Surface Chemistry

Kinetic and Thermodynamic Control by Chemical Bond Rearrangement on a Si(001) Surface

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The (2×1)-reconstructed Si(001) surface, where the surface lattice structure undergoes a reconstruction in which adjacent silicon dimers pair together and form dimers through a σ bond and a π bond,[1] is intriguing in that the chemistry at the surface is frequently analogous to that in organic chemistry owing to its covalent nature. Alkenes, for example, are known to bind to silicon dimers on the Si(001) surface to produce four-member ring analogs in a similar way to [2+2] cycloaddition reactions in organic synthesis.[2] The mechanisms of cycloadditions on the surface have also been argued in terms of orbital symmetry in a similar fashion to organic chemistry.[3] However, it seems likely that adsorbate formation and organic synthesis are different in that it is usually difficult to control the product distributions of surface species on the Si(001) surface, that is, the relative efficiencies of specific reactions to side reactions, by changing reaction temperature. The selectivity of reactions has previously been discussed for the adsorption of 1,3-cyclohexadiene,[4] 2,3-dimethyl-1,3-butadiene,[5] and unsaturated ketones[6] on the Si(001) and Ge(001) surfaces. Those studies have investigated whether the degree of selectivity is determined by thermodynamic or by kinetic factors. However, the conversion from kinetically controlled reactions into thermodynamically controlled ones for the same organic compound by means of heating has not been observed on the Si(001) surface to date. This may be because the binding of organic molecules to the silicon surface is usually strong, which makes reactions irreversible.

Herein we report that the driving force that determines the product distribution for acetone adsorbed on the Si(001) surface can be changed from kinetic to thermodynamic by reversible binding upon raising the surface temperature. The results presented are of interest not only because controlling the degree of selectivity is of importance for future applications of organic-functionalized semiconductors, but also because it is found that the binding of organic molecules to the Si(001) surface is in fact reversible.

Figure 1 depicts two bonding configurations of a four-member-ring and a dissociation species which are produced when the acetone molecules are adsorbed on the Si(001) surface.[7] The relative efficiencies of the two reactions shown in Figure 1 were investigated using scanning tunneling microscopy (STM) in the surface temperature range from 340 K to 440 K (Figure 2a and b). Two separate features labeled A and B are visible in Figure 2, although their ratio differs between the images (see below). The A-type feature is a protrusion which appears to be centered above a silicon dimer. The B-type feature has a protrusion and a depression on a silicon dimer. It is suggested that these two features can be attributed to the four-member-ring and the dissociation species depicted

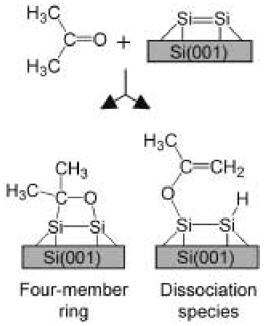

Figure 1. Reactions of acetone with the Si(001) surface. The molecules are bound to the surface to give a mixture of the four-member-ring and dissociation species.[7]

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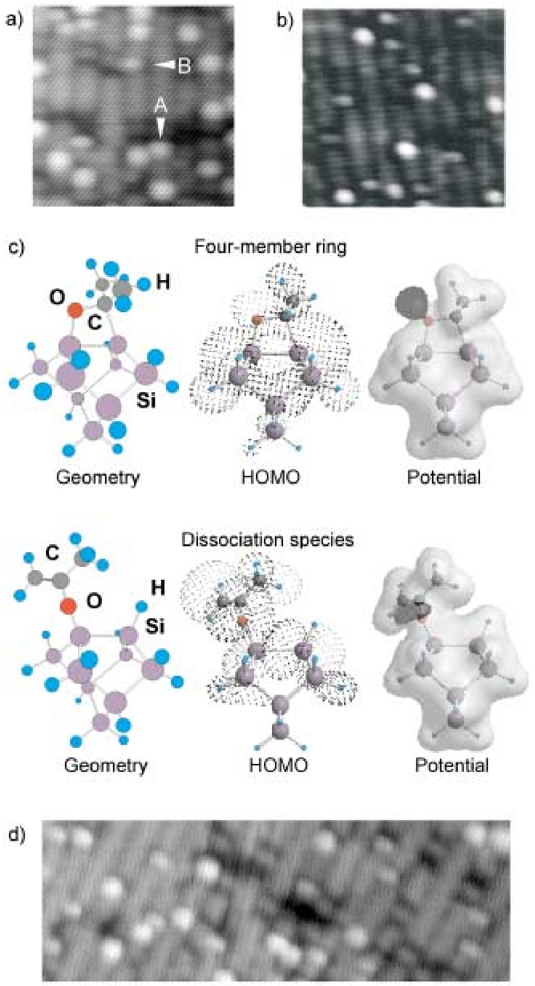

Figure 2. a), b) STM images obtained by exposing Si(001) samples at a) 365 K and b) 440 K to 0.3 L of acetone. The images were acquired with a tunneling current of 0.10 nA and a sample bias of −3.0 V. c) Optimized geometries, probability amplitudes of the HOMO, and electrostatic potentials. Gray and black surfaces for the electrostatic potentials show a difference in plus and minus signs for differential of the potentials. d) STM image obtained after annealing the sample at 420 K.

in Figure 1. Although the images in Figure 2a and b were taken with a sample bias of −3.0 V, it was found that the A-type and B-type features also had similar appearances at a sample bias of −2.0 V. With a sample bias of −2 V, the H−Si bond is imaged more darkly than intact silicon dimers on the Si(001) surfaces.[8] Therefore, it is expected that the dark image in the B-type features can be attributed to the Si−H group in the dissociation species. The A-type features can then be ascribed to the four-member ring.

STM images reflect the local density of states which exist near the Fermi level and tunneling barrier of a sample surface.[9] Therefore, the highest occupied molecular orbital (HOMO) and the electrostatic potentials were calculated using density functional theory (DFT) for the acetone molecules bound to the [Si_9H_{12}] clusters shown in Figure 2c. This procedure was used to confirm the assignment of the A-type and B-type features which were observed in the filled-state images at negative sample biases. Figure 2c shows the optimized geometries, the probability amplitudes of the HOMO, and the electrostatic potentials calculated for the two surface species. The contour surfaces of the HOMO and the electrostatic potential for the four-member ring protrude over the adsorption site, which is in good agreement with the STM images of the A-type features where a protrusion is observed on a silicon dimer. On the other hand, the Si−H group in the dissociation species has a reduced HOMO density and an electrostatic potential which is lower than those for the entire four-member ring and for the vinyl ether group in the dissociation species (Figure 2c), which is in good agreement with the STM images of the B-type features where dark and bright halves are observed on a silicon dimer (Figure 2a, b). Comparison with previous STM studies on the hydrogen-atom-terminated Si(001) surface[8] and calculations of the HOMO and the electrostatic potential both support the idea that the A-type and B-type features are associated with the four-member-ring and the dissociation species, respectively.

In the images in Figure 2a and b, it can be seen that adsorption at 365 K produces predominantly in the four-member-ring species and adsorption at 440 K predominantly the dissociation species. To elucidate the connection between the product distribution and the reaction temperature, the product ratios were examined for Si(001) samples exposed to the compound at 340, 365, 380, 400, and 440 K. Figure 3a shows the distributions of the observed surface species, that is, the ratios of the four-member-ring: the dissociation species: the unidentified species. The relative efficiency of the dissociation reaction is enhanced when the reaction temperature is raised.

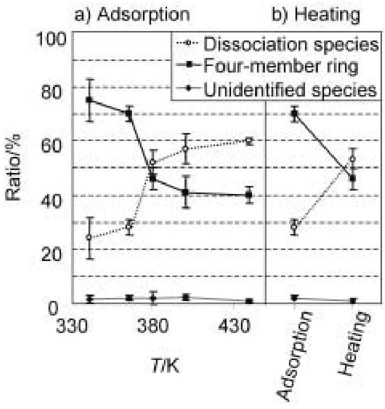

Figure 3. Product distributions of the four-member-ring, the dissociation species, and the unidentified species. The data were obtained by counting 440–1010 adsorbates in the STM images. a) The distributions for the Si(001) samples exposed to 0.3 L of acetone at various temperatures. b) The distributions for the Si(001) sample exposed to acetone at 365 K (left, adsorption) and subsequently annealed to 420 K (right, heating).

The surface species formed on the Si(001) surface were annealed to see whether the reactions were reversible. Figure 2d shows an image which was obtained by heating the Si(001) sample at 420 K for 90 s after it had been exposed to 0.3 L (1.0×10^{-8} Torr·30 s) of acetone at 365 K. Comparing the image in Figure 2d with that in Figure 2a, it can be seen that annealing to 420 K leads to an increase in the dissociation species. Figure 3b shows the product distribution before and after annealing to 420 K. The counting statistics show that successive heating at 420 K varies the ratio of dissociation species:four-member ring from 28:70 to 46:53, which reveals that the acetone molecules bound to the surface undergo changes upon subsequent heating. This result indicates that the reactions are reversible. Additionally, the STM images show that annealing at 420 K does not significantly alter the total coverage of the molecules. Exposing the Si(001) sample at 365 K to acetone resulted in coverages of 0.08 and 0.02 molecules per dimer for the four-member ring and the dissociation species, respectively, while subsequent heating at 420 K resulted in coverages of 0.04 and 0.06 molecules per dimer for the four-member ring and the dissociation species, respectively. The successive heating therefore appears not to decrease the sum of the coverages, which suggests that desorption of the molecules does not occur upon annealing.

To understand the energetics of the adsorption, the DFT calculations were carried out using the [Si_9H_{12}] cluster models. The calculations predict that the adsorption energies of the four-member-ring and the dissociation species are 34.6 kcal mol^{-1} and 43.1 kcal mol^{-1}, respectively. The results of the calculations which show that the cycloaddition species is less stable than the dissociation species can be explained by the formation of a strained four-member ring in the cycloaddition reaction. Based on the experimental and computational data, it seems that the major surface species is changed from an energetically unfavorable species to an energetically favorable one when the reaction temperature is increased.

Since the experimental data suggest that the reactions are reversible, it is possible to consider that the adsorption is kinetically controlled at a low temperature and thermodynamically controlled at a high temperature. Kinetic control preferentially provides the less stable species, that is, the four-member ring at low temperature, if the activation energy for the cycloaddition is smaller than that for the dissociation. On the other hand, thermodynamic control gives rise to the dissociation species in preference to the four-member-ring species at high temperature, if the activation energy for the reverse reaction of dissociation is larger than that for the reverse reaction of cycloaddition. Because the STM images show that the desorption of the surface species does not explain the temperature dependence of the product distribution, it is expected that the conversion between the four-member ring and the dissociation species takes place via intermediates which are weakly bound to the surface (Figure 4). It seems that the rearrangement of chemical bonds via the intermediate on the surface enables competition between the kinetic and thermodynamic dominance. Using DFT calculations, it has recently been proposed that carbonyl compounds react with the Si(001) surface via a precursor in which the carbonyl oxygen center binds to the surface silicon atom through a dative bond.[10] Thus, the studies presented herein imply that the precursor, theoretically predicted in the recent reports, connects the cycloaddition reaction with the dissociation reaction on the potential energy surface.

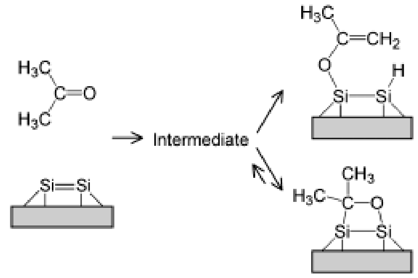

Figure 4. Adsorption mechanism. Conversion between the four-member rings and the dissociation species via intermediate formation accounts for the reversible binding.

In conclusion, we have found evidence that it is possible to control the product distribution on the Si(001) surface by changing the determinant factor from kinetic to thermodynamic control, which is a result of the reversible binding of the surface species. These results suggest approaches for future applications to increase the degree of selectivity in the attachment of organic molecules to the Si(001) surface.

Experimental Section

All experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure of 5×10^{-11} Torr. Clean Si(001) surfaces (1–10 ohm cm resistivity, B-doped) were prepared by a published method.[11]. Acetone (Aldrich, 99.9+ % purity) was subjected to several freeze–pump–thaw cycles prior to introduction into the UHV chamber. The temperatures of the samples were measured with an infrared optical pyrometer, followed by calibration using a thermocouple attached to an identical test sample. Exposures are expressed in Langmuir units (1 L = 1×10^{-6} Torr s). The DFT calculations were performed for the acetone molecules bound to the [Si_9H_{12}] clusters which have one exposed silicon dimer, using Gaussian 98 (B3LYP hybrid DFT method and 6-31 + G(d) basis sets).[12]

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