



Full length article

Organic functionalization of silicene with formaldehyde and propanaldehyde

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ABSTRACT

We have studied the addition reaction of aldehydes on silicene by means of periodic density functional theory. The reaction is initiated at a dangling bond, formed by removing a hydrogen atom from the surface. An incoming unsaturated molecule can attach to the surface by reacting with the dangling bond and forming an intermediate carbon radical state. After abstraction of a neighboring H atom, the molecule becomes stable and a new dangling bond is formed. Thermodynamics and kinetics suggest that adsorption is highly probable to occur. Even more, comparisons with the addition reaction of aldehydes on H-Si(111) and the adsorption of hydrocarbons on silicene, suggest that reaction of aldehydes on silicene is even more favorable. This might be explained in terms of the enhanced polar ambient in silicene with respect to the H-Si(111) surface in the first case, and by the higher stability of Si-O bonds with respect to Si-C bonds in the later. Also, calculations suggest that the attachment of a second molecule is also favorable, indicating the possibility of a chain reaction.

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1. Introduction

The experimental discovery of graphene [1] has gained so much attention in the last decade because of the exotic properties that this material shows. Some of these features are linear dispersion at the K point, massless Dirac fermions, and anomalous quantum hall effect, among others [2,3]. Moreover, since strictly two dimensional structures were theoretically predicted to be unstable, the experimental discovery of graphene meant a breakthrough in our understanding of two dimensional materials. A brief review of its new physics and potential applications is discussed in Ref. [4].

Graphene exotic electronic features have drawn the attention of scientists because of the possibility to design novel electronic devices based on this material. However, its implementation faces some serious drawbacks, such as the inability to grow large area graphene sheets, the lack of a band gap, and the need for retooling the electronic industry processes currently based on silicon. It has been found that other group IV elements, such as silicon (Si) and germanium (Ge), form two-dimensional structures like graphene,

but with a vertical displacement between neighboring atoms [4,5]. These new two-dimensional structures also exhibit massless Dirac fermions and linear dispersion at the K point near the Fermi level, and a negligible band gap [6].

The two-dimensional silicon analogue of graphene is often called silicene. Experimentally, it has been successfully grown on metal substrates such as Ag(110), Ag(111) [6–9], Ir(111) [10], and on ZrB₂ thin films [11] by means of molecular beam epitaxy. Even though the substrate induces deformation on the silicene lattice, theoretical calculations using the electron localization function have shown that most of the localized electron density lies between silicon atoms and not at the silicene substrate interface [10]. This means that the substrate is not chemically bonded to silicene, so it can be considered a two dimensional material.

Another trend towards silicene experimental synthesis is based on wet chemistry methods. In a first attempt to synthesize silicon nanosheets, Nakano and coworkers employed topotactic synthesis using Mg doped CaSi₂ from the Zintl phase with further exfoliation. However, due to the process, the material obtained was found to be capped with oxygen (O) and it contained appreciable amounts of Mg [12]. In recent years the same approach has been used to obtain stable organic modified silicene with *n*-decylamine and alkyl compounds [13,14].

Further modification of silicene, in order to change its properties, seems a good idea. The surface chemistry of Si(111) has been

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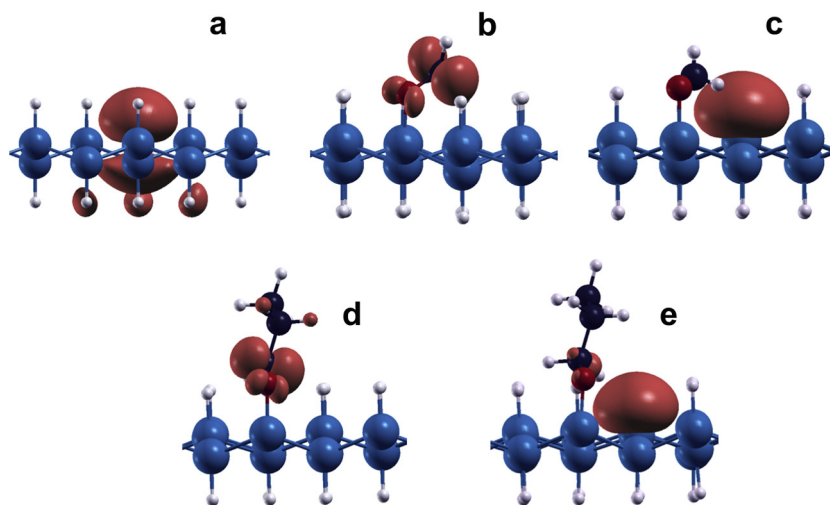


Fig. 1. Spin density isosurfaces at the initial state (a) and for the addition reactions for formaldehyde at the IS (b) and FS (c), and with propanaldehyde IS (d) and FS (e).

Table 1
Total energies from different states along the reaction pathway in the addition reactions of formaldehyde and propanaldehyde on the silicene and H-Si(111) surfaces.

Surface	Molecule	Initial State (eV)	Intermediate State (eV)	Transition State (eV)	Abstraction Barrier (eV)	Final State (eV)
Silicene H-Si[111]	Formaldehyde	0.0	-1.14	-0.82	0.32	-1.76
	Formaldehyde	0.0	-0.81	>-0.3	>0.51*	-1.63
Silicene H-Si[111]	Propanaldehyde	0.0	-1.84	-1.50	0.34	-2.50
	Propanaldehyde	0.0	-0.69	-0.22	0.47	-1.31

Results from H-Si[111] were taken from reference [18].

vastly explored. Organic chemistry, known for its wide repertoire of chemical transformations, has been previously put at work on the modification of this surface with successful results. When hydrogen reacts with the Si(111) surface, the silicon atoms in the resulting hydrogenated surface are in positions similar to those in an ideally bulk terminated Si(111) surface. This similarities suggest that the H-Si(111) chemistry may be used to functionalize silicene. Moreover, the vast field of organic chemistry applied to functionalize silicene may bring in valuable tools for tailoring silicene electronic properties at will.

One possibility for silicene modification is based on the surface radical reactions of the hydrogen (H) terminated Si(111) surface with unsaturated organic molecules, that have been previously experimentally and theoretically explored [15–19]. First of all, we begin with a hydrogen-terminated silicene (Silicene) surface. One way to initiate the free radical reaction is by removing a hydrogen atom with the tip of a scanning tunneling microscope [20]. This will yield a surface vacancy with a highly reactive unpaired electron. In this paper, the surface with a vacancy plus a totally decoupled molecule will be called the initial state, and its total energy will be set to zero. The highly reactive dangling bond will react with a nearby molecule at the unsaturated bond, where one of the molecule's atoms will be bonded to the surface and the unpaired electron will be localized at the molecule. This is called the intermediate state (IS). The dangling bond, now localized at the molecule, may abstract the nearest neighbor H atom from the surface, and a new dangling bond at the silicene surface will be created. This last step creates a new dangling bond on the silicene surface where another molecule may further react, which is called the final state (FS). The structures, together with the spin isosurfaces at each of the reaction steps mentioned above for the two molecules can be pictorially seen at Fig. 1. The viability of the reaction depends on both thermodynamic and kinetic factors, such as the relative total energies of products and reactants, as well as the activation energy. Theoretical calculations of the radical reaction

described above have been previously reported for various surface-molecule systems: H-Si(111)[18,19], H-graphene [21], H-silicene [22], H-germanene[23], and H-Ge(111) [24].

In the present work we have studied the functionalization of silicene with formaldehyde and propanaldehyde following the radical initiated chemical reaction described above, by means of periodic density functional theory. We found that both molecules are likely to complete the reaction. The self propagating character of the radical reaction in both systems was confirmed. The rest of this paper is organized as following: in Section 2 we described the methods, in Section 3 we present our results and discussion and in Section 4 we conclude the article.

2. Theoretical method

Calculations were performed using periodic density functional theory (DFT), within the Car-Parrinello molecular dynamics [26] approach by means of the *Quantum Espresso* computational package [27]. The exchange and correlation energies were calculated using the Perdew-Burke-Ernzerhoff GGA functional [28], pseudopotentials were used to describe electron-ion interactions [29]. We have used a plane wave expansion, with kinetic energy cutoffs of 25 and 200 Ry for the wavefunctions and electron density, respectively. A 5×4 supercell with 40 silicon atoms was used for all calculations: bare and silicene structural optimization, addition surface reaction of formaldehyde and propanaldehyde along the entire reaction pathway. Before hydrogenation, the calculated vertical distance between two adjacent Si atom in silicene was 0.44 Å, value that was increased to 0.72 Å after hydrogenation. The supercell's vacuum distance was greater than 10 Å in all calculations. In all previous works the rupture of a γ Si- γ H bond and the formation of a β C- γ H bond were observed when searching for the minimum energy path (MEP); for this reason the β C- γ H bond distance was chosen to be our reaction coordinate. To implement this into our calculations, we generated a set of configurations between

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