Direction-dependent Intermolecular Interactions: Catechol on TiO$_2$(110)-1×1

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ABSTRACT

The adsorption of a submonolayer of catechol (C$_6$H$_6$O$_2$) on the rutile TiO$_2$(110)-1×1 surface has been investigated by Scanning Tunneling Microscopy (STM). The catechol molecules are preferentially adsorbed on the surface 5-fold coordinated Ti$^{4+}$ sites, and occupy two neighboring lattice Ti sites. No preference for adsorption at surface step edges is observed at room temperature. A statistical analysis of intermolecular distances demonstrates that the interaction between the molecules strongly depends on the surface crystallographic direction: catechol molecules exhibit attractive interaction along [011], while they repel each other along the [001] direction. The attractive interaction is proposed to be caused by the coupling of π bonding electrons and the repulsive interaction is possibly mediated by substrate.

Keywords: Scanning Tunneling Microscopy, TiO$_2$(110), Catechol

1. INTRODUCTION

TiO$_2$ is used in various technological applications and is widely studied to obtain fundamental insights into oxide surface chemistry. [1, 2] For example, TiO$_2$ is often used in solar energy conversion, where the material is adopted as the electrode in dye-sensitized solar cells. [3-5] The band gap of TiO$_2$ is ~3.2eV, located in the ultraviolet region. A monolayer of an organic dye deposited on the TiO$_2$ surface modifies the electronic structure by inducing band gap states. This enables the harvesting of visible light. [3]

Catechol on the rutile TiO$_2$(110)-1×1 surface has recently been studied as a model dye molecule. [5-11] In particular the correlation between molecular adsorption geometries and electronic properties has been determined by combining scanning tunneling microscopy (STM), ultraviolet photoemission spectroscopy (UPS), and theoretical calculations based on density functional theory (DFT). [8] In the catechol (C$_6$H$_6$O$_2$) molecule, two OH groups substitute two neighboring hydrogen atoms at the benzene ring. The most typical functional groups of organic dyes are OH groups, thus catechol represents one of the most simple model dyes. It has been determined [8] that a single, isolated C$_6$H$_6$O$_2$ adsorbs on TiO$_2$(110) by splitting off the two H atoms from the OH groups, which are donated to undercoordinated surface bridging oxygen (O$_{2c}$) atoms. The catechol is anchored to two neighboring surface Ti$_{5c}$ atoms via the two remaining O groups in a bridging bidentate configuration. A full catechol layer deposited on a TiO$_2$(110) surface forms a 4×1 superstructure, where the catechol molecules alternate by assuming of two kinds of adsorption geometries: either partly dissociated with one Ti-O bond (monodentate) or fully dissociated catechol with two Ti-O bonds (bridging bidentate). [8] It turns out that only the bidentate molecules have their HOMO orbitals located within the band gap of TiO$_2$, contributing to sub-band gap photon absorption. [8] The interactions between the adsorbed catechol molecules an is important for molecular self-assembly, and is investigated here in detail.

2. EXPERIMENTS

The experiments were carried out with a room temperature STM (Omicron) in ultrahigh vacuum (UHV) with a base pressure of about 1 × 10$^{-10}$ mbar. The UHV chamber is also equipped with a low-energy electron diffraction (LEED) optics and an ion gun for sputtering. The TiO$_2$(110) crystal (M.T.I. Co.) was loaded into the UHV chamber via a fast-entry loadlock, and outgased to ~400 °C prior to cleaning. The surface was cleaned in-situ in the UHV chamber with standard procedures consisting of Ar$^+$ sputtering and annealing to ~630 °C. The surface cleanliness and structure were checked with STM and LEED prior to dosing catechol (purity 99% from Alfa Aesar). The catechol powder was purified by a few freeze-pump-thaw cycles prior to use; the pure catechol exhibited a yellowish color. The sample was radiatively heated by a filament mounted at its back side. The STM experiments were performed with a wet chemically...
etched W tip, and the constant current mode was adopted. The sample was typically biased with ~+1.5V (imaging empty states) and a typical tunneling current was about 0.1nA. The STM images were processed with the free software WSxM.

3. RESULTS

The stoichiometric TiO$_2$(110)-1×1 surface is composed of alternate rows of 5-fold coordinated Ti$^{4+}$ atoms (Ti$_{5c}$) and 2-fold coordinated bridging oxygen (O$_{2c}$) atoms, running along [001], as shown in Figure 1(a). Upon thermally annealing in UHV, the TiO$_2$(110)-1×1 surface is slightly reduced by forming bridging oxygen vacancies (O$_v$’s) on the bridging oxygen sites (labeled as O, in Fig. 1(a)). At room temperature a water molecule adsorbs at an oxygen vacancy site and dissociates into H and OH, with the OH filling the O$_v$ and the H adsorbing on top of a neighboring surface O$_{2c}$ atom.[13-17] Thus two hydroxyls are formed upon adsorption of one water molecule. Before dosing catechol, the slightly reduced TiO$_2$(110)-1×1 surface was fully hydroxylated by background water from the UHV chamber. Figure 1(b) shows a typical STM image of the hydroxylated TiO$_2$(110) surface. Even though the O$_{2c}$ rows are geometrically lower than Ti$_{5c}$ row, Figure 1 (a), the Ti$_{5c}$ atoms are imaged as bright while the O$_{2c}$ are dark in empty-states STM, due to electronic effects.[2, 18] Note that all the protrusions on the oxygen rows in Fig. 1(b) are due to hydroxyl groups formed upon water dissociation; no O vacancies are shown in the Figure 1(b).

Figure 2(a) shows a large scale overview of a submonolayer (~0.12 ML) of catechol dosed on TiO$_2$(110) at room temperature. The catechol is distributed fairly uniformly across the TiO$_2$ terraces. No preference for adsorption on step-edges is observed at room temperature for all coverages. The catechol adsorbed on TiO$_2$(110) terrace is thermally stable: upon annealing to 140°C, there is no apparent change in the distribution of the molecules (compare Figures 2(a) and (b)). After annealing to 320°C, more catechols appear at the step-edges, as shown in Figure 2(c); this re-distribution is likely due to enhanced mobility at elevated temperature. In addition, when comparing Figure 2(c) and (a), the total number density is also slightly decreased, which might be due to the thermal desorption. In a previous XPS study[19], it was found flashing the full layer of catechol to 327°C decreased the total C 1s intensity by 15% -- 30%, consistent with the STM observation. In addition, the carbon-oxygen shoulder for C 1s was largely removed, and the remaining carbon peak resembled the graphite structure. Regarding to the STM observations, we suspect that the features observed at the step edges after annealing to 320°C might represent such a decomposed carbonaceous species.

Figure 3(a) shows a high-resolution image of a low coverage (~0.05 ML) of catechol, dosed on the TiO$_2$ surface at room temperature (ref [8]). The big, bright protrusions are adsorbed catechols and the smaller protrusions are the hydroxyl groups. By overlaying a TiO$_2$(110) lattice mesh on the STM images, it is clearly shown that each catechol molecule occupies two neighboring Ti$_{5c}$ sites (see the right panels). This is consistent with the theoretical calculations reported previously: the catechol is dissociated via breaking the two OH groups, and forms two Ti-O bonds with two substrate Ti$_{5c}$ atoms, as shown in the inset of Figure 3(b). [8]

The catechol is found to preferably form pairs across the Ti$_{5c}$ rows, with two catechols sitting next to each other in two neighboring Ti rows. Figure 3(b) shows a higher coverage (~0.12 ML) of catechol; the position of the substrate Ti rows and hydroxyls can still be clearly identified. Different from Figure 3(a), longer catechol chains, rather than pairs, are formed across the Ti$_{5c}$ rows. However, at both coverages the catechol molecules prefer to stay apart from each other along the [001] direction.

To further investigate the interactions between the catechol molecules, the distributions of the distances between two nearest catechol neighbors were analyzed. For the in-row distribution (along the [001] direction), the distances between two catechols sitting on the same Ti$_{5c}$ row were measured (see inset in Figure 4(a) upper panel). For the across-row distribution, the distances between two catechols sitting on two neighboring Ti$_{5c}$ rows were measured (see inset in Figure 4(a) lower panel). Only catechol pairs with distances smaller than 80 Å are considered; pairs that are further apart are neglected. In total, more than 1000 pairs were analyzed. Figures 4(a) and (b) show the statistical results for the 0.05 ML and 0.12 ML coverages, respectively. For comparison, the green lines in Figures 4(a) and (b) show the statistics expected for a one-dimensional random distribution. The random distribution $f_{ran}$ can be described by equation [20]

$$f_{ran} = \frac{n!}{N-n+1} \left[ \frac{N-n+1}{\sqrt{N}} \right]$$

where $N$ is the 1D box size, $n$ is the number of particles, and $r_s$ is the pair distance. Here the particle density equals to n/N. For The $f_{ran}$ in Figures 4 (a,b), the number of N and n were set to the same values as the in experiment; any influence stemming from boundaries in STM images was neglected.
As shown in Figure 4, the one-dimensional random distribution decreases monotonously with distance. In contrast to a maximum at the nearest neighbor distance (~7.0 Å or two lattice unit cells) expected for the random distribution, the catechol in-row distribution shows a peak located at about 14.0 Å in Figure 4(a). For the coverage range considered in this work, this peak maximum is also found to be weakly dependent on the coverage; e.g., for the higher coverage in Figure 4(b) it is located at 10.5 Å. On the other hand, the across-row distribution exhibits two maxima. One maximum is located at zero, and the other one at the same position as the in-row-distribution.

This distributions indicate that the catechol molecules repel each other over a range of ~4 lattice units (4 × 3.5 Å) along the Ti5c rows. The peak at zero for the across-row distribution implies the formation of catechol pairs across the bridging oxygen rows, as is already apparent when inspecting the STM images in Figure 3. The second peak, located at the same position as the in-row distribution, can be understood as the interplay of the in-row repulsive interactions and the across-row attractive interactions.

4. DISCUSSION

It is interesting to consider how the distribution of catechol molecules across the surface evolves, starting from the small coverages, considered here to the full monolayer described in our earlier publications. [6] The latter is shown for comparison in Figure 5. It consists of a closely-packed 4×1 superstructure, where all Ti5c lattice sites are occupied by catechol molecules. (This amounts to half a monolayer coverage, i.e., one catechols per two Ti5c’s). As is apparent in Figure 5(b), every other molecule appears displaced towards the neighboring O2c rows in alternate directions. From UPS and DFT results it is known that these molecules are include an angle of ~30° with respect to the surface normal and are tilted alternatingly to the left and right (i.e., towards [1T0] and [1T0]). Also, neighboring catechol molecules form H-bonds; they re-gain one H from an O2c atom (inset in Figure 5) and form a ‘D1’ configuration rather than the fully-dissociated ‘D2’ configuration that is more stable at lower coverages.

The results for low coverage of catechol presented here clearly show a repulsive interaction along the rows. The reason for this repulsive force could have multiple causes: in addition to H-H repulsion and steric hindrance between neighboring, upright benzene rings, the preferred bidentate bridging configuration induces strain in the substrate. Electronic effects could play a role as well, as catechol is known to modify the electronic structure. Clearly, this long-range (3 – 4 lattice constants) repulsive interaction must be overcome before the short-range H-bonding can set in, which stabilizes the molecules in the 4×1 superstructure.

On the other hand, the attractive interaction between catechol neighbors across the rows, which first leads to pairs and then to short, [1T10]-oriented chains, is preserved throughout all coverages. When (across-row) neighbors are tilted in a parallel fashion, the π-bonding between neighboring benzene rings is maximized. For larger coverages, this also allows for a minimization of steric hindrance in the closely-packed 4×1 superstructure.

The adsorption geometry of catechol on TiO2(110) is quite different from that of benzene. It was found that benzene adsorbed on TiO2 with its molecular plane parallel to the surface [21], and no apparent benzene pairs were observed. Since at low-coverage catechols stand upright on the Ti rows with their ring upright and its plane along [001] and the molecular ring parallel to the Ti rows, a pairing across the rows makes the overlap of the π orbital highest (compared to the benzene on TiO2). The stacked catechol chain observed at higher coverage (Figure 3(b)) also supports that π orbital coupling is significant.

5. SUMMARY

In summary, the interactions between catechol molecules adsorbed on a TiO2(110) surface have been studied via a statistical analysis of intermolecular distances at submonolayer coverages. It was found that the interaction between catechol molecules is strongly dependent on the substrate orientation: attractive across, and long-range repulsive along [001]-oriented Ti5c rows. With increasing coverage the average molecule-molecule distance along the rows decreases until, at very high coverage, short-range, attractive H-bonding sets it. This interplay between attractive and repulsive forces is helpful for understanding organic molecule self-assembly on an oxide surface.
6. ACKNOWLEDGMENT

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![Ball-and-stick model of the TiO₂(110)-1×1 surface.](image-a)

![STM image of clean TiO₂(110)-1×1 surface.](image-b)

Fig. 1. (a) Ball-and-stick model of the TiO₂(110)-1×1 surface. (b) STM image of clean TiO₂(110)-1×1 surface. The size is 15 nm × 15 nm. $V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 0.1$ nA.

![STM images showing TiO₂(110) surface.](image-c)

Fig. 2. STM images (50 nm × 50 nm) showing (a) the TiO₂(110) surface with close-to-full coverage of catechol (~0.12ML), and (b), (c) the same surface after annealing to 140°C and 320°C respectively. The annealing time was about 10 min. $V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 0.1$ nA.
Fig. 3. Catechol adsorbed on the TiO$_2$(110)-1×1 surface with a coverage of (a) ~0.05 ML (8.5 nm × 8.5 nm) and (b) ~0.12 ML (8.5 nm × 8.5 nm). The left panel and right panels show the same STM images without and without a lattice grid superimposed, respectively. The inset shows the adsorption geometry of a single catechol molecule on TiO$_2$(110), as determined in ref. [8].

Fig. 4. In-row distributions along the substrate [001] direction (upper panel) and across-row distributions along the substrate [1 1 0] direction (lower panel) of nearest-neighbor catechol pair distances determined for coverages of (a) 0.05 ML and (b) 0.12 ML. Two of the corresponding STM images are shown in Fig. 3(a) and (b) respectively. The green lines show the one dimensional random distribution.
Fig. 5. (a) Large scale STM image (30 nm × 30 nm) of the 4×1 superstructure of the full layer catechol on TiO$_2$(110). The inset shows two adsorption geometries: D1: monodentate and D2: bidentate as determined in ref. [8]. (b) High-resolution STM image of the catechol 4×1 superstructure. The substrate atoms are imposed: black balls are Ti$_{5c}$ atoms and white balls are bridging O atoms. (c) LEED pattern of the catechol 4×1 superstructure. $E_{\text{el}} = 50$ eV.

REFERENCES


