Supporting Information

Adsorption and Reaction of Methanol on Anatase TiO$_2$(101)

Single Crystals and Faceted Nanoparticles

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Figure S1. High-resolution STM image of pristine anatase SC TiO$_2$(101) surface. The white rectangle represents the surface unit cell. The bright protrusions in the STM image correspond to O$_{2c}$-Ti$_{5c}$ pair. Part of the image is overlaid with surface structure. The steep edge of the sawtooth of anatase TiO$_2$(101) surface is across [10\bar{1}] direction.

Figure S2. Arrangements of the sample for TPD and IRAS measurements. (a) Anatase SC TiO$_2$(101) sample with size (7×5×2 mm$^3$) mounted on a tantalum plate holder using Aremco cement and thin tantalum wires at the corners. (b) The IR beam normally comes to the shorter (5mm) side of the sample at 20° to the [10-1] azimuth at glancing angle to the (101) surface (5°). (c) Secondary electron image of the sample with a dosed H$_2$O film (white spot). The molecular beam $\varnothing$ 7.3 mm (umbra), centered on the sample and larger than the sample.
Figure S3. (a) Transmission electron microscopy (TEM) image (a), (b) Scanning electron microscopy (SEM) image, (c) X-ray diffraction pattern (XRD) pattern (c) and in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectrum (d) of anatase F-NP TiO$_2$(101).
**Figure S4.** The schematic illustration of methanol molecule orientation on the TiO$_2$(101) surface. The switching of the hydrogen bonding between the two equidistant step-up O$_{2c}$ atoms is likely responsible for the symmetric dumbbell appearance of methanol monomer in the STM images. Under-coordinated Ti$_{5c}$ atoms are shown in light blue and O$_{2c}$ atoms – in red. Carbon and hydrogen in methanol molecule are dark and light gray, respectively.

**Figure S5.** Bias dependent STM images of 0.12 ML of methanol on anatase SC TiO$_2$(101). The appearance of methanol molecules changes with increasing bias voltage. At the lowest bias voltage of 0.7 V, methanol molecules appear as dumbbell protrusions centered on top of Ti$_{5c}$ sites. At the highest bias voltage of 1.3 V, methanol molecules appear as spherical protrusions centered on top of Ti$_{5c}$ sites. All images: tunneling current, I$_t$ = 200 pA.
Figure S6. Methanol coverage determined from the STM images as a function of methanol dose on anatase SC TiO$_2$(101) at 80 K. The linear dependence of the methanol uptake suggests precursor mediated adsorption.

Figure S7. Same area time-lapse sequential STM images demonstrating the onset of sustained diffusion of methanol molecules on anatase SC TiO$_2$(101). Methanol was adsorbed at 80 K, subsequently annealed and imaged at 250 K. Two diffusion events are marked by red arrows.
Analysis of the clustering tendency of methanol:

To quantify the extent of methanol clustering at 80 K, we have analyzed the cluster size distributions. Purple bars in Figure S8 show the cluster size distributions for the images with the methanol coverages of 0.08, 0.12, and 0.19 ML. As the coverage is increased from 0.12 to 0.19 ML, the coverage of methanol monomers increases marginally from 0.09 to 0.10 ML, while the coverage of monomer pairs increases two-fold (from 0.03 to 0.06 ML). Already at 0.19 ML, the coverage of methanol in the chains contributes to ~47 % of the total coverage.

We have further implemented simple kinetic Monte Carlo (KMC) simulations to compare the above experimental cluster distributions with the expected random adsorption. The red bars in Figure S8 show the simulated cluster size distribution for the random adsorption of molecules in

![Figure S8](image)

**Figure S8**: Experimental (purple) and simulated (red bars) methanol cluster size distributions. The purple bars represent the distributions corresponding to the 0.08, 0.12, and 0.19 ML of methanol adsorbed at 80 K. The simulated distributions (red bars) are determined from the KMC simulations assuming random adsorption in the absence of surface diffusion.
the absence of mobility. The comparison between purple and red bars shows a higher population of simulated monomers (1.6 times higher at 0.19 ML) than the population of experimental monomers. Moreover, the population of simulated clusters (monomer pairs, triplets, etc.) decays faster than the populations observed in the experiment. The higher population of methanol molecules in the clusters suggest that methanol has to be mobile during the adsorption at 80 K. However, the onset of sustained diffusion of methanol on anatase TiO$_2$(101) is observed at 250 K. Hence the diffusion at 80 K can only be transient in nature.

Figure S9. The comparison of cluster size distributions of water and methanol on anatase SC TiO$_2$(101). Black and purple bars represent the cluster size distributions determined from the STM images following water and methanol adsorption at 80 K, respectively. The red bars represent the cluster size distributions determined from the KMC simulations assuming random adsorption. The simulated population of monomers is 2.9 times higher than the experimentally observed population of water monomers and 1.9 times higher than the experimentally observed population of methanol monomers. The experimentally observed population of water clusters accounts for 71% of the total water coverage. In contrast, the experimentally observed population of methanol clusters accounts for only 51% of the total methanol coverage. These observations suggest that water molecules have a higher tendency to form clusters than methanol molecules.

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Figure S10. The STM image of SC TiO$_2$(101) prepared by exposing 0.25 ML of methanol at 80 K and subsequently annealing to 290 K. The image was obtained at 80 K. Only a small fraction of molecules (some are highlighted by green arrows) is left on the surface while the majority desorbed. No paired features (see Figure 5, main manuscript) are observed. The paired features are observed only if the initial coverage before annealing is higher than 0.5 ML.

Figure S11. STM image of TiO$_2$(101) prepared by exposing ~22 ML of methanol at 295 K. The image was acquired at 80 K. Only a very small fraction of molecular methanol (0.05 ML) is adsorbed; no methoxy-hydroxy pairs are seen. X marks the cluster of impurities.
Figure S12. Same area tip-manipulation experiments demonstrate that the paired feature is comprised of methoxy and hydroxyl groups. (a) STM image of SC TiO$_2$(101) prepared by exposing 1.5 ML of methanol at 80 K and subsequently annealing to 290 K. In addition to the remaining methanol molecules, a new type of pair features (highlighted by white circles) are seen. The 3.0 V pulses are applied on paired features at the positions indicated by the white arrows. The subsequent STM image in (b) shows the removal of the bigger part of the paired feature, leaving behind protrusions on dark rows (highlighted by white circles in (b)). Such protrusions were previously assigned to the bridging hydroxyls. Thus, the tip-manipulation experiments suggest that the pair features are comprised of methoxy and hydroxyls groups. The STM images were taken at 80 K.

Figure S13. High-resolution STM image of TiO$_2$(101) following the exposure of 1.5 ML of methanol at 80 K and subsequent annealing to 700 K. The image demonstrates that all methoxy-hydroxy pairs and methanol molecules desorbed. The image was obtained at 80 K.
Figure S14. IRAS spectra in p-polarized light for various deuterated methanol (CD$_3$OD) doses on anatase SC TiO$_2$(101). Blue trace represent the spectra for 1.0 ML of methanol adsorbed at 100 K. Green trace represent spectra following annealing 1.0 ML of CD$_3$OD adsorbed at 100 K to 320 K. Red trace represent spectra after repeating the adsorption at 100 K and subsequent annealing to 320 for 10 times (n=10). Spectral changes after n = 10 are marked with asterisks. Spectra of the 10 ML CD$_3$OD ice (purple trace) are shown in the bottom for reference (scaled).
REFERENCES: