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Imaging Adsorbate O−H Bond Cleavage: Methanol on TiO$_2$(110)

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The thermal and photocatalytic oxidation of simple alcohols has been extensively studied on TiO$_2$ surfaces[1−4] as a prototype for the catalytic oxidation of organic contaminants.[5,6] Among them, methanol, one of the simplest organic molecules, is often adopted as a probe.[1,7−10] Experiments have shown that both molecular and dissociative adsorption takes place on defective rutile TiO$_2$(110) surfaces.[1,8,10] Methanol dissociation occurs primarily on bridge-bonded oxygen vacancy (BBOV) defect sites[4,6] with some evidence for methanol dissociation at nondefect sites as well.[1,8] First-principles calculations show that on a stoichiometric surface, the dissociative adsorption of CH$_3$OH can occur via both O−H and C−O bond scission and that it is slightly favored over molecular adsorption.[9,11] However, the atomic level understanding of these systems is still missing. Scanning tunneling microcopy (STM) is an ideal tool that allows us to track the adsorbates on different surface sites. In this study, we employ in situ STM to follow the adsorption and dissociation of methanol on BBOVs of TiO$_2$(110).

Experiments were performed in an ultrahigh vacuum variable-temperature STM chamber (Omicron, base pressure $< 8 \times 10^{-11}$ Torr). The TiO$_2$(110) (Princeton Scientific) was cleaned by cycles of Ar ion sputtering (1 keV, 1 μA) and annealing at 900−1000 K. Methanol (Fisher, 99.9+ %) purified by several freeze−pump−thaw cycles using liquid nitrogen, was introduced on the TiO$_2$(110) surface via a retractable tube doser. While dosing, the W tip was retracted ~1 μm from the surface to avoid shadowing the imaged area. The methanol backing pressure in the pinhole doser was identical for all experiments in this study, allowing us to use the dosing time as a measure of methanol exposure to the sample.

Figure 1 displays a set of STM images obtained from the same TiO$_2$(110) area before and after dosing methanol at 300 K. Figure 1a represents a clean surface before methanol adsorption. The bright rows on Figure 1a are identified as the five-fold coordinated Ti^{4+} ions; the dark rows are the bridge-bonded oxygen (BBO) ions.[6] The bright spots between the Ti^{4+} rows are assigned to BBOVs, believed to act as the primary dissociation centers for the alcohols.[1,4] Special care was taken to avoid hydroxyl contamination from background water.[12] Statistically the number density of BBOVs on this surface is about 8% with respect to the number of Ti^{4+}. The magnified images (insets, Figure 1) highlight the position of six BBOV sites (marked by yellow circles in Figure 1a) to illustrate the processes observed during methanol adsorption.

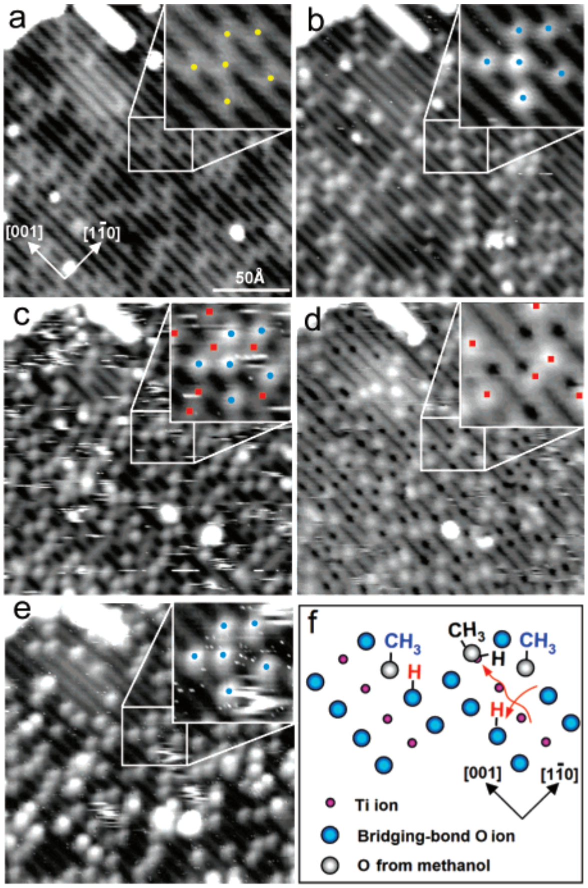

Figure 1. STM images of same area before and after adsorption of methanol on reduced TiO$_2$(110) at 300 K (bias voltage: $+1.0 \pm 0.3$ V, tunneling current: <0.1 A): (a) bare surface; (b) after 80 s exposure to methanol; (c) after 110 seconds exposure to methanol; (d) taken on (c) after spontaneous tip change; (e) after high bias (3.0 V) sweep of (c); (f) schematic model of the adsorption process. Insets show magnified areas marked by squares. Yellow circles show the position of bridge-bonded oxygen (BBO) vacancies. Blue circles show the bright features on oxygen vacancies. Red squares show the features sitting on BBO rows but not related to BBO vacancies.

The surface after an 80 s methanol dose is shown in Figure 1b. The methanol adsorption-induced features appear as bright features on the BBOVs. For this exposure, their coverage is 0.06 monolayer (ML, 1 ML = 5.2×10^{14} cm^{-2}). The spatial location of adsorption sites becomes apparent from comparison of the magnified areas in the insets of panels a and b in Figure 1. The pattern of the bright features (marked with blue circles, inset of panel b in Figure 1) is the same as the BBOV pattern on the clean surface (yellow circles, of panel a in Figure 1), indicating that methanol preferentially adsorbed on BBOVs. Comparing line profiles along the [001] direction shows that the bright features are ~0.8 Å higher than BBOVs (S1) and that the methanol-induced bright features have their maxima located on the original BBOV sites but are asymmetric (S1). This suggests that these features originate from two different chemical species present on neighboring BBO sites, in accord with the previously observed formation of hydroxyl and methoxy species due to dissociative adsorption of methanol.[1] This is shown schematically in Figure 1f (left). The observation of neighboring

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methoxy and hydroxyl pairs is similar to the recently reported neighboring hydroxyl pairs from H_2O adsorption on $TiO_2(110)$.[13]

The same area after an additional 30 s methanol dose is shown in Figure 1c. After this dose, all the BBOVs are saturated. Besides the previously observed features on BBOVs (blue circles, inset of panel b in Figure 1), new features appear (red squares, inset of panel c in Figure 1), also located on the BBO rows but not correlated with the original BBOV sites. They are less bright (hereafter called "gray") than the features present on the BBOVs. In fact, we find that a small fraction of these gray features appeared at the lower methanol dose shown in Figure 1b. In Figure 1c, the coverage ratio between the gray and bright features is 1 ± 0.05. The coverage of bright features increased linearly with the dose time (from 0.06 to 0.08 ML), while that of gray features grew dramatically from 0.01 to 0.07 ML. Additionally, the streaked appearance of this image suggests the presence of highly mobile methanol, most likely bound to Ti^{4+}. To exclude the effect of background adsorption during long sequential dosing experiments (total time 2 h), we dosed the same total amount of methanol in a single dose; the results were the same, i.e., a 1:1 ratio of bright and gray features. We conclude that the gray features are not caused by background contamination.

The different chemical natures of bright and gray features are confirmed in Figure 1d, which shows an identical area and methanol dose to that in Figure 1c. A spontaneous STM tip change led to imaging of the bright features on the original BBOVs as dark depressions (Figure 1d), while the gray features not corresponding to BBOVs remained the same. This contrast reversal is likely a result of an adsorbate pick up by the tip.[14]

Before offering an explanation for the nonlinear increase of the gray features coverage, we present arguments that led to our assignment of gray features as hydroxyl and bright features as methoxy groups. We have carried out separate experiments with H_2O adsorption on BBOV sites. In this case two hydroxyls are formed[12,15] and are imaged identically to the gray features observed after methanol adsorption in Figure 1c. Further, the different responses of the gray and bright features to high tip bias strongly support this assignment. Figure 1e shows an image scanned with 1.3 V after sweeping the area with 3.0 V bias. Almost all the gray features disappeared from the surface after this treatment, while the bright features were not affected. This is consistent with prior literature, as well our own experiments on hydroxyl covered $TiO_2(110)$ surfaces showing that the proton of the hydroxyl groups can be removed by high bias voltage (>2.5 V).[16] On the basis of the hydroxyl (gray) and methoxy (bright) group assignments, we conclude that methanol dissociates on BBOVs via O−H bond scission. In the case of C−O bond scission, the hydroxyl rather than methoxy group would appear on the original BBOV sites.

Below, we further address the nonlinear increase in gray features with exposure. We have already argued that at low exposures (Figure 1b), the methoxy (bright) and hydroxyl (gray) groups occupy neighboring BBO sites (Figure 1f (left)). At this coverage most of the gray features cannot be resolved due to their proximity to bright, methoxy-related features. At high coverages (Figure 1c), all the hydroxyl groups appear to be spatially separated from the methoxy groups (bright/gray = 1:1) as they migrated away from their original geminate sites. We propose that diffusing methanol molecules assist hydroxyl migration, likely through proton "hopping". At CH_3OH coverages below the BBOV coverage, these methanol molecules diffusing on Ti^{4+} rows dissociate after encountering an empty BBOV. At CH_3OH coverages exceeding the BBOV coverage, excess methanol is mobile and leads to the observed dramatic increase in hydroxyl migration. Figure 1f (right) shows a schematic model for methanol assisted hydroxyl migration on $TiO_2(110)$. An analogous migration mechanism has been put forward in the case of water-assisted migration of hydroxyl groups on $TiO_2(110)$[17] and is also consistent with high proton mobility in liquid methanol and water.[18] Repeated imaging of the same area provides additional evidence for the high mobility of hydroxyls at high methanol coverages (S2). We believe this mobility is facilitated by molecular methanol diffusing along the Ti^{4+} rows: as much as 40% of the hydroxyls changed position in two consecutive images (~3 min). In contrast, our analysis of minority gray features in the images with methanol coverages below the BBOV coverage (e.g., Figure 1b) indicates negligible hydroxyl migration (data not shown).

In summary, we present the first atomically resolved images of dissociative methanol adsorption on bridge-bonded oxygen (BBO) vacancies of TiO_2 (110). Imaging of the same area before and after adsorption allowed us to establish that the dissociation proceeds via O−H bond scission. At methanol coverages below the BBO vacancy coverage, the methoxy and hydroxyls occupy primarily neighboring BBO sites. At higher coverages, facile hydroxyl migration assisted by mobile, Ti^{4+}-bound methanol molecules is observed.

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Supporting Information Available: S1: intensity profiles along the BBO row from STM images before and after methanol dose; S2: two subsequent STM images for a 110 s dose of methanol; S3: complete author list of ref 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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