

Unravelling Site-Specific Photo-Reactions of Ethanol on Rutile TiO₂(110)

Supporting Information

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1. Enlarged STM images of Fig. 1 in the main article: Figures S1 to S9.
2. Additional STM experiments addressing the assignments of surface species: Figure S10 and corresponding text.
3. Confirmation of H_{ad} formation in the photo-reaction on EtOH / *r*-TiO₂(110) by TPD measurements: Figure S11 and corresponding text.

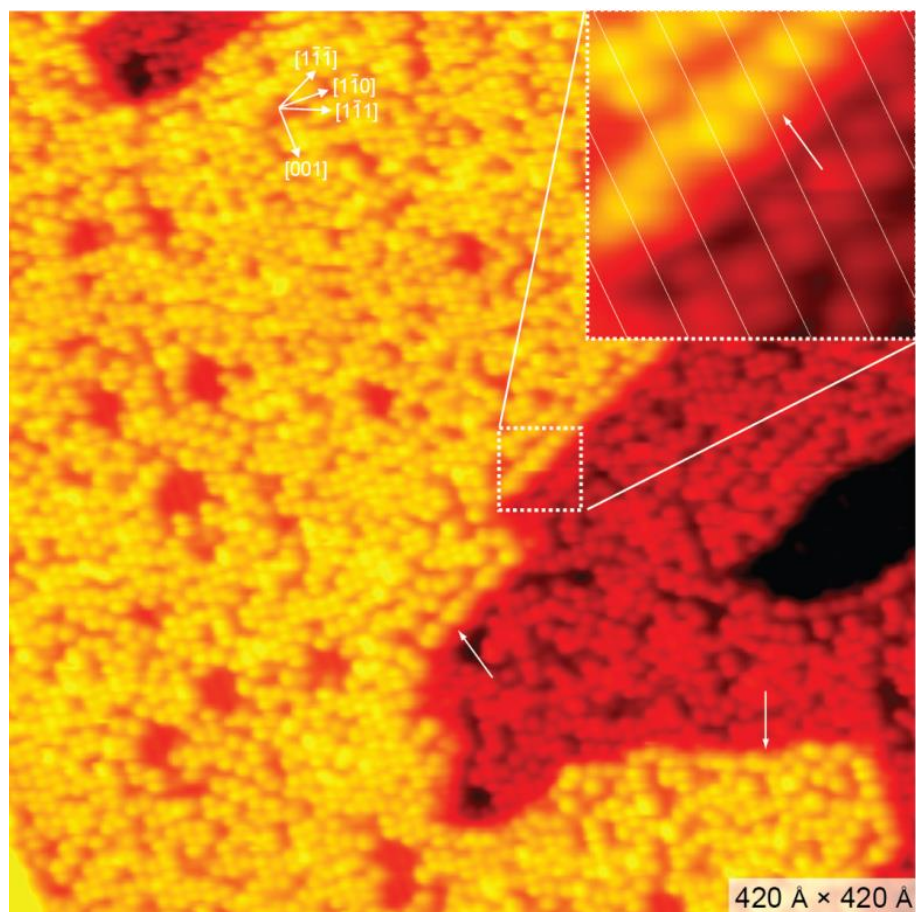


Fig. S1 (see Fig. 1a): STM image ($420 \text{ \AA} \times 420 \text{ \AA}$) obtained after exposing an *r*-TiO₂(110) surface to EtOH at 300 K. Few of the EtO_s ethoxides are indicated by white arrows. In the inset, the Ti troughs are indicated by thin white lines. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

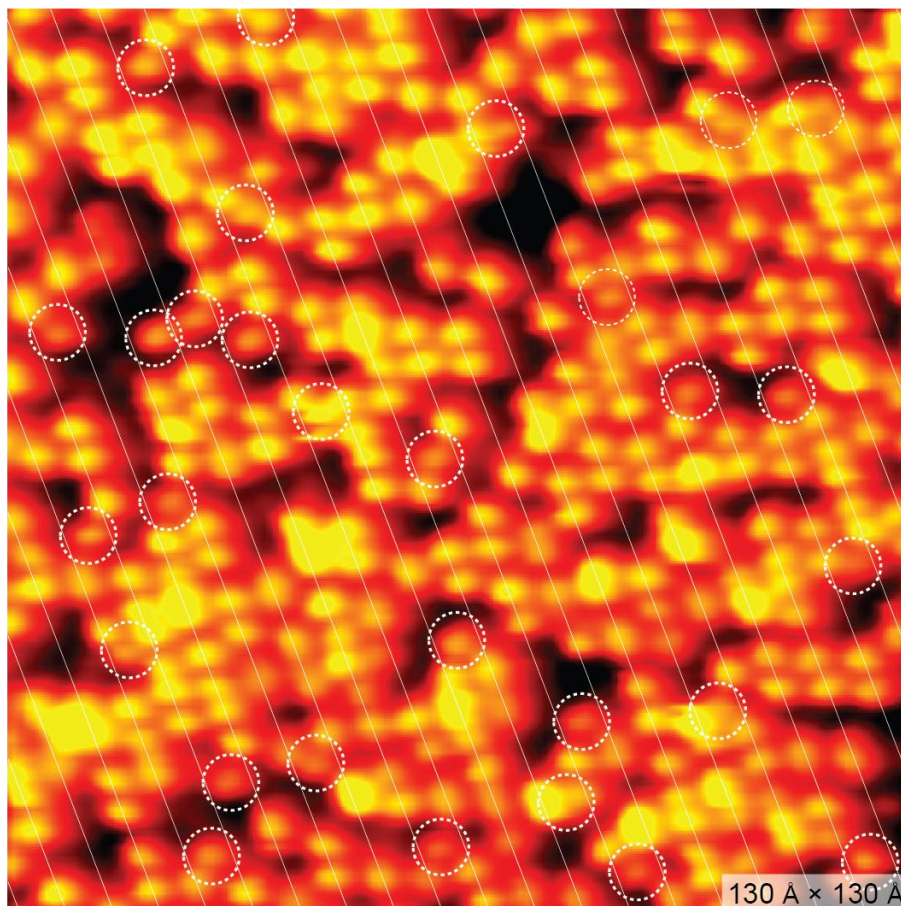


Fig. S2 (see Fig. 1b): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) acquired within the same experiment as the image shown in Fig. S1 after exposing an *r*-TiO₂(110) surface to EtOH at 300 K. The Ti troughs are indicated by thin white lines and EtO_{br} ethoxides by white dotted circles. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

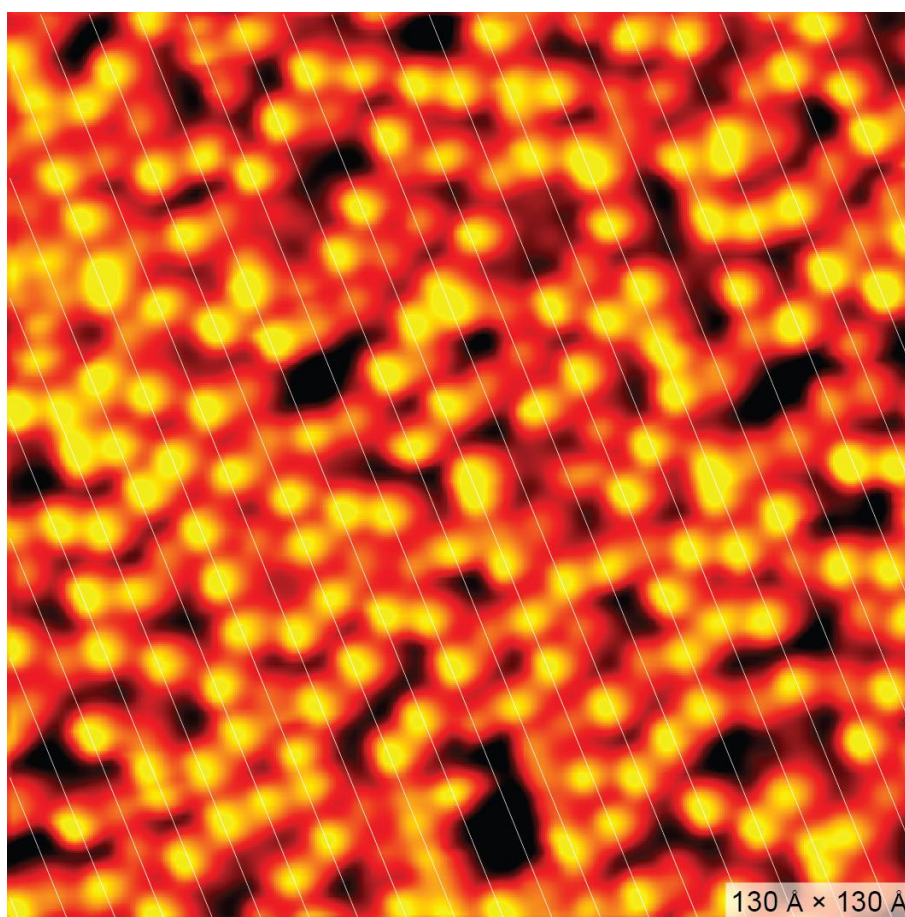


Fig. S3 (see Fig. 1c): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) acquired after exposing an *o*-TiO₂(110) surface to EtOH at 300 K. The Ti troughs are indicated by thin white lines. Note that no EtO_{br} ethoxides were formed on *o*-TiO₂(110), because no O_{br} vacancies exist on this surface. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

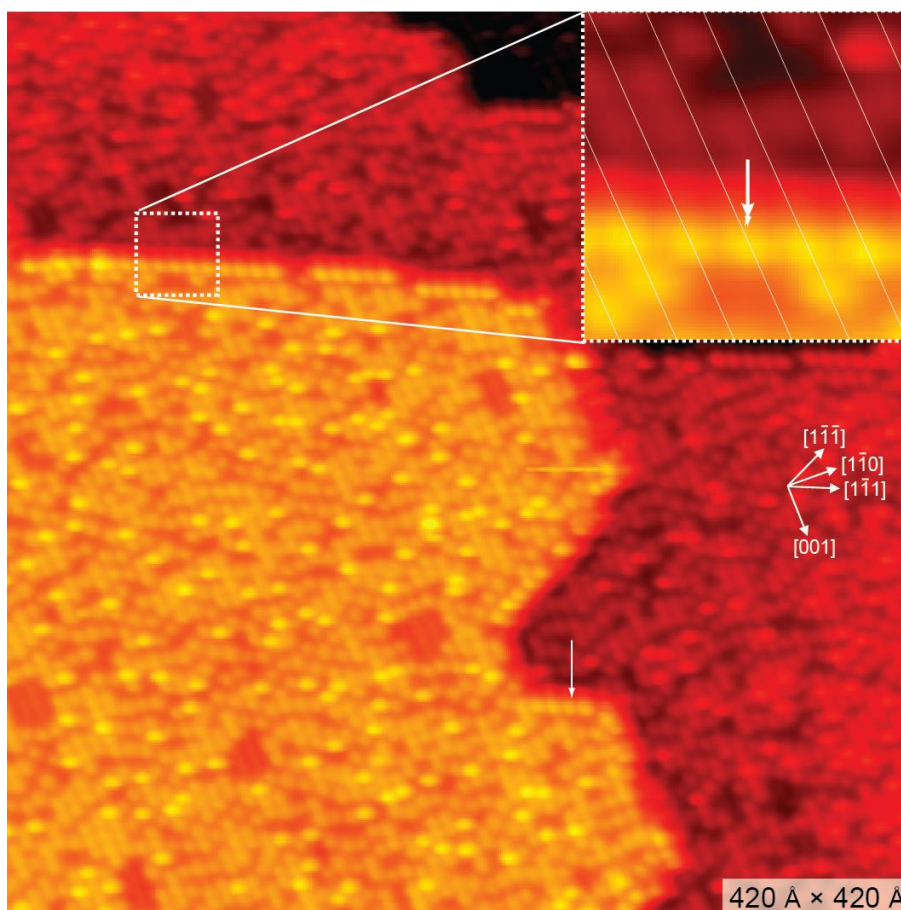


Fig. S4 (see Fig. 1d): STM image ($420 \text{ \AA} \times 420 \text{ \AA}$) acquired after illumination of the EtOH-covered *r*-TiO₂(110) surface with UV-light for 11 min at 290 K in UHV. All the EtOH_{Ti} / EtO_{Ti} species disappeared but not the EtO_{br} and EtO_s ethoxides. Few of the EtO_s ethoxides are indicated by white arrows. In the inset, the Ti troughs are indicated by thin white lines. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

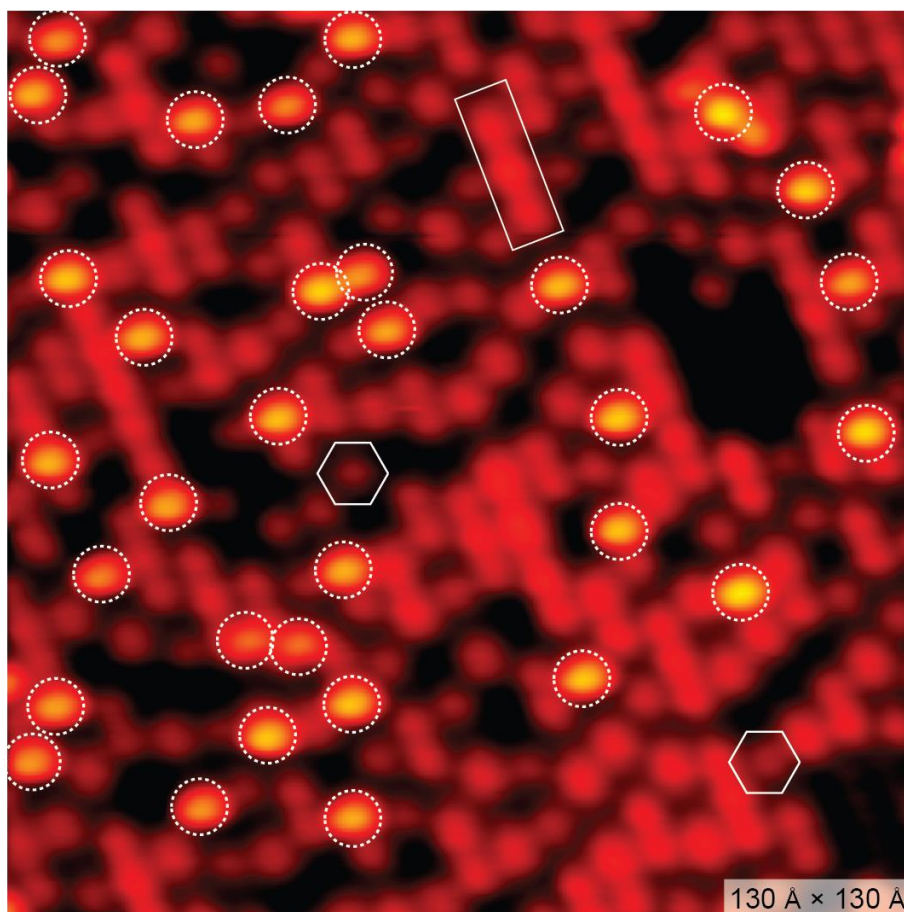


Fig. S5 (see Fig. 1e): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) acquired within the same experiment as the image shown in Fig. S4 after exposing an *r*-TiO₂(110) surface to EtOH at 300 K and UV light illumination. White dotted circles indicate EtO_{br} ethoxides. Few isolated H_{ad} species are indicated by hexagons and “rows of H_{ad} species” by rectangles. Within the rows of H_{ad} species each other O_{br} is capped with an H_{ad} species. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

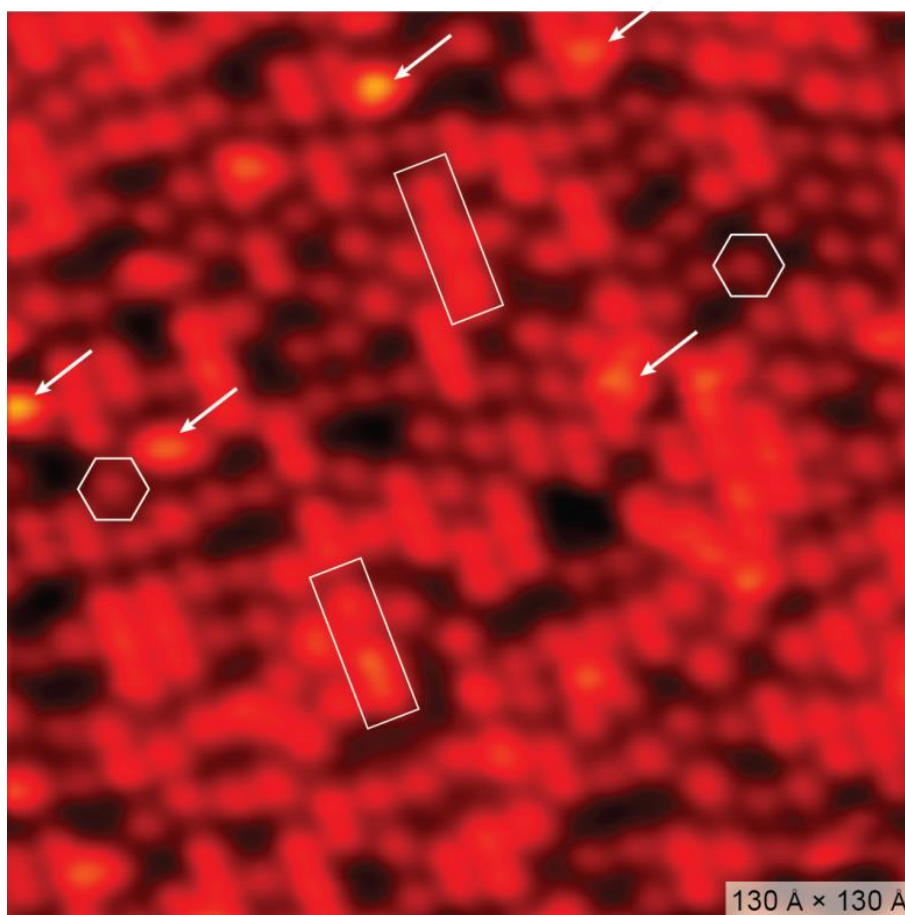


Fig. S6 (see Fig. 1f): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) obtained after illumination of an EtOH-covered *o*-TiO₂(110) surface with UV-light for 11 min at 290 K in UHV. Few isolated H_{ad} species are indicated by hexagons and “rows of H_{ad} species” by rectangles. White arrows indicate water monomers. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

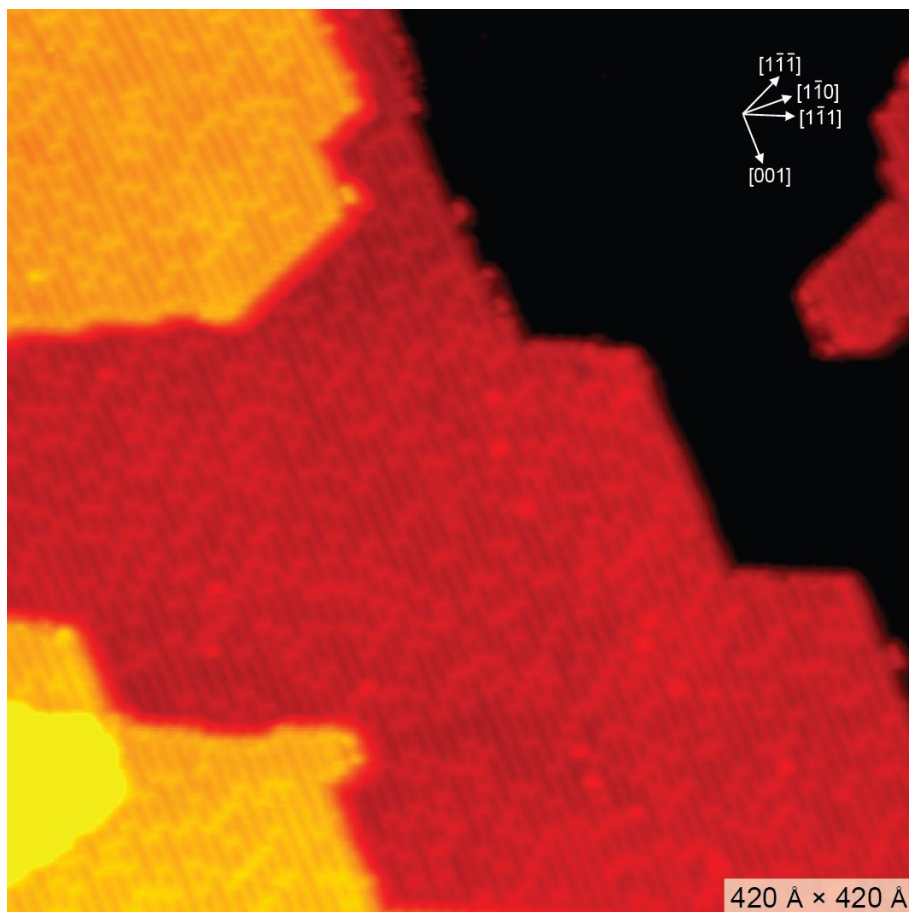


Fig. S7 (see Fig. 1g): STM image ($420 \text{ \AA} \times 420 \text{ \AA}$) acquired after annealing of the $\text{TiO}_2(110)$ crystal for 2 min at $\sim 550 \text{ K}$. The preceding preparations consisted of (i) saturation of $r\text{-TiO}_2(110)$ with EtOH at RT and (ii) UV-light illumination for 11 min at 290 K in UHV. A clean of $r\text{-TiO}_2(110)$ surface resulted characterized by an O_{br} vacancy density about twice as high as the one found on the clean $r\text{-TiO}_2(110)$ surfaces at the very beginning of the experiment. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

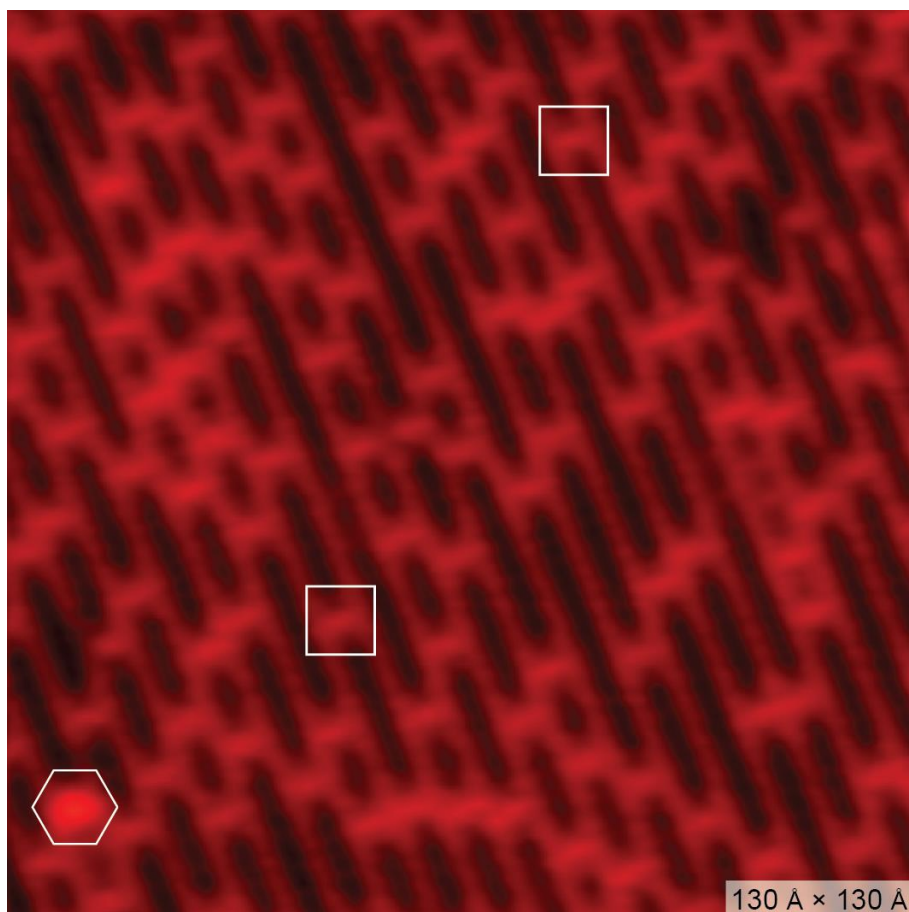


Fig. S8 (see Fig. 1h): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) acquired after annealing of the $\text{TiO}_2(110)$ crystal for 2 min at $\sim 550 \text{ K}$. The preceding preparations consisted of (i) saturation of $r\text{-TiO}_2(110)$ with EtOH at RT and (ii) UV-light illumination for 11 min at 290 K in UHV. A clean of $r\text{-TiO}_2(110)$ surface resulted characterized by an O_{br} vacancy density about twice as high as the one found on the clean $r\text{-TiO}_2(110)$ surfaces at the very beginning of the experiment. Few O_{br} vacancies are indicated by rectangles. Residual, isolated H_{ad} species are indicated by hexagons. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

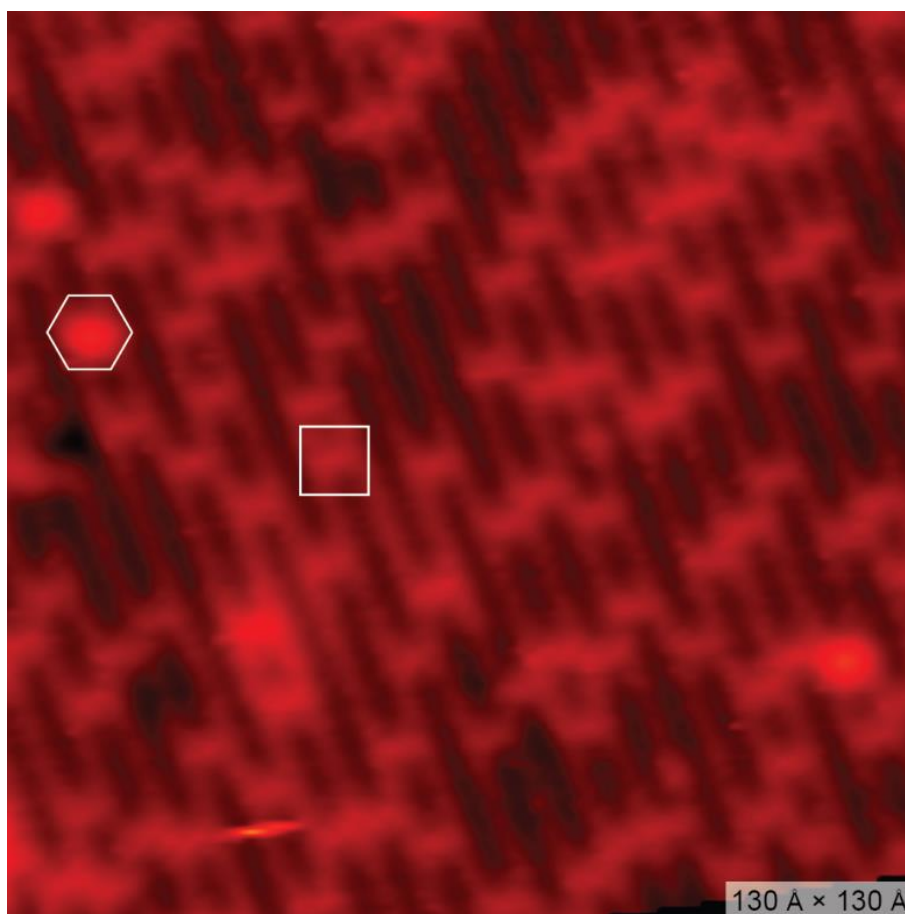


Fig. S9 (see Fig. 1i): STM image ($130 \text{ \AA} \times 130 \text{ \AA}$) acquired after annealing of the $\text{TiO}_2(110)$ crystal for 2 min at $\sim 630 \text{ K}$. The preceding preparations consisted of (i) saturation of $o\text{-TiO}_2(110)$ with EtOH at RT and (ii) UV-light illumination for 11 min at 290 K in UHV. A clean of $r\text{-TiO}_2(110)$ surface resulted characterized by an O_{br} vacancy density about twice as high as the one found on the clean $r\text{-TiO}_2(110)$ surfaces at the very beginning of the experiment. Few O_{br} vacancies are indicated by rectangles. Residual, isolated H_{ad} species are indicated by hexagons. The STM image was collected with a tunnelling current $\leq 0.1 \text{ nA}$ and a tunnelling voltage of $\sim 1.2 \text{ V}$.

Confirmation of the assignments in the STM experiments by means of scanning at

high bias. Considering the situation observed following UV-light illumination of EtOH / *r*-TiO₂(110), we performed several control experiments addressing the assignments of the observed surface species. For example, the assignment of the species in the O_{br} rows to H_{ad} species was further supported by the fact that they can be removed by O₂ exposure^{1,2} and by scanning with a tunneling voltage of $V_t = +3V$ (see ref. 3). Regarding the latter type of control experiment, an example is shown in Fig. S10. First we scanned an area of $80 \text{ \AA} \times 80 \text{ \AA}$ size with our usually used scanning conditions (tunnelling current $I_t \leq 0.1 \text{ nA}$ and a tunnelling voltage V_t of $\sim 1.2 \text{ V}$). The resulting STM image is shown in Fig. S10a. Subsequently, the same area was scanned again, but this time with $V_t = +3V$. We then zoomed out to a larger scanning area ($166 \text{ \AA} \times 166 \text{ \AA}$) and switched back to our usual scanning conditions (see Fig. S10b). In this image, the area that was scanned earlier with a high bias ($V_t = +3V$) is indicated by a white broken square. It can be seen that the EtO_{br} species were not removed during scanning with high bias. However, as expected³, all the H_{ad} species disappeared after scanning with $V_t = +3V$. As a result, the O_{br} rows and the Ti troughs became clearly visible in this area.

In the area scanned with high bias the white lines are superimposed on the Ti troughs. By extrapolating the white lines to the area outside the white broken square it becomes evident that the many new species that appeared after UV-light illumination ascribed to H_{ad} species are indeed centered at the O_{br} rows (i.e. between the lines), as expected for the H_{ad} species³. Moreover, it can be seen that the EtO_{br} are centered about the O_{br} rows. Also this result is expected, since the EtO_{br} species are formed via EtOH

dissociation at O_{br} vacancy sites⁴. The described control experiment further supports the assignments given in the main text.

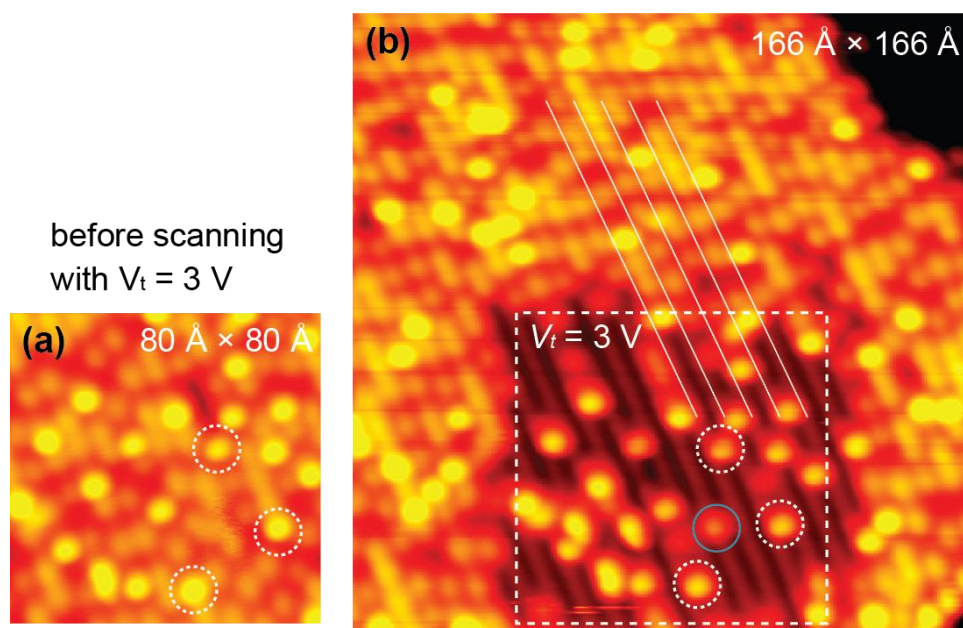


Figure S10: (a) STM image ($80 \text{ \AA} \times 80 \text{ \AA}$) acquired within a similar experiment as the image shown in Fig. S4 after exposing an $r\text{-TiO}_2(110)$ surface to EtOH at 300 K followed by UV light illumination at 290 K. The most apparent protrusions arise from EtO_{br} ethoxides, three of which are indicated by white dotted circles. The other protrusions arise from H_{ad} species. After this image was acquired, we scanned the same surface area again but this time with an increased bias of $V_t = +3$ V, resulting in the removal of H_{ad} species. (b) STM image ($166 \text{ \AA} \times 166 \text{ \AA}$) acquired after scanning with $V_t = +3$ V in the indicated area (same as in (a)). The white lines are superimposed on the Ti troughs in the squared region scanned with high bias. By extending these white lines to the area outside the square it becomes clear that the EtO_{br} species and the H_{ad} species are located at the O_{br} rows between the Ti troughs (thin white lines), confirming their assignments. In (b), the same three EtO_{br} species are indicated as in (a). In addition, a newly appeared species in a Ti trough (probably a water monomer from the background) is indicated by a blue circle.

Confirmation of H_{ad} formation by TPD measurements. The water-TPD spectra ($m/z = 18$) displayed in Fig. S11 further corroborate the formation of H_{ad} species in the photo-reaction on EtOH / r -TiO₂(110). The black TPD spectrum corresponds to EtOH / r -TiO₂(110) and was acquired after UV-light illumination for 11 min. This spectrum shows a small and narrow desorption feature at ~350 K (denoted “ α ”) and a larger and broader feature with a maximum at ~520 K (denoted “ β ”). For comparison, we show a water-TPD spectrum acquired from an h -TiO₂(110) surface (green curve). This surface was prepared by exposing an r -TiO₂(110) surface to water, using the same TiO₂(110) sample. Here, the α -feature is similar as in the previous case, but the β -feature is less intense by a factor of ~2.6. The α -feature arises from water molecules in the residual gas, which adsorb in the Ti troughs^{1,5} while cooling the sample down to ~100 K. The β -feature, however, arises from the recombination of H_{ad} species with O_{br} atoms^{1,5}. Consequently, the integrated area of the β -feature is a measure of the H_{ad} density.

An STM analysis of the h -TiO₂(110) surface corresponding to the green spectrum in Fig. S11 yielded an H_{ad} density of (11 ± 0.5) %ML, which is a factor of ~2.45 less than on the illuminated EtOH / r -TiO₂(110) surface $[(27 \pm 1)$ %ML, see Fig. 1d,e]. Accordingly, the TPD and STM data are in excellent agreement.

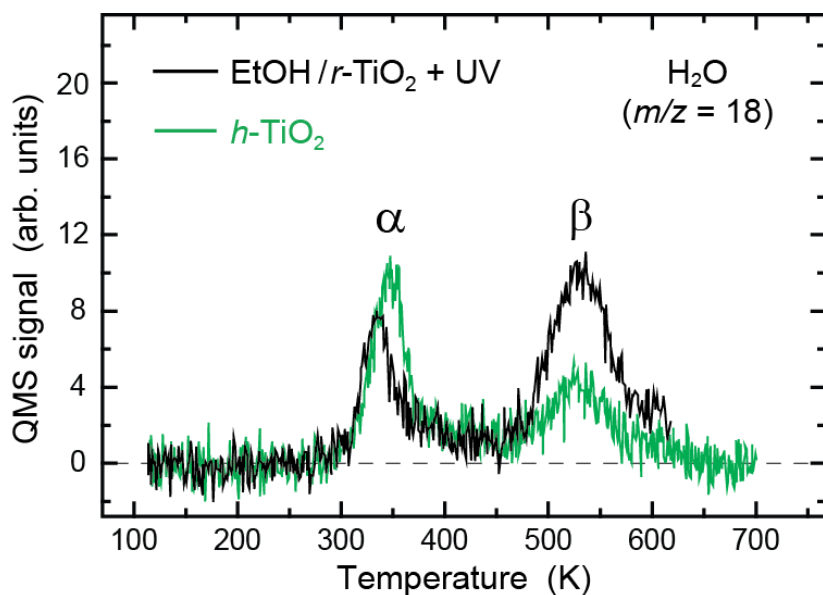


Figure S11: Water-TPD spectra of an illuminated EtOH / *r*-TiO₂(110) surface (black curve) and a non-illuminated *h*-TiO₂(110) surface (green curve). The same TiO₂(110) crystal was used for these experiments.

References of the Supplemental Information:

1. Henderson M. A., Epling W. S, Peden C. H. F. & Perkins C. L. Insights into photoexcited electron scavenging processes on TiO₂ obtained from studies of the reaction of O₂ with OH groups adsorbed at electronic defects on TiO₂(110). *J. Phys. Chem. B* **107**, 534–545 (2003).
2. Matthiesen J., *et al.* Observation of all the intermediate steps of a chemical reaction on an oxide surface by scanning tunneling microscopy. *ACS Nano* **3**, 517–526 (2009).
3. Wendt S., *et al.* Oxygen vacancies on TiO₂(110) and their interaction with H₂O and O₂: A combined high-resolution STM and DFT study. *Surf. Sci.* **598**, 226–245 (2005).
4. Hansen J. Ø., *et al.* Direct evidence for ethanol dissociation on rutile TiO₂(110). *Phys. Rev. Lett.* **107**, 136102 (2011).
5. Hugenschmidt M. B., Gamble L. & Campbell C. T. The Interaction of H₂O with a TiO₂(110) Surface. *Surf. Sci.* **302**, 329–340 (1994).