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Preservation of epoxy groups on surfaces in the covalent attachment of butadiene monoxide on Si(111)-(7×7): the effect of a vinyl substituent†

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Adsorption of butadiene monoxide on Si(111)-(7×7) has been scrutinized by high-resolution electron energy loss spectroscopy (HREELS), scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. The experimental results indicate that surface reaction occurs through a [2+2]-like cycloaddition, which is further supported by the DFT studies.

Molecular electronics with custom-desired properties is emerging as an interesting field due to the limited miniaturization of silicon integrated circuits.¹ An important and essential step in fabricating applicable molecular circuitry is to build large molecular chains. One possible approach to complete this procedure is self-assembly which could be used to directionally construct large molecular patterns or supramolecular arrays.² The 'bottom-up' approach requires that the initial reaction layer should have low surface roughness and uniform distribution of reactive sites to avoid interface defects. The technologically important Si(111)-(7×7) superlattice is a perfect candidate template which consists of triangular faulted and unfaulted subunits for the growth of arrayed nanostructures.³ Recently, much more attention has been directed towards the covalent binding of organic molecules on Si(111)-(7×7) to obtain desired surface modification and functionalization due to its potential applications in

molecular electronics.⁴ The manufacturing technique also demands the proper choice of organic functional groups which can be used to tune the structure, size and properties of adsorbates to achieve the expected molecular nanostructures. A cyclic ether that contains the epoxy group is a good building block for fabricating the molecular chains. It can form rings with various sizes and shapes by selectively assembling the cyclic ether molecules. Two simplest cyclic ether molecules, oxirane and methyl oxirane, served as models to explore the surface-epoxy group interaction. For example, oxirane readily adsorbs on Si(100) *via* breaking the C–C bond to form a Si–C–O–C–Si ring.⁵ Similar reaction was observed for methyl oxirane, which was shown to adsorb through cleavage of the C–O bond in the epoxy group, giving rise to a five-membered ring surface species on Si(100).⁶ In previous studies, the ring of the epoxy group that is supposed to be kept for further modification to form a supramolecular chain breaks due to its large ring-strain.^{5,6} Thus, it is necessary to employ substituent groups to ensure that the first stage of surface attachment takes place in a controlled and selective manner. This work reports another simple cyclic ether molecule of butadiene monoxide that contains two functional groups, epoxy and vinyl groups. Our experimental data and DFT calculations show that butadiene monoxide covalently binds to the surface through a [2+2]-like cycloaddition between the C=C bond and a neighboring adatom–rest atom pair, maintaining the epoxy group in the cycloadduct. The vinyl substituent is introduced as a tool to successfully direct the chemical attachment behaviors of the butadiene monoxide molecules on Si(111)-(7×7).

Fig. 1 shows the HREELS spectra of physisorbed butadiene monoxide by exposing 1.5 L of molecules to the clean Si(111)-(7×7) surface at 110 K and chemisorbed butadiene monoxide by annealing the physisorbed-molecule-covered sample to 300 K. The comparison between these two spectra, with reference to the infrared analysis of liquid phase butadiene monoxide⁷ as well as the theoretical calculations, is summarized in Table S1 (ESI†). Among all the physisorbed vibrational signatures, the characteristic C=C stretching mode can be identified at 1634 cm^{−1}.

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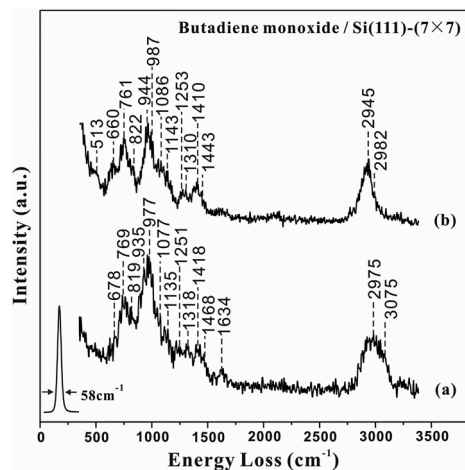


Fig. 1 HREELS spectra of butadiene monoxide/Si(111)-(7×7): (a) physisorbed 1.5 L of butadiene monoxide on Si(111)-(7×7) at 110 K; (b) a saturated chemisorption monolayer by annealing the physisorbed-molecules-covered sample to 300 K, $E_p = 6.23$ eV, specular mode.

Two features at 1251 and 819 cm^{-1} are attributable to ring breathing and ring deformation, respectively.

The vibrational assignments of chemisorbed butadiene monoxide are significantly different. The retention of vibrational features for ring breathing (1253 cm^{-1}) and ring deformation (822 cm^{-1}) suggests that the epoxy groups are preserved in the surface products. The absence of the C=C (1634 cm^{-1}) stretching vibration suggests the direct involvement of C=C in surface binding. It is different from the case of thiophene adsorption on Si(100) where the stretching mode of the C=C bond in the chemisorbed species was not identified in HREELS spectra due to its parallel configuration to the surface plane.⁸ In this study, all the possible adspecies bear a tilted configuration relative to the surface plane. Additional important evidence of the adsorption mechanism is provided by the appearance of a new peak at 513 cm^{-1} , which is ascribed to the stretching mode of a newly formed Si-C⁹ bond.

By combining selectivity and competition of epoxy and vinyl groups in the butadiene monoxide molecules, comprehensive reaction pathways of the complex chemical attachment occurring on Si(111)-(7×7) are sketched in Fig. 2. The vinyl group exposes the interface reaction to a [2+2]-like cycloaddition through the C=C bond (modes I and II), which is supported by the disappearance of the C=C stretching mode and the preservation of ring breathing and deformation, accompanied by the presence of a new vibrational peak for the Si-C bond. Due to the presence of the competitive epoxy group, it may undergo the epoxy ring-opening reaction (modes IV and V). In addition, the [4+2]-like cycloadditions may also occur through the conjugated epoxy and vinyl groups (mode VI). Abundant previous studies^{6a,10} showed that no matter the epoxy ring-opening reaction or the [4+2]-like cycloaddition starts from a dative-bonded precursor state (mode III), which is formed by donating the lone-pair electrons of the oxygen atoms in the epoxy group to the electron-deficient Si adatoms. The last four modes (from mode III to mode VI) are precluded as the absence of the stretching

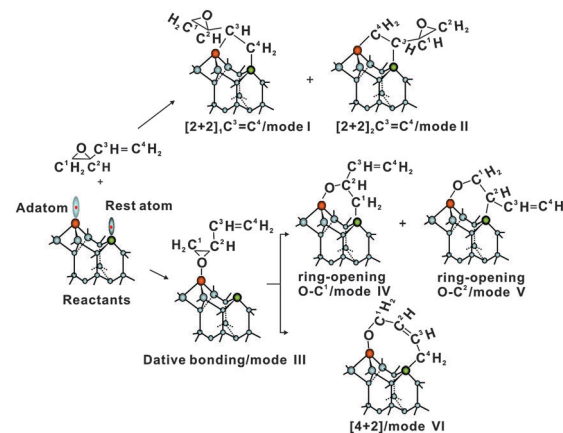


Fig. 2 Schematic representation of possible binding configurations of butadiene monoxide on Si(111)-(7×7) through [2+2]-like cycloaddition, dative bonding, ring-opening reaction and [4+2]-like cycloaddition.

signature of the C=C bond and Si-O bond. Thus, the HREELS results directly support a [2+2]-like cycloaddition mechanism, involving the C=C bond of butadiene monoxide and Si surface dangling bonds.

To acquire detailed information about butadiene monoxide chemisorption on Si(111)-(7×7), atomic-scale STM was performed to elucidate the site selectivity and electronic distribution of the surface reaction. Fig. 3a and b contain STM constant current topographies of the clean Si(111)-(7×7) surface and of the same region after butadiene monoxide exposure at room temperature. All STM images were collected at +1.2 V sample bias. The defect labeled A is used to identify the positions of other adatoms before and upon chemisorptions. Compared to the clean Si(111)-(7×7) surface (Fig. 3a), the chemisorbed molecules preserve the 7×7 reconstruction and produce depressions (highlighted with black circles in Fig. 3b), similar to Si adatom vacancies. The number of the invisible adatoms scales linearly with the molecular exposure. A similar observation was also reported for other small organic molecules chemisorbed on Si(111)-(7×7), including *N*-allylurea,¹¹ ethylene,¹² and benzene.¹³ In all these reaction systems, the adsorption features of darkened adatoms are due to the saturation of the dangling bonds arising

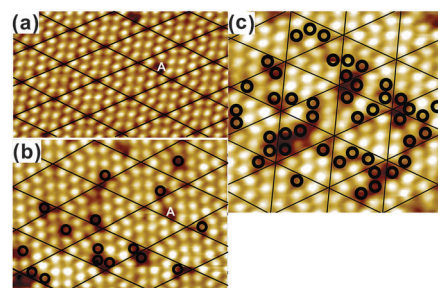


Fig. 3 Constant current STM images ($V_s = +1.2$ V) of (a) clean, (b) butadiene monoxide chemisorbed Si(111)-(7×7) at 300 K, and (c) saturated butadiene monoxide chemisorbed Si(111)-(7×7) at 300 K. The unit cells are outlined with black lines. The mark A in part a and b is used to locate the positions of other adatoms.

from new adsorbate–surface bond formation as well as lack of molecular orbitals close to the Fermi level (E_F). Furthermore, it is evident that the maximum number of reacted adatoms for each faulted or unfaulted half unit cell is three, equals to the number of adjacent adatom–rest atom pairs (Fig. 3c). Thus it is reasonable to deduce that the rest atoms are involved in binding butadiene monoxide to the Si(111)-(7×7) surface.

Statistical analysis of the STM images can provide information about the apparent reactivity difference of individual sites. In common with many other small organic molecules, the butadiene monoxide molecules do not distribute randomly over the available binding sites at low coverage, but prefer to chemisorb on the center adatom sites of faulted halves. At the exposure of 0.3 L, the STM images containing ~134 unit cells reveal that there are ~59 center adatoms and ~44 corner adatoms among the ~103 total reacted adatoms. In addition, ~68 adatom sites occupied by butadiene monoxide are situated in the faulted half while ~35 in the unfaulted half. The site preference has also been observed for several different regions on the same surface. The relative occupancies for the adatoms in faulted halves are about twice of those in the unfaulted halves. Besides, the reactivity ratio of center to corner adatoms is about 1.3. This preferential occupation of reacted sites is attributed to the higher electrophilicity of the faulted subunits.¹⁴ Meanwhile, each center adatom has two possible adjacent rest atoms, compared to only one for each corner adatom. Thus, a larger reaction probability is expected for the center adatoms.

Hence, all the information derived from the spectroscopic analysis and STM imaging suggests that each butadiene monoxide molecule binds to a neighboring adatom–rest atom pair on Si(111)-(7×7) *via* the [2+2]-like cycloaddition.

To further understand the factors controlling the selectivity and competition of surface reactions, DFT calculations were carried out to explore the energetics of all the possible surface products as well as the kinetics for each of the butadiene monoxide reaction pathways on Si(111)-(7×7). The calculated minima of the potential energy surface of the butadiene monoxide/Si₁₆H₁₈ model system based on six possible binding modes are shown in Fig. 4.

The [2+2]-like cycloaddition of butadiene monoxide on Si(111)-(7×7) *via* the C₃=C₄ bond leads to cycloadducts of modes I and II, which lie below the interaction-free reactants with 68.26 and 67.40 kcal mol⁻¹, respectively. Upon molecular binding,

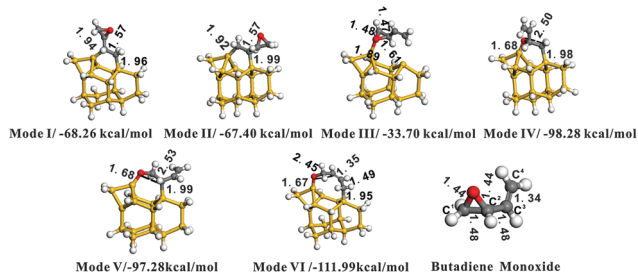


Fig. 4 Optimized structures (selected bond lengths in Å) and energies (RE in kcal mol⁻¹ compared to the interaction-free reactants) of binding configurations for C₄H₆O reacting with the Si₁₆H₁₈ model system. The optimized structure of the butadiene monoxide molecule is also presented.

the C₃–C₄ bond in mode I is elongated to 1.57 Å (also 1.57 Å in mode II), which is characteristic of a C–C single bond.¹⁵ More importantly, there is neither an intermediate nor a transition state along the reaction pathway when searching the potential energy surface. This is in line with previously calculated ethylene on Si(111)-(7×7).¹⁶ Thus, the chemisorption of butadiene monoxide on the neighboring adatom–rest atom pair of the Si(111)-(7×7) surface through the [2+2]-like C=C cycloaddition is kinetically favorable.

The adsorption of butadiene monoxide can also be initiated by forming a dative bond between the lone-pair electrons of the oxygen atom and the electron-deficient Si adatom. The dative-bonded adduct (mode III) is 33.70 kcal mol⁻¹ lower in energy than the interaction-free reactants. Notably, two C–O bonds in the dative-bonded butadiene monoxide are activated for further reaction with the surface dangling bond on the rest atoms. Accordingly, two possible pathways for the cleavage of either the C₁–O or C₂–O bond in Fig. 5 can be uncovered. In the former process involving the C₁–O bond, intramolecular rotation of the Si–O bond within the dative-bonded adduct is required to force the C₁ atom approaching the rest atom site, reducing the steric hindrance. This rotation has to climb at least a barrier of 8.54 kcal mol⁻¹ with respect to mode III to give rise to its isomer (mode III-a) with the formation energy of 25.16 kcal mol⁻¹. From mode III-a, one transition state (TS1) is identified for the ring-opening reaction pathway with an energy increase of 9.13 kcal mol⁻¹ compared to the dative-bonded adduct of mode III-a. Furthermore, the formation energy of mode IV is predicted to be 98.28 kcal mol⁻¹. In mode IV, the length of C₁–O is as large as 2.50 Å, instead of 1.44 Å in the free butadiene monoxide molecule, indicating its cleavage. The splitting C₂–O bond leads to the other ring-opening reaction product of mode V. In order to avoid the steric hindrance from the

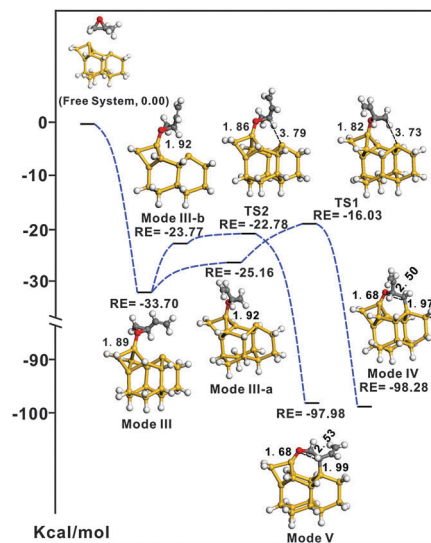


Fig. 5 Potential energy diagram for the ring-opening reaction of butadiene monoxide reacting with the Si₁₆H₁₈ model system *via* cleavage of C–O in the epoxy group (selected bond lengths in Å, and RE in kcal mol⁻¹ compared to the interaction-free reactants).

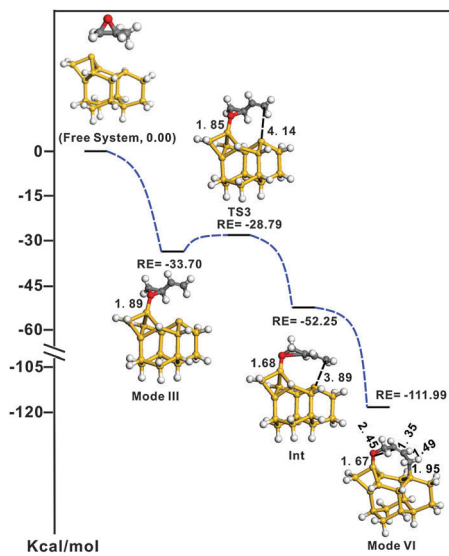


Fig. 6 Potential energy diagram for the [4+2]-like cycloaddition of butadiene monoxide reacting with the $\text{Si}_{16}\text{H}_{18}$ model system (selected bond lengths in Å, and RE in kcal mol^{-1} compared to the interaction-free reactants).

substitutive vinyl group, the first step is to rotate the $\text{C}_2\text{--C}_3$ bond from mode III to another isomer of mode III-b, which requires an activation energy of $9.93 \text{ kcal mol}^{-1}$. After surmounting the transition state (TS2), which is uphill by $0.99 \text{ kcal mol}^{-1}$, the ring-opening reaction product of mode V is thus formed, in which the $\text{C}_2\text{--O}$ bond length is enlarged to 2.53 Å and its thermal stability is increased to $97.98 \text{ kcal mol}^{-1}$ compared with the interaction-free reactants. In addition, mode III can also be the starting point for the [4+2]-like cycloaddition pathway, as shown in Fig. 6. From mode III to mode VI, one transition state (TS3) and one intermediate were identified. The conversion from mode III to the intermediate needs to overcome an activation barrier of $4.91 \text{ kcal mol}^{-1}$ at the transition state of TS3. The intermediate is $52.25 \text{ kcal mol}^{-1}$ lower in energy than the isolated reactants, and no barrier can be found for the transformation from the intermediate to the [4+2]-like cycloadduct of mode VI, which has an exothermicity of $111.99 \text{ kcal mol}^{-1}$. Compared with the bond value of 1.48 Å for $\text{C}_2\text{--C}_3$ in free butadiene monoxide, the length between C_2 and C_3 is shortened to 1.35 Å in mode VI, indicating the conversion from a single bond to a double bond upon chemisorptions. The 1.49 Å value for the $\text{C}_3\text{--C}_4$ bond length demonstrates its single-bond feature. Furthermore, the $\text{C}_2\text{--O}$ bond is broken with a separation of 2.45 Å . It is noted that the thermodynamic stability of the [4+2]-like cycloadduct is significantly higher than that of the ring-opening reaction products via breaking the $\text{C}_1/\text{C}_2\text{--O}$ bond. Moreover, the [4+2]-like cycloaddition pathway requires lower activation energy than that for intramolecular isomerization from mode III to mode III-a/mode III-b,

indicating that the [4+2]-like cycloaddition is also kinetically more favorable compared with the ring-opening reaction.

The surface reactions on silicon surfaces are often kinetically controlled and the reaction pathway producing the most thermodynamically stable product may be kinetically less favorable. Although the [4+2]-like cycloadduct (mode VI) is more thermodynamically stable than the [2+2]-like cycloadducts (modes I and II), the energy barrier of the overall route for the former is $4.91 \text{ kcal mol}^{-1}$ higher than that of the latter as the [2+2]-like cycloaddition pathway via the $\text{C}_3\text{=C}_4$ bond is barrierless. Thus, we conclude that the chemisorption of butadiene monoxide on the $\text{Si}(111)\text{--}(7\times 7)$ surface prefers to react through the [2+2]-like cycloaddition between the $\text{C}_3\text{=C}_4$ bond and the adjacent adatom-rest atom pair, in accordance with the HREELS and STM results.

In conclusion, butadiene monoxide undergoes [2+2]-like cycloaddition through a vinyl group on $\text{Si}(111)\text{--}(7\times 7)$ at room temperature, producing a modified Si surface with the cyclic epoxy group which may act as an intermediate for the fabrication of supramolecular structures or multilayer organic thin films. The vinyl substituent group plays a major role in determining the reaction pathway for molecules with multifunctional groups, further leading to the desired selectivity in organic functionalized silicon surfaces.

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