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Regioselective Cycloaddition Reaction of Alkene Molecules with the Asymmetric Dimer on Si(100)*c*(4×2)

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Abstract: We investigated the adsorption states of 2-methylpropene and propene on Si(100)*c*(4×2) using low-temperature scanning tunneling microscopy. We have found that regioselective cycloaddition reactions (di-σ bond formation) occur between the asymmetric alkene molecules and the asymmetric dimers on Si(100)*c*(4×2). First-principles calculations have elucidated that the regioselectivity is closely related to the structures of precursor species and these precursor species have carbocation-like features. Thus, we conclude that Markovnikov's rule is applicable for the cycloaddition of asymmetric alkene with the asymmetric dimer on Si(100)*c*(4×2).

Introduction

Potential applications enabled by the chemical modification of Si surfaces include coatings, sensors, molecule-based microelectronics, and so forth.[1] The cycloaddition reaction of unsaturated organic molecules with the Si(100) surface is the most important family of chemical reactions for the modification of Si surfaces as well as the Lewis acid−base reaction,[2−5] because stable SiC covalent bonds are formed between molecules and the surface. In the cycloaddition, the asymmetric dimer on the reconstructed Si(100) surface plays an important role, in which a partial charge transfer occurs from a down dimer atom (Sd) to an up dimer atom (Su).[6] Thus, the chemical nature of Sd and Su is electrophilic and nucleophilic, respectively;[3−5] in other words, the asymmetric dimer may act as a zwitterion.

In organic chemistry, the regioselective addition reaction of asymmetric alkene with an ionic molecule like hydrogen halide (HX) is known as "Markovnikov's rule".[7] This reaction undergoes two steps including a carbocation intermediate; first, an electrophilic H^+ reacts with one of the sp^2 carbon atoms that has fewer alkyl substituents, and subsequently a nucleophilic X^- reacts with the other carbon atom. The regioselective product is controlled by the stability of the carbocation intermediate species.[7]

Recently, we found that the cycloaddition reaction of ethylene with the dimer occurs via a π complex precursor state, where π electrons of ethylene are weakly donated to the Sd site.[8] Here, assuming that the cycloaddition from the π complex precursor state to the di-σ chemisorbed species occurs via a carbocation-like intermediate,[9] an asymmetric alkene molecule would show a regioselective cycloaddition to the asymmetric dimer.

In this study, we investigated the adsorption states of 2-methylpropene and propene on Si(100)*c*(4×2) using low-temperature scanning tunneling microscopy (STM) to elucidate the regioselectivity of these molecules on Si(100)*c*(4×2): the cycloaddition reaction with the zwitterion-like asymmetric dimer on Si(100). High-resolution electron energy loss spectroscopy (HREELS) was also used to elucidate the adsorption states. First-principles calculations were performed to interpret the STM images and understand the reaction mechanism in detail.

Experimental and Theoretical Methods

Experiments were carried out in an ultrahigh vacuum system. The Si(100) samples were cut from Si wafers (n-type, 0.005−0.018 Ω cm for STM; p-type, 3−5 Ω cm for HREELS). The clean (100) surface was prepared by flashing the sample to 1500 K under ultrahigh vacuum with a base pressure below 1.2×10^{-8} Pa. The sample was cooled at 80 K using liquid nitrogen. 2-Methylpropene and propene were purified by freeze−pump−thaw cycles. Gaseous molecules were introduced to the vacuum chamber through a pulse gas dosing system. STM measurements were carried out at 80 K using a JEOL SPM-4500A. For HREELS measurements, an energy resolution of 16 cm^{-1} (direct mode) and an incidence angle of 60° with respect to the surface normal were used.[8]

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(1) (a) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413. (b) Buriak, J. *Chem. Rev.* **2002**, *102*, 1271.

(2) Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *J. Chem. Phys.* **1987**, *87*, 7332.

(3) Hamers, R. J.; et al. *Acc. Chem. Res.* **2000**, *33*, 617.

(4) Filler, M. A.; Bent, S. F. *Prog. Surf. Sci.* **2003**, *73*, 1.

(5) Yoshinobu, J. *Prog. Surf. Sci.* **2004**, *77*, 37.

(6) Chadi, D. J. *Phys. Rev. Lett.* **1979**, *43*, 43.

(7) (a) Solomons, T. W. G. *Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1988. (b) McMurry, J. *Organic Chemistry*, 4th ed.; Brooks/Cole Pub Co.: 1996.

(8) Nagao, M.; Umeyama, H.; Mukai, K.; Yamashita, Y.; Yoshinobu, J.; Akagi, K.; Tsuneyuki, S. *J. Am. Chem. Soc.* **2004**, *126*, 9922.

(9) Yoshinobu, J.; Yamashita, Y.; Yasui, F.; Mukai, K.; Akagi, K.; Tsuneyuki, S.; Hamaguchi, K.; Machida, S.; Nagao, M.; Sato, T.; Iwatsuki, M. *J. Electron Specrosc. Relat. Phenom.* **2001**, *114*/*115*, 383.

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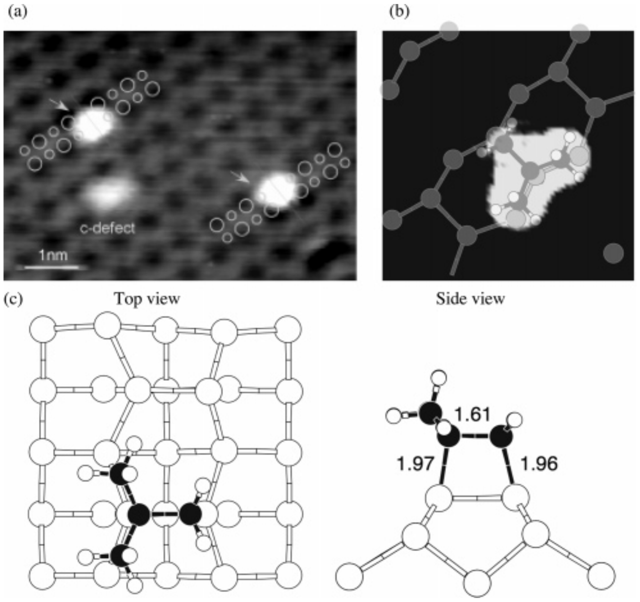

Figure 1. (a) An STM image of 2-methylpropene molecules on Si(100)-$c(4\times2)$ at 80 K. The large and small open circles represent Su and Sd sites of the asymmetric dimer, respectively. $V_s = 2.0$ V, $I_t = 0.085$ nA. (b) A contour map of the integrated LDOS on a plane parallel to the surface ($V_s = 2.3$ V, $z = 11.0$ Å). The topmost hydrogen atoms of the system locate at $z = 10.0$ Å. The gray-scale map is properly adjusted to sharpen the shape of the image. (c) A structure model of adsorbed 2-methylpropene on Si(100)$c(4\times2)$. The calculated adsorption energy is 1.75 eV. The large and small open circles represent silicon and hydrogen, respectively. The filled circle represents carbon. The CC and two SiC bond lengths are shown in angstroms.

Total energy calculations and structure optimizations were performed based on the density functional theory (DFT).[10] A plane wave basis set with 36.0 Ry cutoff energy, exchange-correlation functional with GGA (PBE96), and pseudo-potential approach (Troullier−Martins norm-conserving type for Si atoms, Vanderbilt's ultrasoft type for H and C atoms) were adopted.[11−13] The size of the unit cell was 10.91 Å × 10.91 Å × 15.43 Å. A repeated slab model of Si(100)$\sqrt{8}\times\sqrt{8}$ of six layers thick was used to describe the surface, and cluster model calculations were performed using a super-cell of the same size for the slab model. One sampling *k*-point in the first Brillouin zone (Γ point only) was used for cluster models, and four sampling *k*-points ($2 \times 2 \times 1$) were used for slab models, respectively.

Results and Discussion

Figure 1a shows an unoccupied-state STM image of the 2-methylpropene adsorbed Si(100)$c(4\times2)$ surface. The protrusions on the Si(100)$c(4\times2)$ "bare" surface correspond to Sd sites in the unoccupied state STM image;[5,6] the large and small open circles represent the positions of the Su and Sd, respectively. The bright protrusions indicated by arrows originate from adsorbed 2-methylpropene molecules. Note that very few C-defects (less than a few %) are observed due to the adsorption of water from the residual gases, but they can be discriminated from the adsorbed organic molecules by STM.[14,15] The protrusions of adsorbed 2-methylpropene are obtuse triangle-shaped, and the center of the triangle-shaped protrusion is located at the Su position. One of the three corners of the triangle-shaped protrusion points in the dimer bond direction. By inspection of many protrusions, we have confirmed that more than 96% of the adsorbed 2-methylpropene molecules show the same configuration as shown in Figure 1a. The remaining 4% were not clearly identified.

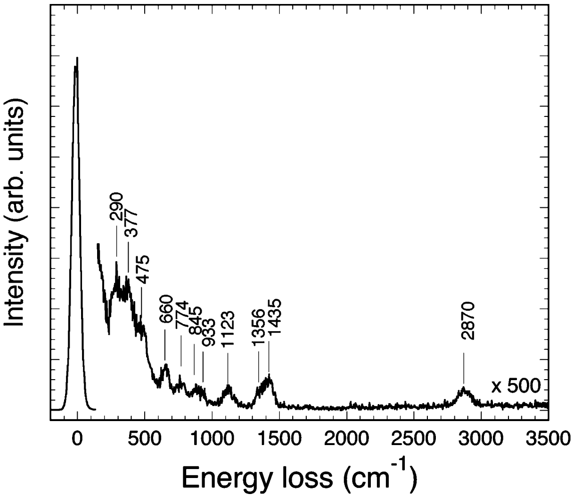

Figure 2. An EELS spectrum of 2-methylpropene on Si(100)$c(4\times2)$ at 90 K (a submonolayer coverage: ~0.1 ML). $E_p = 5.0$ eV.

Table 1. Assignments of Observed Loss Peaks of 2-Methylpropene on Si(100)$c(4\times2)$ at 90 K As Shown in Figure 2[a]

observed peak (cm^{-1})	mode
290	Si surface phonon
377	Si surface phonon
475	Si surface phonon
660	$\nu_{\mathrm{Si-C}}$
774	hindered motion
~900 (845, 933)	$\nu_{\mathrm{C-C}}$, CH_3 deform, CH_2 twist
1123	$\nu_{\mathrm{C-C}}$
1356	CH_2 scissors
1435	CH_3 deform
2870	ν_{CH} (sp^3)

[a] The assignments are based on empirical database[5,16,17] and the present first-principles calculations.

Most alkene molecules form a di-σ bond with the dimer on Si(100) (cycloaddition).[2−5] We elucidated that 2-methylpropene was molecularly di-σ bonded to the Si(100) surface at 90 K based on HREELS results. Figure 2 shows an EELS spectrum of 2-methylpropene on Si(100)$c(4\times2)$ at 90 K. The assignment of observed peaks is summarized in Table 1. The CH stretching mode observed at 2870 cm^{-1} indicates that the hybridization state of the adsorbed species is sp^3.[16,17] Note that the CH_2 (sp^2) stretching mode and the C═C stretching mode of free 2-methylpropene are observed at 3086−2989 and 1661 cm^{-1}, respectively.[17] In the case of π-bonded ethylene on Si(100)-$c(4\times2)$ at 48 K, the CH_2 stretching mode and the C═C stretching mode were observed at 3051 and 1522 cm^{-1}, respectively.[8] However, in the present case, no sp^2-related feature is observed. In addition, a Si−H stretching mode is hardly observed at ~2100 cm^{-1}, which indicates that CH bond scission does not occur. These results indicate that 2-methyl-

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(10) Tsukada, M.; et al. Computer program package TAPP, University of Tokyo, Tokyo, Japan, 1983−2006. Yamauchi, J.; Tsukada, M.; Watanabe, S.; Sugino, O. *Phys. Rev. B* **1996**, *54*, 5586.
(11) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(12) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.
(13) Vanderbilt, D. *Phys. Rev. B* **1990**, *41*, 7892.
(14) Hamers, R. J.; Köhler, U. K. *J. Vac. Sci. Technol., A* **1989**, *7*, 2854.
(15) Hossain, M. Z.; Yamashita, Y.; Mukai, K.; Yoshinobu, J. *Phys. Rev. B* **2003**, *67*, 153307.
(16) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975.
(17) Shimanouchi, T. *Tables of molecular vibrational frequencies; Consolidated Vol. I*; NSRDS-NBS 39, 1972.

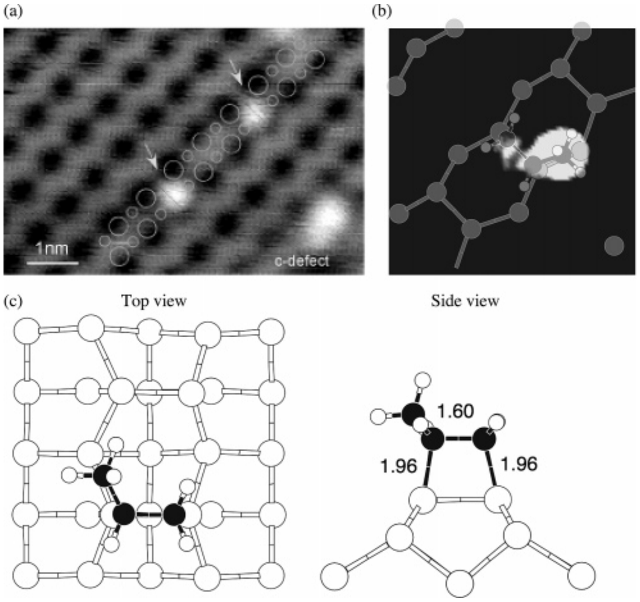

Figure 3. (a) An STM image of propene molecules on Si(100)$c(4\times2)$ at 80 K. Thin solid lines are indicated on the dimer bond direction. $V_s = 2.0$ V, $I_t = 0.085$ nA. (b) A contour map of the integrated LDOS on a plane parallel to the surface ($V_s = 2.3$ V, $z = 11.0$ Å). The topmost hydrogen atom of the system locates at $z = 10.0$ Å. The gray-scale map is properly adjusted to sharpen the shape of the image. (c) A structure model of adsorbed propene on Si(100)$c(4\times2)$. The calculated adsorption energy is 1.90 eV. The large and small open circles represent silicon and hydrogen, respectively. The filled circle represents carbon.

propene is di-σ bonded to the surface without CH dissociation. Thus, we conclude that the observed protrusions in STM images are assigned to chemisorbed 2-methylpropene molecules.

Figure 3a shows an unoccupied-state STM image of the propene adsorbed Si(100)$c(4\times2)$ surface. The bright protrusions indicated by arrows originate from adsorbed propene molecules. Note that Lopinsky et al. reported STM images of propene on Si(100)(2 × 1) at room temperature.[18] In the present STM images, the protrusions are located at the Su side, but they are slightly shifted from the centerline on the dimer bond direction (thin solid lines in Figure 3). By inspection of many protrusions in STM images, we found that more than 95% of adsorbed propene molecules show the same configuration as that in Figure 3a. Note that the slight shift from the centerline to the opposite direction occurs with the same probability (50%).

Previous STM studies attribute the bright protrusions to methyl groups in chemisorbed organic molecules on Si(100).[18−20] This interpretation is confirmed by first-principles simulation of STM images in Figures 1b and 3b, which are calculated from local density of states (LDOS) of theoretically optimized adsorption structures in Figures 1c and 3c, respectively. Because the observed protrusions are always located on the Su side in the present systems, we conclude that the alkene carbon atom having methyl group(s) is selectively bonded to the nucleophilic Su site, while the other carbon atom with two hydrogen atoms is bonded to the electrophilic Sd site.

Such selectivity in the cycloaddition reactions of 2-methylpropene and propene reminds us of Markovnikov’s rule in the addition reactions of hydrogen halides with alkenes in organic chemistry. The modern statement of Markovnikov’s rule is that “the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield more stable carbocation as an intermediate.”[7] On the other hand, recent experimental and theoretical studies have clarified that cycloaddition reaction of some kinds of alkene molecules to the asymmetric dimer on the Si(100) surface proceeds via formation of a π-complex precursor state weakly bonded to the Sd site.[8,21,22] If such precursor states exist in the present systems, and if the states are carbocation-like, we can conclude that Markovnikov’s rule also holds for the present surface reaction.

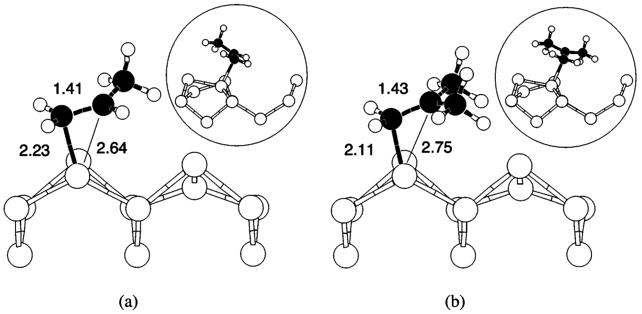

Figure 4. Side views of calculated precursor states of (a) propene and (b) 2-methylpropene on a Si(100) $\sqrt{8}\times\sqrt{8}$ clean surface. Corresponding front views are shown in the circles. These molecules are weakly bonded to the Sd site of the asymmetric dimer. The calculated adsorption energies are 0.50 eV for propene and 0.58 eV for 2-methylpropene. The large and small open circles represent silicon and hydrogen atoms, respectively. The filled circles represent carbon atoms. The CC and two SiC “bond” lengths are shown in angstroms in each figure.

First, to confirm the former part of the above assumption (precursor-mediated reaction), we searched for an adsorption structure other than the final di-σ state for 2-methylpropene and propene by first-principles calculations. After the structure optimization process starting from various initial configurations with different orientations at the Sd site on Si(100), several stable structures were obtained; all of them share some characteristic of a π-complex precursor state. Furthermore, we also found that the end carbon atoms without methyl groups are always closer to the Si atom at the Sd site as compared to the center carbon atoms with methyl group(s) in any case. Typical structures obtained by the calculation are shown in Figure 4a and b. This asymmetric property of the SiC bonds strongly suggests that such precursor states play an important role in the regioselective cycloaddition reactions.

Second, to check that these precursor states have carbocation-like properties, we compared their structures with an ideal carbocation intermediate in Markovnikov’s rule. In a free 2-methylpropene molecule, the C═C double bond length is calculated to be 1.36 Å. By the addition reaction of one H^+ to the end carbon atom, the C═C double bond is elongated to 1.49 Å due to π electron donation, but it is still much shorter than the normal C−C single bond (1.56 Å) in 2-methylpropane. At the same time, the remaining C−C single bonds are shortened from 1.53 to 1.49 Å because of the electron resonance effect. Such change in the bond lengths is a typical feature of a carbocation, which plays a central role in Makovnikov’s rule. On the other hand, in the case of the precursor state of 2-methyl-

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(18) Lopinski, G. P.; Moffatt, D. J.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **1998**, *392*, 909.
(19) Hossain, M. Z.; Machida, S.; Yamashita, Y.; Mukai, K.; Yoshinobu, J. *J. Am. Chem. Soc.* **2003**, *125*, 9252.
(20) Hossain, M. Z.; Machida, S.; Yamashita, Y.; Mukai, K.; Yoshinobu, J. *J. Phys. Chem. B* **2004**, *108*, 4737.
(21) Cho, J. H.; Kleinman, L. *Phys. Rev. B* **2003**, *68*, 245314.
(22) Lu, X. *J. Am. Chem. Soc.* **2003**, *125*, 6384.

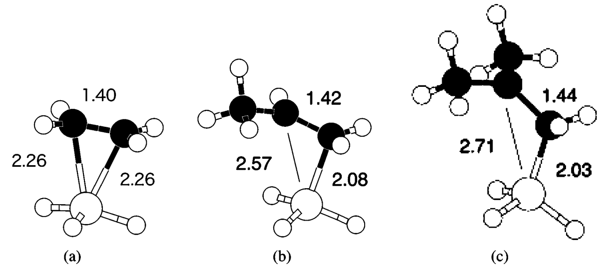

Figure 5. Calculated structures of (a) ethylene, (b) propene, and (c) 2-methylpropene interacting with a SiH_3^+ cluster. The large and small open circles represent silicon and hydrogen atoms, respectively. The filled circles represent carbon atoms. The CC and two SiC "bond" lengths are shown in angstroms in each figure.

propene on the surface, the C═C double bond is elongated to 1.43 Å, while the other C−C bonds in the molecule are slightly shortened from 1.53 to 1.51 Å. The same tendency is found in the case of propene, too. In addition, the end carbon atoms without methyl groups in Figure 4a and b show sp^3-like geometrical features; on the other hand, the carbon atoms with methyl groups have sp^2-like geometrical features. In fact, we have obtained differential charge distributions showing that the electron density at the carbon atom with methyl group(s) decreases by interacting with Sd site. Thus, these results indicate that Markovnikov's rule works even in the present surface reaction.

Finally, we discuss the steric hindrance effect as a result of the presence of a surface. One of the differences between conventional gas/liquid phase and surface reactions is that steric hindrance is often more important in the latter. Here, we theoretically investigated the structures of "alkene + $(SiH_3)^+$". This is the simplest model of the precursor states on the Sd site that has an unoccupied orbital, and at the same time, SiH_3^+ plays a role of H^+ (electrophilic reagent) in Markovnikov's rule. As shown in Figure 5a, an $(\text{ethylene}+SiH_3)^+$ cluster has two weak SiC bonds of the same length (2.26 Å). On the other hand, in the cases of propene and 2-methylpropene, the SiC bond between the Si part and the carbon atom without methyl groups becomes obviously shorter than the other SiC "bond" (Figure 5b and c). This is the same feature as the precursor on a surface (Figure 4a and b). We also confirmed that the final structures as shown in Figure 5 do not depend on initial configurations. Because there is no steric hindrance from the surface in these cluster models, we conclude that the asymmetry of SiC "bonds" is purely caused by the electronic effect.

Summary

In summary, we have found that regioselective cycloaddition reactions occur between the asymmetric alkene molecules (propene and 2-methylpropene) and the asymmetric dimer on Si(100)*c*(4×2). First-principles calculations show that the carbocation-like precursor states play an important role in these reactions. The regioselectivity of these reactions can be explained by the asymmetric structure of the precursor states. Thus, Markovnikov's rule is applicable for the cycloaddition of asymmetric alkene molecules to the asymmetric dimer on Si(100)*c*(4×2).

Acknowledgment. Financial support was provided in part by a Grant-in-Aid for Scientific Research on Creative Research B and Priority Areas "Electron Transport of Nano-link Molecules" from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan and also by CREST (JST). K.O. is supported by the program "The 21st Century COE Program for Applied Physics on Strong Correlation" at the University of Tokyo.

JA066285I