bond (db) sites for initiation of the reaction, we assume from scratch that one unsaturated Si db is present on the surface. Using a recently proposed¹⁹ and implemented²⁰ method for finding chemical reaction pathways, we study important aspects of the addition reaction that are not easily accessed by experiments, such as the barrier for the initial

attachment of the molecule to the surface and for the successive H-abstraction process by the carbon radical, as well as the evolution of the electronic charge and spin densities and of the electronic energy levels in the course of the reaction. While contributing to a better fundamental understanding, these results may be useful for improving the ability to control the formation of functionalized silicon structures.

2. Method

Periodic DFT calculations have been performed within the Car–Parrinello approach,^{21,22} using the gradient-corrected Perdew, Burke, and Enzerhof (PBE)²³ functional. Electron–ion interactions are described using a Troullier–Martins²⁴ pseudopotential for Si and ultrasoft pseudopotentials²⁵ for C and H. The electronic states are expanded in plane waves with kinetic energy cutoffs of 25 and 200 Ry for the wave function and charge density, respectively. As the systems of interest have a spin-unpaired electron, both spin-restricted and spin-unrestricted calculations have been carried out.

In our periodic supercell approach, the surface is modeled as a slab of six (111) layers with eight silicon atoms per layer, forming a (4 × 3) surface cell in the (111) plane. Molecules are adsorbed on the upper surface of the slab, where a monolayer of H atoms is also present to saturate part of the Si dangling bonds. On the slab's bottom surface, all Si db's are saturated by H atoms. The four topmost Si layers of the slab as well as the H monolayer and the adsorbed molecules are fully relaxed, whereas the two lowest Si layers and the saturating H atoms are fixed at the ideal positions in order to simulate a bulklike environment (the Si–H distance was previously optimized). To check finite size effects, stable and metastable configurations have been reoptimized using a larger slab model with 12 Si atoms/layer. The results are found to be very similar to those obtained with the smaller supercell. In the geometry optimizations, the residual forces acting on all mobile atoms are always smaller than 10^{−4} atomic units.

To study the reaction pathways and activation energies, we have applied the string method,¹⁹ as implemented by Kanai et al.²⁰ in the context of the Car–Parrinello molecular dynamics. The string method allows one to determine the minimum energy pathway (MEP) in a reaction where both the initial (A) and final (B) states are known. Let us call φ a generic path (string) connecting A and B, which are usually local minima in the potential energy surface of the system of interest. By definition, a MEP is a path φ^* which satisfies

$$(\nabla V[\varphi^*])^\perp = 0 \quad (1)$$

where $(\nabla V)^\perp$ is the component of the potential energy gradient orthogonal to φ^* . A local maximum on the MEP is a saddle point on the potential energy surface of the system and thus corresponds to a transition state (TS) of the reaction.

It is convenient to describe the path using a parametric representation in terms of a scalar variable α defined along the path $\varphi = \varphi(\alpha)$. Following ref 19, we choose α to be the normalized arc length along the path: in this case $0 \leq \alpha \leq 1$, and the two end-states A and B correspond to $\alpha = 0$ and $\alpha = 1$, respectively. A simple way to determine the MEP is to evolve φ using a steepest descent dynamics:

$$\varphi_t = - [\nabla V(\varphi(\alpha;t))]^\perp + \lambda(\alpha;t)\hat{t}(\alpha;t) \quad (2)$$

Here the time t labels string configurations during the dynamics, $\varphi_t = \partial\varphi/\partial t$, $\hat{t} \equiv d\varphi/d\alpha/|d\varphi/d\alpha| = \varphi_\alpha/|\varphi_\alpha|$ is a unit vector tangent to the string, and $\lambda(\alpha;t)$ is a Lagrange multiplier that is introduced to satisfy

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Table 1. Calculated Bond Lengths (Å) and Bond Angles (deg) for the Molecules of Interest in This Work^a

	C–C	C–H	∠H–C–H	∠H–C–C
C ₂ H ₂	1.21 (1.203)	1.08 (1.06)		
C ₂ H ₄	1.34 (1.339)	1.10 (1.087)	117 (121.3)	
phenylacetylene	1.21	1.08		
styrene	1.35	1.10	117	114

^a Experimental results, in parentheses, are taken from *Handbook of Chemistry and Physics* 83rd ed., CRC Press, Boca Raton, 2002.

the constraint that the parametrization is preserved when the string deforms. This constraint is expressed by $d/d\alpha |d/d\alpha \varphi(\alpha)| = 0$, which states that the infinitesimal change in the arc length is constant along the string, thus ensuring that the local elastic stretching energy is distributed uniformly along the string.

In practice, the continuous string $\varphi(\alpha)$ is represented by a discrete set of “replicas” $\varphi(n)$, with integers $n = 0, \dots, P$. In most of our calculations, 10 replicas were used. The Lagrange multipliers are calculated iteratively by imposing the constraint,²⁰ and a second-order damped dynamics²⁶ is used instead of the steepest descent dynamics of eq 2. The electronic and nuclear degrees of freedom are simultaneously optimized using the Car–Parrinello damped dynamics equations of motion, and the potential energy is obtained “on the fly” from the DFT energy functional. A detailed description of our implementation of the string method is given in ref 20.

As a reference for the results to be presented below, in Table 1 we summarize the main structural parameters of the molecules of interest in this work. Experimental bond distances and angles are satisfactorily reproduced by our calculations, particularly the C–C triple- and double-bond lengths.

3. Results

3.1. Reaction Pathway for C₂H₂. The potential energy profile and selected configurations along the MEP for the addition of C₂H₂ to a H-terminated Si(111) surface with one Si dangling bond are shown in Figure 1A, where the results of both spin-unpolarized and spin-polarized calculations are presented. While the energetic and structural results of the two calculations are very similar along most of the pathway, there are nonnegligible differences in the activation barriers. Thus in the following, when mentioning energy values, we shall always refer to the more realistic spin-polarized results.

The pathway in Figure 1A consists of two parts separated by an intermediate metastable state (a local minimum in the system’s potential energy surface). It was determined by performing two separate string calculations, each involving 10 replicas, one from the initial to the metastable state and the other from the metastable to the final state. The initial state is a configuration with the C₂H₂ molecule lying parallel to the surface at a distance of 15 Å above it. At this position, the molecule and the surface are completely decoupled; for example, the C–C and C–H distances in the molecule are the same as in the isolated molecule. The intermediate state, shown in the inset (c) of Figure 1, corresponds to a Si–CH=CH radical and no Si db’s present on the surface. This state is found to be 0.64 eV more stable than the initial one, while the final state, shown in the inset (e), is as much as 2 eV more stable than the initial state. In the final state the original empty Si db site is replaced by a vinyl-silicon species (Si–CH=CH₂), while a new empty Si db is formed at a nearest neighbor surface site.

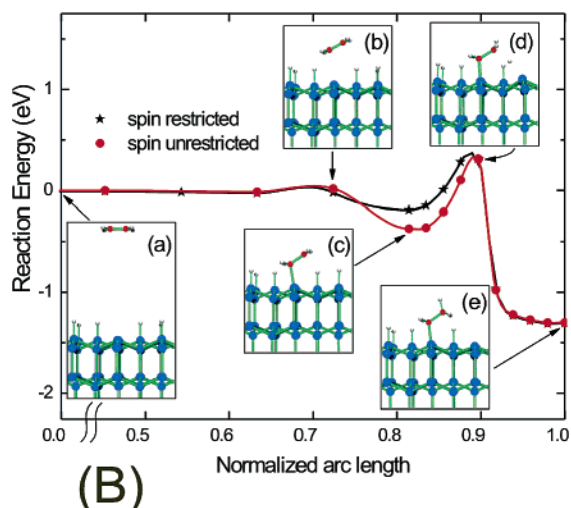
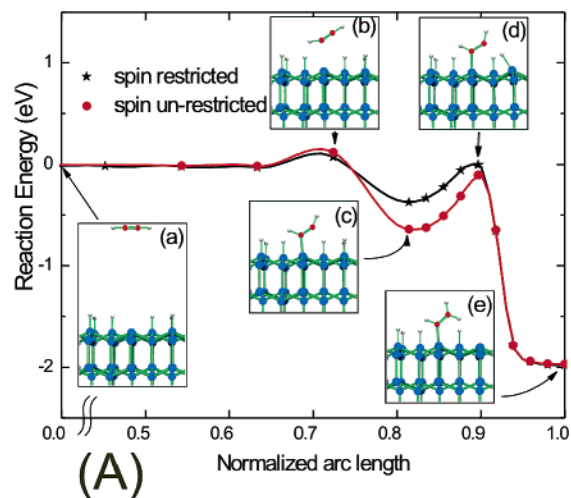


Figure 1. Potential energy profile along the MEP for the reaction of (A) acetylene, and (B) ethylene with the H-Si(111) surface. Black and red lines correspond to the spin unpolarized and spin polarized calculations, respectively. The zero of energy corresponds to the noninteracting surface + molecule system. Silicon atoms are blue, carbons are red, and hydrogens are white.

It appears from Figure 1 that the C₂H₂ molecule has to overcome a very small (~0.15 eV) energy barrier to attach to the surface and reach the intermediate metastable state. This barrier is related to the breaking of a π bond in the molecule and the subsequent change in hybridization, from sp to sp^2 , that the carbon atom closer to the surface must undergo to become bonded to it. The C–C bond in the intermediate state has a length $d_{C-C} \approx 1.29$ Å, a value between a double and a triple bond, and is tilted by $\theta \approx 37^\circ$ with respect to the surface plane, while the C–Si bond length is 1.92 Å. The activation barrier for hydrogen abstraction (saddle point (d)) is 0.54 eV, substantially larger than the first one, so that it is this process that represents the rate-limiting step for the reaction. The energy of the H-abstraction TS, however, is still below the initial zero of energy (see also Table 2), indicating that the process of H-abstraction is more likely than the desorption of the adsorbed radical back into the vacuum. Thus the adsorbed radical will transform into an adsorbed Si–CH=CH₂ species, with a huge stabilization energy of almost 2 eV with respect to the initial state. In the final state, the calculated C–C bond length and tilt angle are $d_{C-C} \approx 1.34$ Å and $\theta \approx 40^\circ$, respectively.

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Table 2. Local Minima and Transition State Energies (eV) in the Addition Reaction of Alkynes and Alkenes to the H-Si(111) Surface^a

	initial state	1st transition state	intermediate state	2nd transition state	final state
C ₂ H ₂	0.0	0.15	-0.64	-0.10	-1.97
C ₂ H ₄	0.0	0.04	-0.38	0.33	-1.30
phenylacetylene	0.0	-	-0.97	-0.72	-1.89
styrene	0.0	0.0	-0.81	-0.51	-1.02

^a For each molecule, the energy zero corresponds to the noninteracting molecule + surface system.

In the MEP of Figure 1A, the initial, intermediate, and final states were chosen so as to have the C–C bond of the organic molecule lying in a plane perpendicular to the surface and passing through adjacent surface Si atoms. Since in the initial state the molecule and the surface are completely decoupled, the initial relative orientation of the molecule is not important. However, for the transition from the intermediate to the final state the relative orientation of the molecule may change the energy barrier. We have thus calculated the MEP for metastable and final configurations rotated by 30° with respect to those shown in Figure 1A. The resulting MEP is qualitatively similar, except for a slightly (~0.1 eV) larger H-abstraction barrier, due to the larger distance between the H adatom and the unpaired electron of the radical. This does not change our conclusions on the viability of the investigated pathway for the formation of a stable adsorbed Si–CH=CH₂ species. No sizable barrier between different orientations of the molecule in the final state is found.

To monitor the formation and breaking of bonds during the addition reaction, we have analyzed the electronic charge and spin densities for selected atomic configurations along the MEP. We consider the atomic configurations in Figure 1, plus an additional configuration near the second transition state. In Figure 2A, we present contour plots of the total charge density, $\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})$, where $\rho_{\uparrow}(\vec{r})$ and $\rho_{\downarrow}(\vec{r})$ are the charge densities for spin up and down electrons, respectively. The charge density in the initial state, shown in panel (a), clearly reflects the strong triple bond between the two carbon atoms. Panels (b) and (c) show the charge density at the transition and intermediate metastable states, respectively. A reduction of the electron density between the carbon atoms can be observed, indicating a weakening of the C–C bond. In panels (d) and (e), due to the abstraction of the nearby hydrogen atom, the C–C bond is further weakened, now becoming a double bond.

The evolution of the total spin density, $\sigma(\vec{r}) = \rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r})$, along the MEP is shown in Figure 2B. In the initial and final states the spin density is localized at the hydrogen vacancy. At the first transition state (b), σ is distributed between the hydrogen vacancy and the outer (β) carbon atom of the organic molecule. At the intermediate state, the spin density σ is completely localized at the β -carbon atom of the acetylene molecule, indicating the presence of a radical. At the second transition state (d–d1), σ is again distributed between the organic molecule and the new hydrogen vacancy, until it becomes completely localized at the silicon db site in the final state.

To gain insight into the electronic properties, it is also useful to consider the evolution of the electronic density of states (namely the distribution of Kohn–Sham eigenvalues) along the MEP. Starting from the noninteracting molecule + H-Si(111)

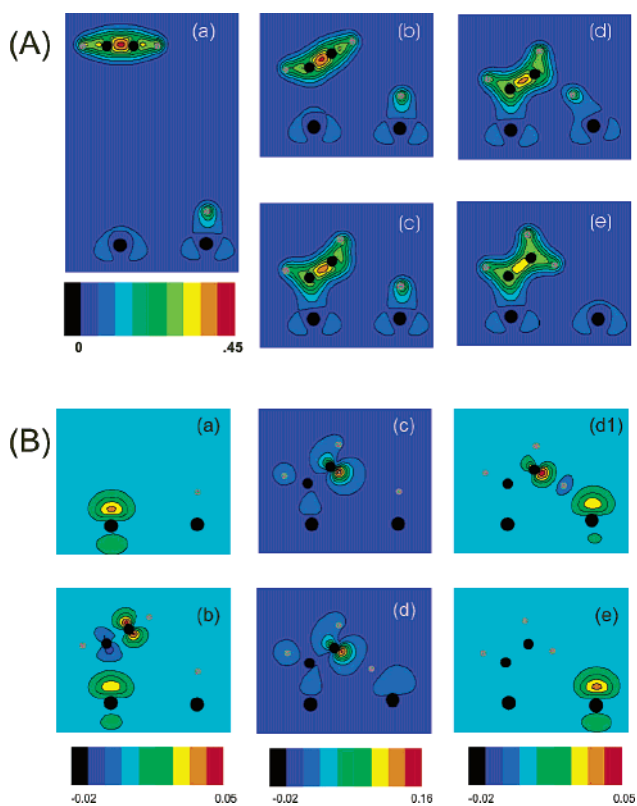


Figure 2. Total charge, $\rho(\vec{r}) = \rho_{\uparrow}(\vec{r}) + \rho_{\downarrow}(\vec{r})$ (A), and spin, $\sigma(\vec{r}) = \rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r})$ (B), densities in a plane perpendicular to the surface and passing through the C–C molecular bond. The charge density plots refer to the states in the inset of Figure 1A. The spin density plots include an additional state, marked as d1, for which the system HOMO–LUMO gap (see Figure 4) attains its minimum value along the MEP. In B, plots (c) and (d) have different color scales, due to larger spin densities.

surface with one dangling bond (top panels), in (a) we show the total density of states (DOS), where the black and red lines refer to the up- and down-spin electrons, respectively. Note that the only difference between the two curves is close to the gap: for up-spin electrons the dangling bond is occupied, while in the down-spin DOS the dangling bond is empty. In panel (b), the DOS projected onto the 2p orbitals of the α - and β -carbon atoms is shown. Since in the initial state, the two atoms are equivalent, their projected DOS (PDOS) are identical. Also, there is no difference between spin-up and spin-down states. The molecular highest occupied molecular orbital (HOMO) corresponds to the 2-fold degenerate π bonding states, while the lowest unoccupied molecular orbital (LUMO) corresponds to the π^* antibonding states.

The picture is quite different in the intermediate state (middle panels of Figure 3). The α - and β -carbon atoms are no longer equivalent, and due to the presence of the spin-unpaired electron, there are differences between spin-up and spin-down PDOS. Panel (d) shows that all peaks in the carbon PDOS are broadened by the interaction with the Si substrate. For the β -carbon, in particular, the highly reactive radical gives rise to peaks close to the edges of the H-Si(111) band gap.

In the final state (bottom panels of Figure 3), there is again no difference in the carbon spin-up and spin-down PDOS; by contrast, the presence of a Si dangling bond gives rise to different up- and down-spin total DOS near the band gap. With respect to the isolated acetylene molecule, the peaks in the carbon PDOS are broadened and shifted by the interaction with

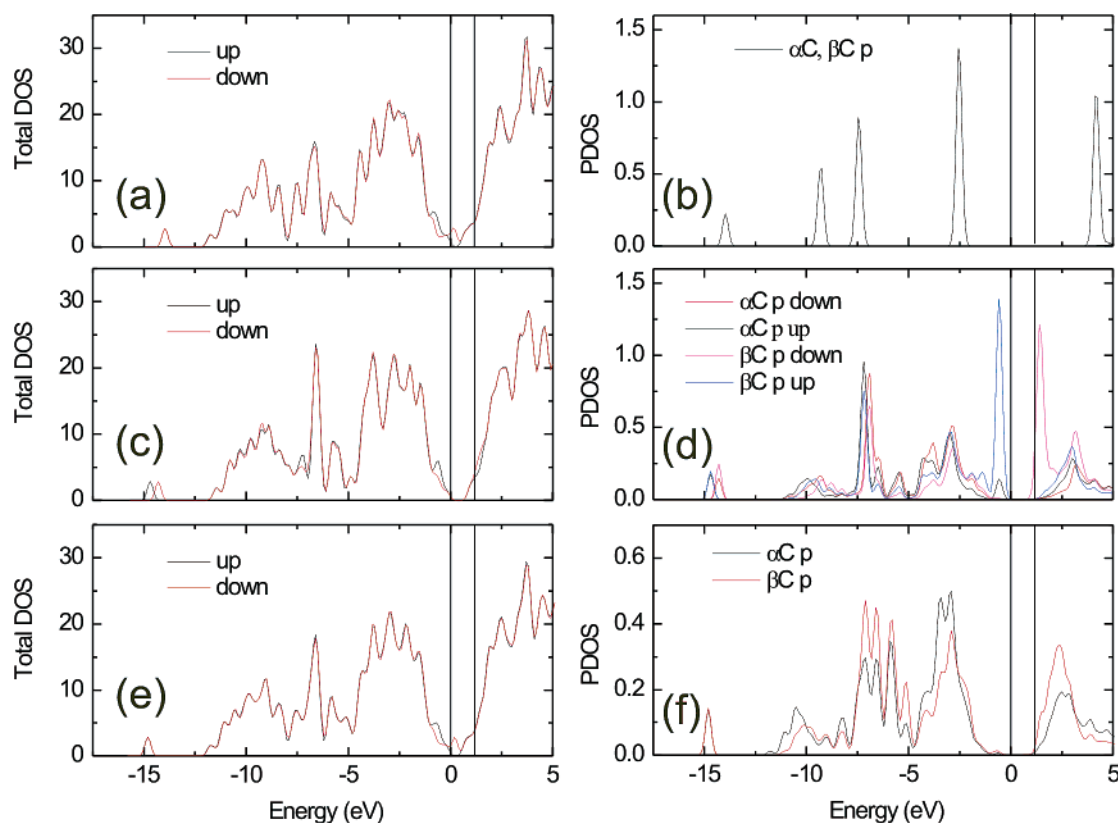


Figure 3. Density of states for selected atomic configurations along the MEP for the addition of acetylene to the H-Si(111) surface with one unsaturated Si db. Top panels: initial state, corresponding to the noninteracting surface + molecule system. Middle panels: intermediate metastable state. Bottom panels: final state. Panels (a), (c), (e): total DOS. Panels (b), (d), (f): DOS projected onto the 2p states of the α - and β -carbon atoms. Vertical lines indicate the band gap of the fully hydrogenated Si(111) surface.

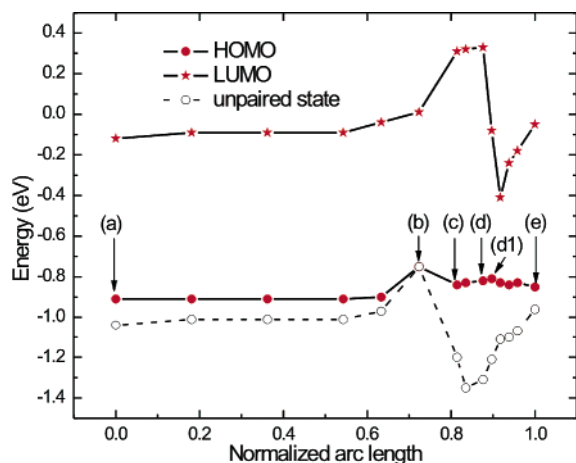


Figure 4. HOMO and LUMO of the interacting molecule + surface system along the MEP for the addition of acetylene to the H-Si(111) surface with one unsaturated Si db. Empty circles show the spin-unpaired occupied state.

the Si surface, with some empty states showing up near the bottom of the conduction band.

A more detailed view of the electronic structure around the gap is given in Figure 4. This shows the energies of the HOMO and LUMO of the interacting surface + molecule system along the MEP, as well as the energy of the occupied spin-unpaired state, which corresponds to the silicon dangling bond in the initial and final states of the transition. It appears that the typical HOMO–LUMO gap is on the order of 1 eV. However, as in most chemical reactions, the gap becomes narrower close to the transition states: a small reduction occurs at the first

transition state (b), and an even larger reduction takes place close to the second transition state (between d and d1).

3.2. Reaction Pathways for Ethylene, Styrene, and Phenylacetylene. The MEP for ethylene was calculated with the same procedure used for acetylene. Although the two MEPs seem qualitatively similar (see Figure 1B), the quantitative differences in the energies and barriers are quite substantial (see Table 2). The initial attachment of C_2H_4 to the surface, where the molecular π bond breaks and a new C–Si bond is formed between the molecule and the surface, is almost barrier-free. However, the stabilization energy of the intermediate state with respect to the initial one is found to be very small, only 0.38 eV, about one-half the corresponding value for acetylene. By estimating the lifetime of the intermediate state as $\tau \approx \nu^{-1} \exp(\Delta E_{des}^\ddagger/kT)$, where ΔE_{des}^\ddagger is the desorption barrier ($\Delta E_{des}^\ddagger = 0.42$ eV, corresponding to the sum of the adsorption barrier, 0.04 eV, and the stabilization energy of the intermediate, 0.38 eV), and ν is a typical attempt frequency that we assume of the order $10^{13} s^{-1}$, we find $\tau \approx 2 \mu s$ at room temperature. On the other hand, the activation barrier for hydrogen abstraction is rather large, ~ 0.71 eV, indicating that it is very unlikely that a H-abstraction event will take place during the short lifetime of the intermediate state, even if this may lead to an adsorbed complex about 1 eV more stable. Instead, the adsorbed radical is more likely to desorb back into the gas phase. This is consistent with recent experimental results for H-Si(100), where no stable structure was observed to form by the reaction with gas-phase propylene.¹ On the basis of DFT cluster calculations, this finding was attributed to the low stabilization energy of

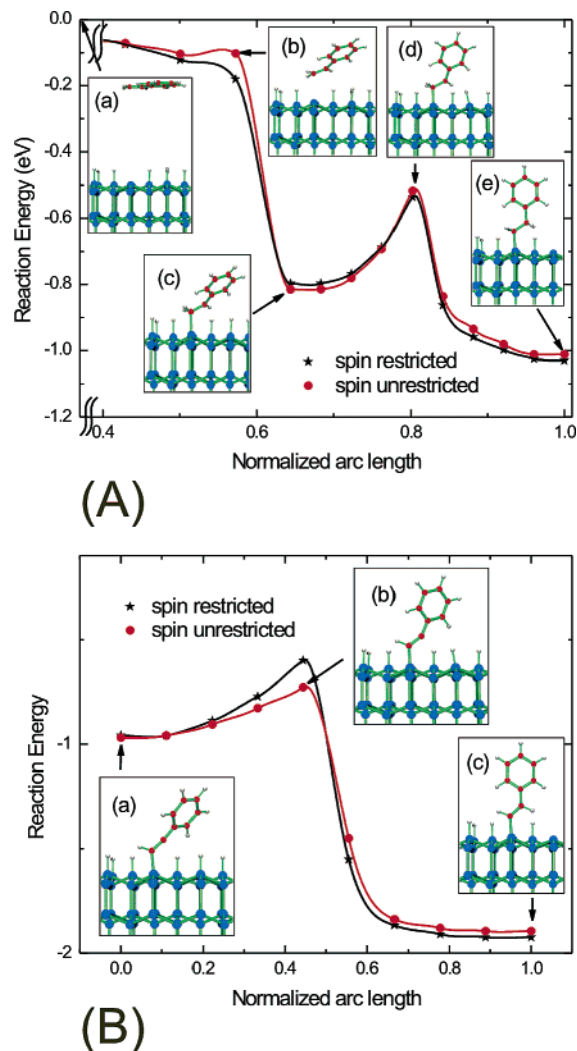


Figure 5. Potential energy profile along the MEP for the reaction of (A) styrene and (B) phenylacetylene with the H-Si(111) surface. For phenylacetylene, only the MEP for the H-abstraction from a neighboring Si-H species is shown. Black and red lines correspond to the spin unpolarized and spin polarized calculations, respectively. The zero of energy corresponds to the noninteracting surface + molecule.

the intermediate state for propylene adsorption on H-Si(100), for which a value of 0.4 eV was calculated. This value is very close to our result for C_2H_4 on H-Si(111), suggesting that an instability similar to that observed for propylene on H-Si(100) may be typical of short chain linear alkenes on hydrogenated silicon surfaces.

Turning now to styrene, the potential energy profile together with selected configurations along the MEP are shown in Figure 5A. We started again with the molecule at large distance from the surface and the molecular plane parallel to the surface, so that in the approach toward the surface the molecular π bonds can more directly interact with the surface dangling bond. Not only does this result in an almost vanishing adsorption barrier for the initial attachment of the molecule to the surface, but also the presence of the phenyl ring causes a strong stabilization of the intermediate, 0.81 eV, as found as well in DFT cluster calculations.¹⁰ Moreover, the barrier for H-abstraction is reduced to only 0.3 eV, indicating that this process should readily occur at room temperature, leading to a stable adsorbed species. We notice that our computed H-abstraction barrier is much smaller than that found in previous theoretical investigations of styrene

on H-Si(100),^{15,16a,17} which may be due to a not fully optimized MEP in those studies (see also below). Thus our results provide strong support for the interpretation that the styrene islands observed in STM experiments arise from a surface radical chain-reaction.¹⁰

As shown in Figure 5A, the structure of the styrene molecule along the reaction pathway is quite interesting. The structures of both the intermediate metastable state and the transition state for H-abstraction are significantly different with respect to those reported in previous theoretical studies,^{15,17} which is likely the reason for our lower calculated H-abstraction barrier. In the intermediate metastable state, the molecule is slightly bent; the $\alpha C-\beta C$ bond has a length $d_{C-C} \approx 1.47$ Å, a value between a single and a double bond, and is tilted by $\theta \approx 25^\circ$ with respect to the surface plane, while the C-Si bond length is 1.96 Å; the bond between the β -carbon atom and the closest carbon of the phenyl group forms a 38° angle with the surface. The structure of the molecule is evidently such as to optimize its bonding with the surface and also facilitates the successive abstraction of a H atom from a neighboring Si-H group. Detailed structural parameters for the intermediate and transition states are given in the Supporting Information.

Finally, for phenylacetylene we considered only the last part of the reaction, i.e., abstraction of the hydrogen atom from a neighboring site. This pathway is found to be qualitatively similar to that of styrene, with some quantitative differences, which are summarized in Table 2 and shown in Figure 5A. The intermediate state is more stable for phenylacetylene, 0.97 vs 0.81 eV for styrene, which can be related to the stronger bond between the C and Si atoms (the Si-C bond length is 1.93 and 1.96 Å for the alkyne and the alkene, respectively). Also the H-abstraction barrier is slightly lower for phenylacetylene, with the same trend found for the C_2H_2 vs C_2H_4 molecules. The larger difference between the two molecules is in the total exothermicity of the reaction: for phenylacetylene this is ~ 1.9 eV, which is almost twice that obtained for the addition of styrene, in line with the exothermicity difference between C_2H_2 and C_2H_4 .

4. Summary and Conclusions

Using periodic DFT calculations, we have studied the addition reaction of alkyne and alkene molecules (C_2H_2 , C_2H_4 , phenylacetylene, and styrene) to a hydrogenated Si(111) surface with one H-vacancy. Our results are in agreement with the available experimental observations and provide detailed information on the reaction pathways and barriers. In particular, our calculated reaction pathways confirm the suggestion^{9,10} that the reaction occurs via an intermediate state with lower potential energy than the noninteracting molecule + surface system. This intermediate state is characterized by the presence of a carbon-based radical, which may abstract a hydrogen atom from a neighboring surface Si-H group and thus give rise to the formation of a stable organic group as well as a db at a neighboring Si site. It is essential that the intermediate is sufficiently stabilized with respect to the initial state, and that the barrier for H-abstraction is lower than that for desorption, for the stable organic group to be efficiently formed. This is not the case for ethylene, for which we find that the intermediate is rather shallow and, at the same time, the H-abstraction barrier is quite high. A similar result is likely to hold for most short chain linear alkenes. In such cases

no stable organic species can be formed, as indeed it has been experimentally observed for propylene interacting with the hydrogenated Si(100) surface.¹ By contrast, our calculations indicate that the radical surface reaction mechanism is viable for the phenyl-stabilized styrene and phenylacetylene molecules. However both the lower H-abstraction barrier and larger overall reaction exothermicity suggest that the reaction with terminal alkynes should be faster and should also lead to a more stable organic overlayer.

Acknowledgment. We thank R. Pascal and S. Bernasek for useful discussions. Calculations were performed on the IBM-SP3 computer of the Keck Computational Materials Science

Laboratory in Princeton. This work was partially supported by NSF through Grant DMR-0213706 to the MRSEC-Princeton Center for Complex Materials and Grant No. CHE-0121432.

Supporting Information Available: Main optimized geometrical parameters of the initial, intermediate, transition, and final states along the minimum energy pathways for the reaction of H-Si(111) with C₂H₂, C₂H₄, phenylacetylene, and styrene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA046702W