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Chemisorption

Visualization of Complex-Anion Site Conversion on a Metal Oxide Surface[**]

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Molecular adsorption on a metal oxide surface differs fundamentally from that on a metal surface because complex-anion formation is a potential outcome. These species are technologically important. For example, they are likely to be involved when sulfur dioxide is removed from a gas stream by sorption onto a dispersed oxide. Despite the importance of such processes, there is still relatively little understanding of molecular adsorption on metal oxides at the microscopic level. One of the best studied adsorption systems in which complex anions are involved is SO_2 on the model oxide substrate $TiO_2(110)1\times1$.[1] This system has been examined experimentally with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy[2] and photoemission spectroscopy.[3–6] Density functional theory (DFT) calculations have also been used to provide insight into the important factors influencing complex-anion formation.[6–8] The spectroscopic results indicate the formation of SO_3^{2-} (sulfite) and SO_4^{2-} (sulfate) like species above 120 K, the relative concentrations of which are dependent on the temperature of the substrate.[3] The DFT results point to the pivotal role of oxygen vacancies in stabilizing both sulfite and sulfate adsorbates. Herein, we use variable-temperature scanning tunneling microscopy (STM) to follow the reaction of SO_2 with $TiO_2(110)$ between 120 and 420 K. We image a new phenomenon, namely, conversion of the complex-anion site. This conversion appears to be driven by stabilization of the adsorbates by the oxygen vacancies at elevated temperatures and is consistent with theoretical predictions.[7]

Figure 1 a shows an STM image of $TiO_2(110)$ at 120 K prior to exposure to SO_2. The bright rows, which lie in the [001] substrate azimuth, arise from tunneling into fivefold-coordinated Ti atoms.[1] Figure 1 b shows part of the same area of the surface following exposure to 0.2 L (1 langmuir $= 1.32\times10^{-6}$ mbar s) SO_2. A number of small, bright features randomly distributed over the substrate terraces appear, three appearing in the area imaged in Figure 1 b. These features are ascribed to sulfite species on the basis of the spectroscopic data[3,5] and are imaged close to the Ti rows.

Bridging oxygen vacancies were recently shown to play an important part in the reaction of H_2O with $TiO_2(110)$.[9,10] Defects on other oxide surfaces, such as MgO(001),[11] were

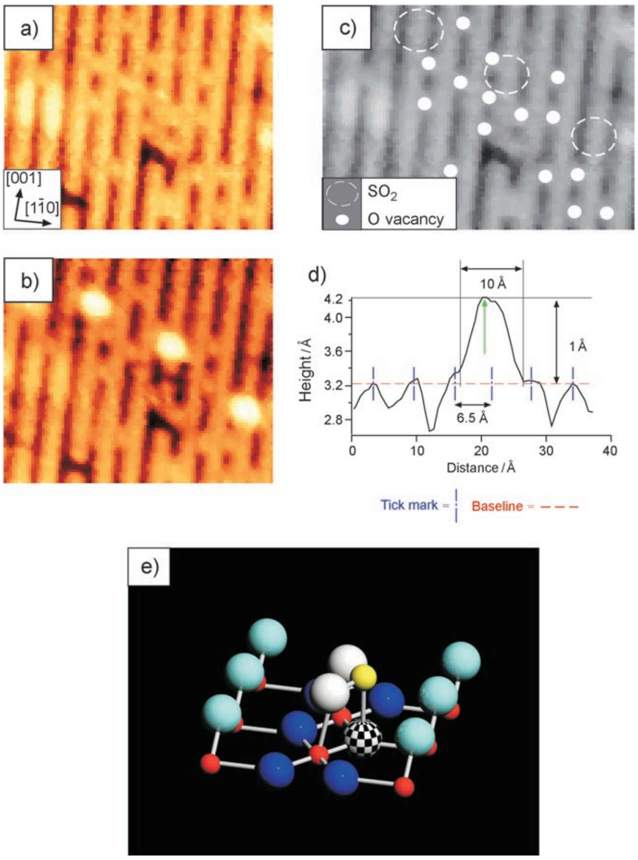

Figure 1. STM images (1.55 V, 1 nA) of $TiO_2(110)1\times1$ at 120 K: a) 110×90 Å^2 image of the surface prior to SO_2 dose. Bridging oxygen vacancies are visible as bright spots in the dark rows. b) The same area following exposure to 0.2 L SO_2 at 120 K, showing three adsorbate-induced features. c) Image (a) with defect positions marked (filled circles) and the adsorbate positions from image (b) superimposed (dashed circles). d) Line profile over an adsorbate. The tick marks over the baseline represent the positions of the fivefold-coordinated-Ti rows (bright). The green arrow indicates the position of the adsorbate. e) Side view of a sulfite geometry predicted to be stable on a perfect surface. Red spheres: Ti; dark-blue spheres: in-plane O atoms; turquoise spheres: bridging O atoms; checkered sphere: complex-anion O atom that occupies a position close to that of O atoms on the perfect clean substrate; white sphere: sulfite O atoms; yellow sphere: sulfur atom. The surface unit cell dimensions are 3.0×6.5 Å^2; the shorter dimension is in the [001] direction, corresponding to the rows of fivefold-coordinated Ti atoms.

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also shown to play an important role in bonding adsorbed species. On $TiO_2(110)$, oxygen vacancies are known to have a typical concentration of about 5% ML (1 monolayer (ML) corresponds to the number of surface unit cells) when $TiO_2(110)$ is prepared in ultrahigh vacuum.[1] At room temperature, water dissociates in the vacancies to produce two bridging hydroxyl species that are typically separated by about 6 Å, or two lattice spacings along the [001] azimuth. This process is activated and does not occur at 120 K.[12] As we will show below, this temperature dependence of vacancy interaction is mirrored by SO_2.

To investigate the influence of O vacancies on the adsorption process, we looked in more detail at the STM images recorded from the same area before (Figure 1 a) and after (Figure 1 b) adsorption. The positions of the bridging oxygen vacancy defects appear as bright spots in the dark rows.[1] Exposure of the surface to 0.2 L SO_2 at 120 K produces three new features that we ascribe to SO_3^{2-}. Figure 1 c is a schematic representation of the molecular adsorbate positions relative to the oxygen vacancies. The three adsorbates (hollow dashed circles) are separated from the nearest O-vacancy positions (highlighted by filled white circles) by between 5 and 10 Å. This separation tends to rule out a significant interaction between the adsorbate and the vacancies at 120 K, because a more uniform separation would be expected if there were such an interaction.

A line profile measured perpendicular to the Ti rows and over a single sulfite adsorbate (Figure 1 d) indicates that sulfite has an apparent height of 1 Å above the Ti rows. The diameter is about 10 Å, a value that will be dominated by tip convolution effects. Consecutive images reveal that the adsorbate is immobile at this temperature. Because a spherical feature is imaged in STM, tunneling is most likely into orbitals associated with the S atom. On this basis, the line profile in Figure 1 d indicates that the S atom, which corresponds to the position of the peak maximum associated with the adsorbate (indicated by a green arrow in the line profile), is laterally displaced along $[1\bar{1}0]$ by about 1 Å with respect to the Ti row.

DFT calculations predict a stable SO_3^{2-} species on "perfect" $TiO_2(110)$ (i.e., a surface without bridging oxygen vacancies). In this case, the SO_2 molecule is bound to the substrate through all three atoms: the S atom to an in-plane oxygen atom and the two SO_2 oxygen atoms each to a fivefold-coordinated Ti atom (Figure 1 e).[6–8] This model is consistent with the position derived from STM, as the S atom is laterally displaced from the Ti row by about 1 Å. It is also in line with the polarization dependence of the S *K*-edge NEXAFS of the SO_3^{2-} species, which points to a geometry in which the C_3 axis is oriented towards the surface normal.[2] Furthermore, increased exposure of the surface to SO_2 should result in a saturation coverage corresponding to a 2×1 overlayer. This is precisely what we observe experimentally (not shown). There is nothing in our STM results to point to the formation of a disordered overlayer, as suggested by the photoemission and photoelectron diffraction work of Sayago et al.[5] This difference could possibly result from a difference in sample preparation or from damage by the X-ray beam in the photoemission work.

Subsequent heating of the ordered 2×1 overlayer to 300 K in the STM stage resulted in the removal of the majority of adsorbates from the surface (Figure 2 a). The remaining adsorbates have a coverage of 0.05 ML and continue to be situated close to the Ti rows. An analysis of the apparent heights of 107 adsorbate features in the image in Figure 2 a did not indicate the bimodal distribution expected on the basis of NEXAFS[2] and photoemission[5] data. These spectroscopic results indicate that both sulfite and sulfate should be present after annealing to room temperature. For example, the NEXAFS results point towards a 50:50 mixture of sulfate and sulfite species after annealing an overlayer from 100 to 300 K. On the basis of results obtained from a surface annealed to higher temperature (see below), it seems likely that the sulfate-like species are removed from the surface under the tunneling conditions employed to obtain the image in Figure 2 a. The average height of the adsorbates above the bright rows in Figure 2 a is 2 Å. As this height differs from that in Figure 1 a (1 Å), it implies that there is a change in the adsorbate. Moreover, the coverage in Figure 2 a is 0.05 ML, which is comparable to the O-vacancy concentration. It therefore seems likely that there is sufficient mobility for sulfite species to migrate to sites adjacent to vacancies. This migration would allow the sulfite species predicted by DFT

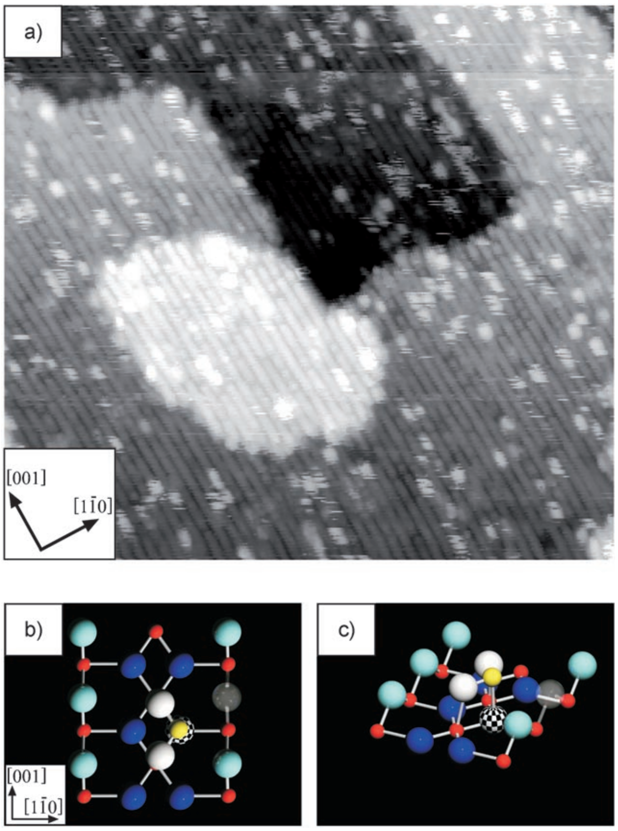

Figure 2. a) 300×270 Å² STM image (2 V, 1 nA) of $TiO_2(110)1\times1$ at 300 K following a total exposure of 8 L SO_2 at 120 K. b) Top and c) side view of a sulfite geometry predicted to be stable adjacent to a vacancy. The vacancies are shown as translucent spheres; all other colors as in Figure 1.

calculations to be stabilized by the proximity to a vacancy.[7] The difference in the apparent height of sulfite when adjacent to a vacancy arises from its different electronic structure. A model of this moiety is shown in Figure 2 b,c. Some adsorbate features on the surface imaged in Figure 2 a appear "scratched". This result suggests that the adsorbates maintain some degree of mobility, which is probably induced by the tip. This behavior is not observed in the image of sulfite in Figure 1 d, presumably because of the lower temperature.

A major change occurs to the adsorbate upon annealing the surface imaged in Figure 2 a to 420 K and cooling to 300 K (Figure 3 a). The new features are assigned to sulfate-like species on the basis of the spectroscopic measurements.[2] Although there are a few species centered on the bright rows, most of the remaining species had shifted in position and appear to reside over the dark rows in the image, which correspond to the positions of bridging oxygen atoms. Many of these new adsorbate features have a characteristic half-moon shape, heights that vary between 1.5 and 2.7 Å with respect to the Ti rows, and a coverage of about 0.025 ML. These features could only be imaged if the tunneling current was reduced from 1 nA to 0.1 nA. At 1 nA, the act of scanning removed the adsorbate from the surface. Although a stable sulfate species is not predicted by calculations of the perfect surface, they are favored if associated with O vacancies.[7] A model of one such species is shown in Figure 3 b,c in which the S atom bonds to bridging O atoms adjacent to two bridging oxygen vacancies.[7] As this species is centered over the bridging oxygen row, it is consistent with the STM images of sulfate. We speculate that the half-moon motif arises because in this case we are tunneling into oxygen-derived orbitals. Furthermore, the lower coverage of SO_4^{2-} (0.025 ML) compared with SO_3^{2-} (0.05 ML) may reflect the enhanced stability of the sulfate species when adjacent to more than one bridging oxygen vacancy.[7]

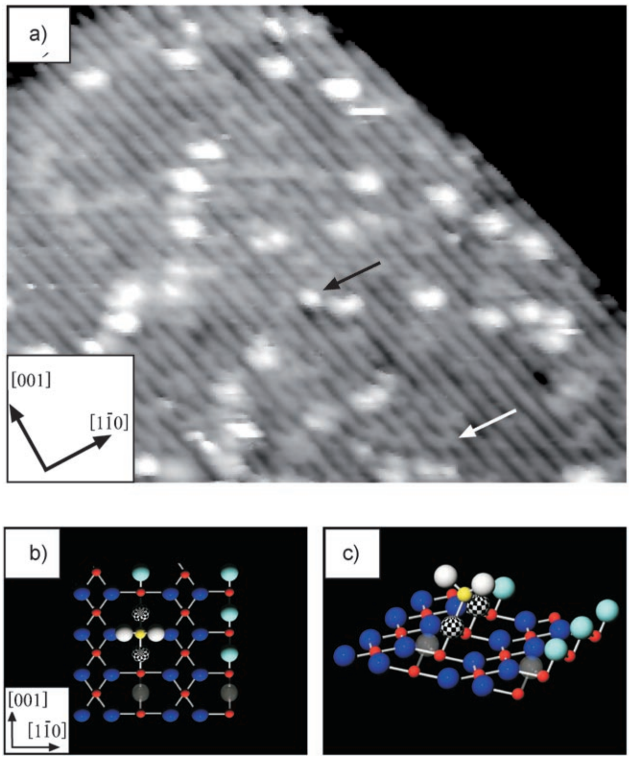

Figure 3. 180×140 Å^2 STM image (2 V, 0.1 nA) of $TiO_2(110)1\times1$ at 300 K following a total exposure of 8 L SO_2 at 120 K and annealing to 420 K for 2 min. The white and black arrows denote an oxygen vacancy and a minority SO_3^{2-}-like adsorbate, respectively. b) Top and c) side view of a stable sulfate geometry when the molecule is adjacent to two bridging oxygen vacancies. White spheres: sulfate O atoms; see Figure 1 legend for other colors.

In summary, we have shown that there is a change in the adsorption site as sulfite is transformed into sulfate on $TiO_2(110)$ by increasing the temperature in the range 120–420 K. The site of the adsorbate is determined by using STM. There is also an intermediate, which consists of sulfite adjacent to a bridging oxygen vacancy. We observe SO_3^{2-} species to be initially formed at 120 K at regular lattice sites close to fivefold-coordinated-Ti rows. The adsorbate does not appear to interact with oxygen vacancies at this temperature. The position of the adsorbate is consistent with a species predicted to be stable by DFT calculations in which the two O atoms in the SO_2 molecule bridge adjacent fivefold-coordinated Ti atoms.[6–8] The S atom bonds to an in-plane O atom. Sulfite saturates with a 2×1 overlayer, which is also consistent with this bridging configuration. Raising the temperature of the ordered overlayer to 300 K results in the removal of SO_3^{2-}species and leaves only about 0.05 ML SO_3^{2-} on the surface. This particular concentration points to the involvement of O vacancies. Thermal activation in the form of a barrier to diffusion may prevent this interaction at lower temperature, as was found for the dissociation of water at O vacancies.[1] Annealing the overlayer to 420 K transforms the sulfite-like species into sulfate-like species. This change in adsorption site is evidenced by a shift in position of the adsorbate from the fivefold-coordinated-Ti rows to bridging O rows.

Experimental Section

Measurements were performed by using an Omicron GmbH variable-temperature scanning tunneling microscope operating at a base pressure of approximately 1×10^{-10} mbar. The rutile $TiO_2(110)$ sample was vacuum annealed at 900 K for 30 min to reduce the bulk and then cleaned in situ by cycles of argon-ion bombardment (500 eV) and annealing at 1050 K. The surface cleanliness and ordering were checked by Auger electron spectroscopy, low-energy electron diffraction (LEED), and STM. SO_2 (99.98 % purity) was admitted to the STM chamber through a high-precision leak valve. All images presented were recorded by using a tungsten tip in the constant-current mode and a positive sample bias.

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