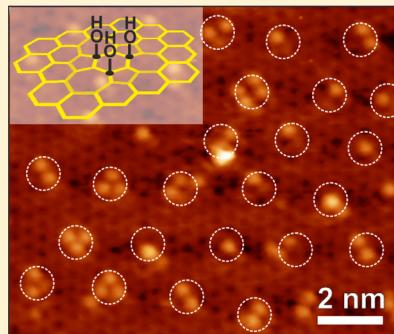


Tuning Spatial Distribution of Surface Hydroxyls on a Metal-Supported Single-Layer Silica

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ABSTRACT: Using scanning tunneling microscopy and infrared reflection absorption spectroscopy, we studied adsorption of water on a single-layer silicatene grown on Ru(0001). Surface hydroxylation occurs exclusively on defect sites, resulting in isolated silanols (Si–OH). By modifying the defect structure of the overlayer, we have provided a means of tuning spatial distribution of surface hydroxyls to fabricate periodic arrays of silanols on a metal-supported single-layer silicatene. We have visualized the surface hydroxyls directly with atomic resolution to determine their preferential adsorption sites, which involve Si at the junction nodes of three nonequivalent silica polygons. Our results open up the possibility of patterning surface hydroxyls via the engineering of nanometer scale defect sites, which may then serve as potential templates for supported active species on oxide surfaces.



SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

It is generally accepted that surface-bound hydroxyl groups play a crucial role in absorption, geochemistry, and catalysis of silica-based materials.¹ These species exist as either isolated or hydrogen-bonded silanols (Si–OH)^{2,3} and are known to act as anchoring sites for catalytically active species.⁴ Therefore, the concentration and spatial distribution of silanols may affect the density, morphology, and hence the functional properties of silica-supported clusters.

Although numerous studies have been carried out to gain a better understanding of silica hydroxylation and the relevant surface structures related to such processes, an atomistic description remains challenging because of the structural complexity and diversity of the silica surfaces, which typically exist in glassy (amorphous) states. To study the surface properties of silica at the molecular level with surface-sensitive experimental tools, model systems have recently been introduced, which are also well-suited for theoretical studies.⁵ The structural motif of the models is a layer of corner-sharing [SiO₄] tetrahedra,^{6,7} forming a 2-D honeycomb network, referred to as silicatene by analogy to graphene and silicene.⁸

Previous studies⁹ showed that water does not chemisorb on regular, siloxane (Si–O–Si) terminated surfaces, with hydroxylation occurring solely at ill-defined defects present within double-layer silicatene. Despite this, a direct visualization of surface silanols on silicatene is still missing. Furthermore, if defects govern hydroxylation, then the spatial distribution of silanol groups could, in principle, be controlled by patterning defects on the silica surface. To validate this concept, we have created samples that consist of periodic hydroxyl arrays decorating topological defects on single-layer silicatene grown on Ru(0001). Using scanning tunneling microscopy (STM) and infrared reflection absorption spectroscopy (IRAS), we directly identify silanol species and their adsorption geometry on surface defects.

Figure 1 displays typical STM images of “as-prepared” single-layer silicatene upon hydroxylation. The sample was first exposed to water (D₂O) vapor at ~100 K, which forms a thin ice film, as monitored by IRAS. Upon heating to 300 K in ultrahigh vacuum (UHV), the ice film sublimes but leaves behind isolated silanol species, which are readily distinguished by IRA spectrum (inset in Figure 1a). Concomitantly, the atomically sized protrusions, missing on the pristine samples, appear in the STM images. On the basis of this correlation, we assign the protrusions (which are ~1 Å in height, depending on tunneling conditions) to surface hydroxyls. The shortest distance between these protrusions is ~5 Å, that is, the length of the unit cell of the silicatene on Ru(0001) (= 5.42 Å), indicating that these species are isolated in nature, in agreement with the IRAS results.

Figure 1b shows that domain boundaries provide the majority of the active sites for water dissociation and binding, ultimately resulting in their decoration. Figure 1a shows that hydroxyls may also be formed on the step edges along the perimeter of “holes” within the film, which expose the metal substrate. Very few hydroxo species are observed on the regular terraces, presumably on the “point” defects, and all of the previously mentioned observations are consistent with a defect-mediated hydroxylation mechanism.

Annealing of single-layer silicatene to 1100 K in UHV leads to severe surface reconstructions.⁸ The surface of such samples exhibits a 2-D array of structural (triangular (T) and rectangular (R)) defects, which are shown in Figure 2 together with their polygonal representations. The T-defect of three-fold symmetry resembles the blister defect previously observed for haeckelite-

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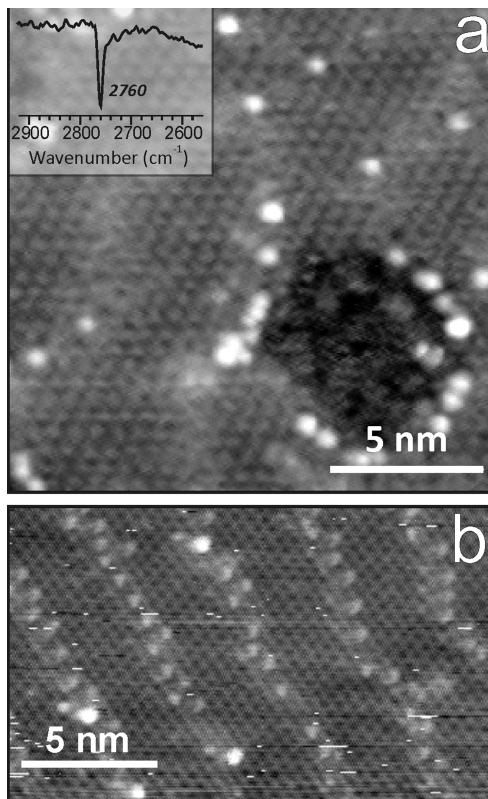


Figure 1. STM images of the “as-prepared” single-layer silicatene upon subsequent hydroxylation with D_2O . Surface hydroxyls appear as protrusions decorating primarily the holes, exposing a Ru(0001) substrate (a) and domain boundaries (b). Only a few hydroxyls are seen on terraces. The inset displays the OD-stretching region of an IRA-spectrum with a sharp peak at 2760 cm^{-1} characteristic for isolated silanols (tunneling parameters: sample bias 1.5 V, current 0.1 nA).

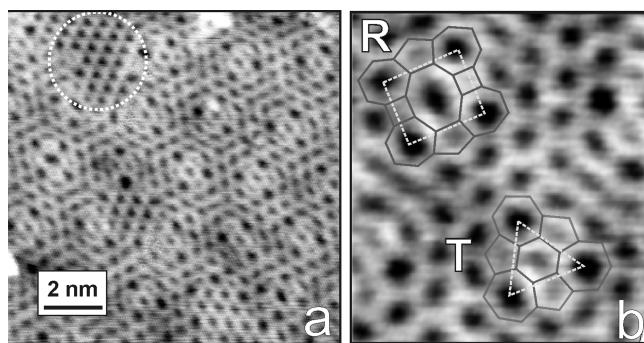


Figure 2. (a) STM image of the silicatene reconstructed into the haecelkelite-like structure upon annealing at 1100 K in UHV, resulting in an array of periodic defects zoomed in panel b. Two types of defects are observed, that is, rectangular (R) and triangular (T). Its polygonal representations are shown. (Nodes of polygons indicate positions of the Si atoms in the silicatene.) The dashed circle in panel a marks the unreconstructed domain for comparison (tunneling parameters: 1.5 V, 0.1 nA).

type structures of graphene and is formed by three pentagons and three heptagons surrounding one hexagon.¹⁰ (Nodes of polygons indicate positions of the Si atoms in the silica network; see ref 8 for the details.) The R-defects are composed of one octagon surrounded by two pentagons, two tetragons, and four heptagons, thus exhibiting two-fold symmetry. Note

that the T-defects dominate the surface under the conditions studied.

Hydroxylation of the haecelkelite-type silicatene (henceforth referred to as “*h*-silicatene”), using the same procedure as for the “as prepared” films, results in atomically sized bright protrusions ($\sim 0.7 \text{ \AA}$ in height, and 3 \AA in diameter) and their aggregates (mostly dimers and trimers; see Figure 3), which are

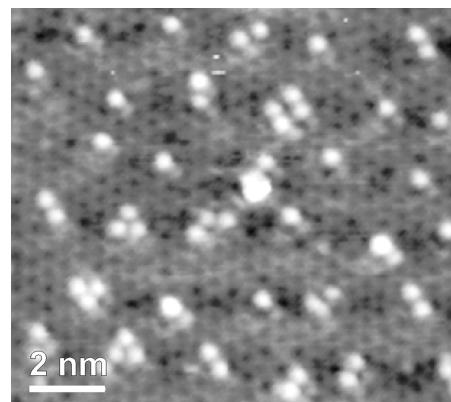


Figure 3. STM image of the *h*-silicatene after hydroxylation showing atomic protrusions of surface hydroxyls and their aggregates hexagonally arranged with the same long-range periodicity as of topological defects shown in Figure 2 (tunneling parameters: 1.3 V, 0.1 nA).

arranged on the surface following the same long-range periodicity (ca. 24 \AA) as the topological defects on the pristine *h*-silicatene. Indeed, triangular trimers, seen in Figure 3, clearly resemble the symmetry of the T-defects. It is noteworthy that the distance between the protrusions in dimers is the same as in trimers, and those dimers are preferentially oriented in the same directions as the triangle edges, thus suggesting that the dimers are associated with the T-defects unsaturated by hydroxyls. The rectangular clusters, formed by four protrusions (see the top portion of Figure 3), which are tentatively thought to be associated with the R-defects, were rarely observed due to low concentration of R-defects in our samples.

High-resolution STM images, displayed in Figure 4, allow us to directly localize the position of silanol species with respect to the T-defects identified in these images. The corresponding polygonal representation revealed that the OH-associated protrusions are preferentially located above the Si atoms at the nodes formed by a pentagon, hexagon, and heptagon (five-, six-, and seven-membered rings, in other notation). Such species can also be observed outside the triangles formed by centers of three heptagons, but they are still located over the S,6,7-junctions. Therefore, the STM results show a strong preference of the S,6,7-sites over other possible sites on the T-defects.

The preferential adsorption sites on the R-defects are more difficult to establish because of their minority. Figure 5a shows an example where two equivalent S,7,8-sites expose OH species. In another example shown on the right in Figure 5b, the 4,7,8- and 4,6,7-sites expose hydroxyls. Finally, using the mutual orientation of T and R defects on bare surfaces, we could reconstruct the R-defect underneath the rectangle of protrusions seen in the top-right portion of Figure 3. In this case, 4,7,8- and S,7,8-sites are hydroxylated (Figure 5c).

It is worth mentioning that the polygonal schemes applied here are based on previous STM images of the pristine *h*-

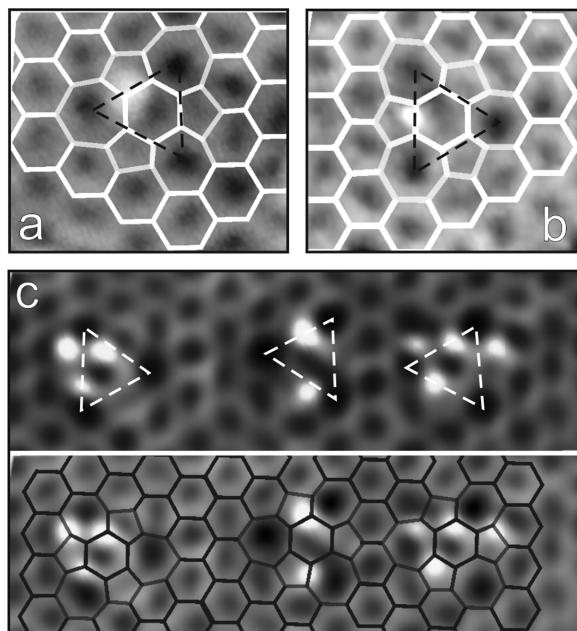


Figure 4. Series of high-resolution STM images and corresponding polygonal representations of the T-defects (marked by dashed triangles), illustrating the preferential formation of OH species over Si atoms on the 5,6,7-sites. In panel b, the OH-related protrusion is apparently located in the bridge position between the 5,6,7-sites (tunneling parameters: 1.3 V, 0.1 nA).

silicatenes, for which the theoretical calculations and optimized geometry of the T- and R-defects are still missing. This may explain some of the deviations between the OD protrusions and the positions of the polygonal nodes. In addition, one might anticipate additional lattice distortions induced by OH species. Finally, rotation of the OH bond around the Si–O bond axis in silanol and (not yet proven) hopping of species between quasi-equivalent sites could also contribute to the images recorded at room temperature. Interestingly, when more than two OD protrusions are observed on the T- (and R-) defects, they are well-separated and located in meta and para positions of the silica polygons. The formation of two ODs in an ortho geometry is never observed and, therefore, seems unfavorable. In this respect, it is instructive to recall that the commonly discussed hydroxylation mechanism proceeds through “opening” the strained Si–O–Si bonds at the surface, which ultimately results in two adjacent silanol groups in ortho positions.^{2,11} This seems to not be the case for the single-layer silicatene.

Now we address the IRAS results. Hydroxylation of the *h*-silicatene results in the sharp IRAS signal at 2760 cm^{-1} (Figure 6), that is, at the same frequency as observed for the original

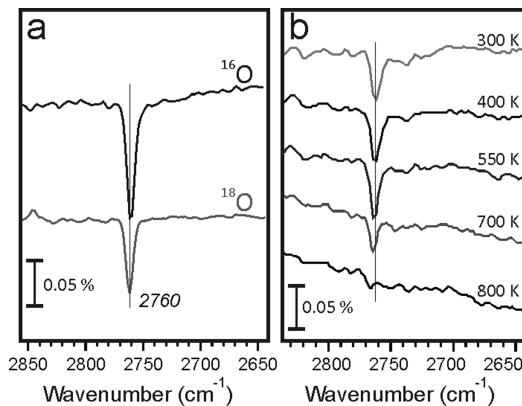


Figure 6. (a) $\nu(\text{OD})$ region in IRA-spectra of *h*-silicatene, prepared with $^{16}\text{O}_2$ (top line) and $^{18}\text{O}_2$ (bottom line), hydroxylated with D_2^{16}O . Only the band at 2760 cm^{-1} , assigned to ^{16}OD species, is observed irrespective of the oxygen isotope the silicatene is made of. (b) Series of IRA-spectra obtained upon thermal flash to the specified temperature (in UHV). All spectra were obtained at 300 K and are offset for clarity.

silicatene (inset in Figure 1a), suggesting that the isolated silanols on both surfaces are virtually identical in nature. The silanols are quite stable and disappear upon heating to $\sim 800\text{ K}$, as shown in Figure 6b. For comparison, silanols on the “as-prepared” silicatene sample disappear at considerably higher temperatures, ca. 1050 K .

In addition, we have performed isotopic experiments by preparing the silicatene with $^{18}\text{O}_2$ for comparison. After hydroxylation with D_2^{16}O , only the band at 2760 cm^{-1} assigned to the ^{16}OD stretching mode is observed for both surfaces. Therefore, hydroxyls form exclusively from the adsorbed water molecules and do not undergo scrambling with the lattice oxygen atoms. Because the single silicatene layer is bound to the metal Ru(0001) support via the $(\text{O}_3)\text{Si}-\text{O}-\text{Ru}$ linkages and hydroxo species are imaged on top of the Si atoms, the results suggest breaking of the Si–O bond, pointing toward the Ru surface, and subsequent flipping of the Si atom on top to bind OH from the water as possible reaction steps. However, the second H from the water should form another hydroxyl with a silica lattice oxygen atom, which is not detected in our IRAS experiments. The fate of the second OH remains puzzling. Furthermore, the same results have been obtained in isotopic experiments with a double-layer silicatene,⁹ thus suggesting a similar mechanism for both systems. One possible explanation involves the specific geometry of the second OH that becomes IRAS-invisible due to the well-known metal selection rules. Also, a metal support underneath an ultrathin film may play a role in the adsorption processes, for example, through recombinative desorption of weakly bound H_2 . This issue

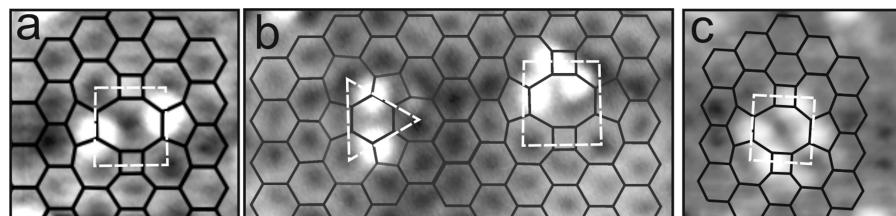


Figure 5. (a–c) Series of high-resolution STM images overlapped with polygonal representations showing OH species on the R-defects, which are marked as dashed rectangles. Panel b additionally shows the T defect (tunneling parameters: 1.3 V, 0.1 nA).

needs to be further investigated, in particular, by theoretical calculations.

In summary, our results provide compelling evidence that the formation of silanols on silica occurs exclusively on surface defects. Under the conditions studied, the silanols are isolated in nature and preferentially form on specific sites, defined by the junction nodes of three nonequivalent polygons within the silica framework. It has been shown that patterning the surface defects allows for tuning of the spatial distribution of surface hydroxyls, ultimately resulting in a 2-D array. The latter surface can be used as a template for anchoring active species on oxide supports.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript

Notes

The authors declare no competing financial interest.

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