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Cycloaddition Reaction of 1,3-Butadiene with a Symmetric Si Adatom Pair on the Si(111)7×7 Surface

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The interactions of organic molecules with semiconductor surfaces recently have taken much attention because of potential applications such as molecular switching devices and functionally treated surfaces.[1,2] The study has been focused on unsaturated hydrocarbons and heterocyclic aromatics on the two representative surfaces, Si(001)2×1 and Si(111)7×7. The most chemical reactions on the surfaces have been ascribed to [2+2]-like and [4+2]-like cycloaddition reactions between molecules and Si pairs through various pathways such as concerted and stepwise ones. In the reactions, Si pairs were disclosed to behave differently from a simple alkene, which boosted the study of the roles of Si pairs.[2−4] Up to now, molecules have been reported experimentally to react with asymmetric Si pairs, asymmetric dimers on Si(001)2×1, and adatom−restatom pairs (AR pair hereafter) on Si(111)7×7.[5,6] Here, the Si═Si bond of a Si dimer on Si(100)2×1 with a σ bond coupled with a weak π bond is similar to the C═C bond of organic molecules, while Si(111)7×7 is composed of 12 adatoms, 6 restatoms, and 1 corner atom, with spatially inequivalent dangling bonds.[5,6] The asymmetric Si pairs have a common characteristic that charge transfer within the Si pairs, from the lower atom to the upper atom on the asymmetric Si dimer and from the adatom to the restatom on the Si AR pair, makes them behave as an electrophile−nucleophile pair. For this reason, theoretical studies of cycloaddition reactions on Si surfaces have been focused on the asymmetric electrophile−nucleophile pairs. This naturally leads to a question of what if a symmetric Si pair playing as a dielectrophile or a dinucleophile takes part in a cycloaddition reaction. In this communication, we fist report experimentally using scanning tunneling microscopy (STM) that a symmetric Si adatom pair on Si(111)7×7 reacts with 1,3-butadiene through a cycloaddition reaction. The symmetry of the Si adatom pair is expected to influence significantly a reaction pathway of a cycloaddition product, as also discussed in the study of a cycloaddition reaction on a symmetric C dimer of C(100).[7]

STM images were acquired using a commercial variable-temperature STM (Omicron, Germany). Figure 1 shows STM images of Si(111)7×7 after exposure to 0.1 Langmuirs (L) of 1,3-butadiene at room temperature. Si adatoms with a binding energy of 0.5 eV are sensitive at a low positive sample bias (V_s). Thus, the bright protrusions in the STM image acquired at $V_s = 0.5$ V (Figure 1a) originate from Si adatoms with unsaturated dangling bonds.[8] In the STM image, some Si adatoms are not imaged and look to be desorbed, leaving a defect. If the dark site is due to a simple defect, it should look dark at both filled- and empty-state images. At the filled-state STM image with $V_s = -1.0$ V (Figure 1b), the dark sites are shown with other bright protrusions located at different positions from Si adatoms. This indicates that the dark sites originate from Si adatoms bonding with 1,3-butadiene rather than simple defects, as observed for other molecule additions on Si(111)7×7.[9] A closer insight reveals the adsorption of 1,3-butadiene to produce three different dark sites. This indicates that the number of adsorption sites of 1,3-butadiene is three; the three sites are denoted as A, B, and C in Figure 1. We counted the number of the three adsorption sites so that we found that the reaction rate of the three adsorption sites is 8:1:3 (A/B/C), which reveals that 1,3-butadiene prefers A site energetically rather than B and C sites.

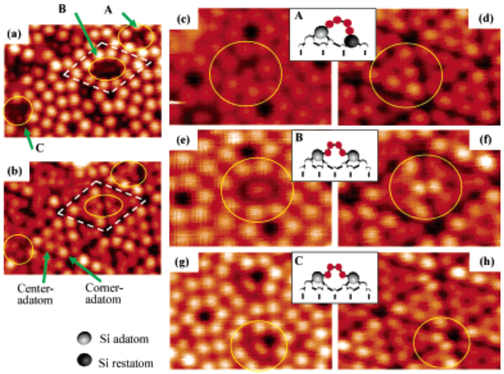

Figure 1. STM images of Si(111)7×7 after exposure to 0.1 L of 1,3-butadiene with $V_s = 0.5$ (a) and -1.0 V (b), where white dashed lines denote the unit cell of Si(111)7×7 and yellow circles indicate the adsorption sites of 1,3-butadiene. The STM images of the three different adsorption sites, A (c)−(d), B (e)−(f), C (g)−(h) were also acquired at different $V_s =$ 1.0 (c)−(e)−(g) and −2.0 V (d)−(f)−(h).

1,3-butadiene on Si(100)2×1 and Si(111)7×7 is known to form a [4+2]-like or a [2+2]-like cycloaddition product reacting with two Si atoms with unsaturated dangling bonds.[3,4,10] Thus, adatoms and restatoms on Si(111)7×7 are involved in the cycloaddition reactions with 1,3-butadiene. Figures 1c−d, e−f, and g−h are empty- and filled-state images of A, B, and C sites, respectively. The empty-state image (Figure 1c) with $V_s = 1.0$ V of the A site reveals 1,3-butadiene reacting with one Si adatom. Because 1,3-butadiene bonding with only one Si adatom is unstable energetically, it is expected to react with a neighboring Si restatom near the Si adatom, resulting in a [4+2]-like or a [2+2]-like product. This is supported by the filled-state image with $V_s = -2.0$ V (Figure 1d) of A site, where Si restatoms are imaged at-between Si adatoms on clean Si(111)7×7, showing that the neighboring Si restatom fades away. As a result, it is obvious that 1,3-butadiene at A site forms a [4+2]-like or a [2+2]-like product with the Si AR pair. For the reaction of 1,3-butadiene with the Si AR pair, Lu et al.[10] suggested theoretically that a [4+2]-like reaction is energetically favorable over a [2+2]-like reaction. This is also supported by Tao et al.,[11] suggesting that a [4+2]-like product is matched geo-

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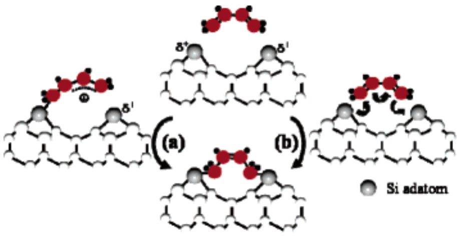
metrically with the Si AR pair and, consequently, is with less strain in comparison to a [2+2]-like product.

The other two sites (B and C) were neither predicted theoretically nor observed experimentally. The empty- and filled-states of B (Figure 1e,f) and C sites (Figure 1g,h) reveal 1,3-butadiene to react with two Si adatoms, which fades the adatoms away in the images. 1,3-butadiene, located at B site, forms a cycloaddition product reacting with the center-adatom pair, while 1,3-butadiene of C site gives rise to a cycloaddition product reacting with the corner-adatom pair. The two adsorption sites are nearly identical, except that the binding energy of the center adatom is lower than one of the corner adatoms by 0.3 eV.[12] It is unusual that 1,3-butadiene gives rise to a cycloaddition reaction on the symmetric Si pair, the Si adatom pair, because unsaturated hydrocarbons and heterocyclic aromatics on the two representative Si(111)7×7 and Si(100)2×1 surfaces have been reported to form a cycloaddition product reacting with an asymmetric Si pair, an asymmetric Si dimer, and a Si adatom–restatom pair.

1,3-butadiene at B and C sites may give rise to one of [4+2]-like and [2+2]-like products, as expected from the studies of cycloaddition reactions on the asymmetric Si pairs of Si(111)7×7 and Si(100)2×1.[3,4,10] Because a [2+2]-like product of 1,3-butadiene is geometrically optimized through one C–C bond within a Si pair, one C–C bond length of 1.5 Å is too short to bond with the adatom pair with a distance of 6.7 Å.[11] In the [4+2]-like product, the positions of carbon atoms of 1,3-butadiene in the [4+2]-like product may be distorted for carbon atoms to bond with the adatom pair with a long distance of 6.7 Å. Besides, the cycloaddition products of B and C sites are imaged as an ellipse and a dumbbell in the empty-state and filled-state images, respectively. Because the two images are not found on clean Si(111)7×7, the possible origins of the ellipse and dumbbell images are the C═C π*-orbital (or Si–C σ*-orbital) and the C═C π-orbital (or Si–C σ-orbital), respectively, with binding energies close to E_F, while the C–C σ*- and σ-orbitals are excluded as origins because of their binding energies at least below −10 eV and above 8 eV, respectively.[4,13] For the dumbbell image, the planar shape of the C═C π-orbital resembles an ellipse, while that of the two Si–C σ-orbitals resembles a dumbbell. Moreover, the energy level of the Si–C σ-orbital on C_2H_2/Si(100) is closer to E_F by 2 eV in comparison to that of the C═C π-orbital on C_2H_2/Si(100).[13] For the ellipse image, the planar shape of the C═C π*-orbital is like a dumbbell, as observed for the Si–Si π*-orbital of a Si dimer on Si(100)2×1, while the two Si–C σ*-orbitals with dumbbell shapes could be overlapped in a planar shape, resulting in the ellipse image. Besides, the binding energy of the Si–C σ*-orbital on C_2H_2/Si(100) is similar to that of the C═C π*-orbital on C_2H_2/Si(100).[13] These imply that the dumbbell and ellipse images may be due to the Si–C σ-orbital and the Si–C σ*-orbital, respectively, which needs to be studied further in the future.

The symmetric adatom pair is considered as a dielectrophile. This deviates distinctly from an asymmetric adatom pair with one electrophile and one nucleophile, which have been studied experimentally and theoretically up to now. The charge distributions of the Si pairs play a critical role in determining a reaction pathway.[3,7] The stepwise reaction pathway (see Scheme 1a) is initiated by a nucleophilic attack of the C═C bond of 1,3-butadiene on the positively charged Si atom, for examples, the lower atom of an asymmetric Si dimer and the adatom of a Si AR pair. The positive charge transferred from the Si atom results in a zwitterionic intermediate with a positively charged carbocation, which sequentially reacts with a negatively charged atom of the asymmetric Si pair. Thus, the stepwise reaction is not plausible on the Si adatom pair with two positively charged Si atoms. Here we do not exclude that a stepwise reaction can happen through another intermediate. In comparison, the concerted reaction (see Scheme 1b) requires a negligible charge asymmetry of a Si pair to form two Si–C bonds simultaneously. For these reasons, 1,3-butadiene is expected to form a [4+2]-like product through the concerted reaction pathway on the symmetric adatom pair, while the stepwise reaction pathway is favorable for the [4+2]-like reaction on the asymmetric AR pair.

Scheme 1. Stepwise (a) and Concerted (b) Reaction Pathways of the [4+2]-Like Cycloaddition Reaction of 1,3-Butadiene on the Symmetric Si Adatom Pair



In summary, the studies of cycloadditon reactions on two representative Si(100)2×1 and Si(111)7×7 have been focused on the asymmetric Si pairs, the asymmetric dimer on Si(100)2×1 and the AR pair on Si(111)7×7, because cycloaddition reactions were found experimentally only on the asymmetric Si pairs. Therefore, this first experimental observation of the cycloaddition reaction on the symmetric Si pair, the Si adatom pair on Si(111)7×7, will shed light on and provide further insight into the study of the dependence of a cycloaddition reaction on the symmetry of a Si pair.

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