Supporting Information: Methanol on anatase TiO$_2$(101), mechanistic insights into photocatalysis

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Reaction of methanol with oxygen

In the main text we have discussed activation of methanol by a reaction with terminal OH groups. In previous works, adsorbed O$_2$ was mostly used for methanol activation.$^1$ Here we discuss activation of methanol by reaction with O$_2$ on anatase (101), and show analogous experimental data to those presented in the main text.

The results in Figure S1 shows XPS and TPD data for reaction of methanol with O$_2$ – the same process, as performed with the OH groups in Figures. 6 and 7c of the main text. The XPS peak
positions and heights are almost identical in both cases. The reaction products detected by TPD are also very similar.

The reaction with O$_2$ was also observed by STM, see Figure S2. The surface was exposed to 1 L O$_2$ at T = 10 K, followed by exposure to 0.1 L methanol at 110 K and annealing to 350 K for 10 minutes. The resulting STM image (Figure S2a) shows a surface containing only methoxy groups as a single reaction product. Figure S2b shows the same area after 28 minutes of illumination by UV light. The photoreaction proceeds in an identical as in the main text (Figure 4). The methoxy species are again partially converted to formaldehyde.

The reaction pathway is more complicated, though. The thermally activated step – reaction of methanol with O$_2$ – has multiple possible pathways. O$_2$ rarely dissociates on the anatase (101), even at room temperature. The O=O bond breaking becomes feasible, however, when the O$_2$ accepts a proton and forms OOH$^\cdot$. The first step of the reaction is

$$\text{O}_2^\cdot + \text{CH}_3\text{OH} + e^- \rightarrow \text{OOH}^\cdot + (\text{CH}_3\text{O})^-$$  \hspace{1cm} (2)

The OOH can undergo a series of reactions described in ref. 2, where it dissociates and further reacts with water, provided that the substrate can provide enough excess electrons:

$$\text{OOH}^- \rightarrow \text{OH}^- + (\text{O}_2)_o$$  \hspace{1cm} (3)

$$\text{(O}_2)_o + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$$  \hspace{1cm} (4)

Here the (O$_2$)$_o$ is so called the bridging oxygen dimer, which is essentially an O adatom incorporated in the surface layer. 3 The final product of this reaction cascade are terminal OH groups, which can react with methanol via the reaction in Equation (1) of the main text. Alternatively, both metastable reaction products, OOH and (O$_2$)$_o$, can react with methanol directly. XPS data in Figure S1 show that the major reaction product is again the methoxy species; hydrogen atoms are not removed from the methyl group.

According to the reaction scheme in Equations (2-4), each chemisorbed O$_2$ molecule initially adsorbed at the surface results in the formation of 4 methoxy groups, regardless of the exact reaction cascade. The O$_2$ either first reacts with water, providing terminal OH groups, or directly enters reactions with the methanol. The result is the same, as the terminal OH group has a higher affinity to protons then methanol, allowing the reaction in Equation (1) of the main text. In our case, the amount of chemisorbed O$_2$ is determined by the availability of excess electrons in the sample (i.e. by its reduction state and extrinsic doping), though excess electrons can also be obtained by
photoexcitation. The availability of excess electrons is the determining factor for the resulting concentration of methoxy groups.

In computations, we also considered the case where the OOH group from reaction (2) does not dissociate, but abstracts another H atom from the methoxy group, forming $H_2O_2$. This reaction mechanism is possible, see the pathway in Figure S3. It is likely occurs in samples that have a low concentration of excess electrons (non-reduced material).

\[ \text{Received by the electron} \rightarrow \text{OOF}^* \rightarrow \text{OOF} + \text{H} \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{OOF} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{OOF} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]

\[ \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}_2^+ \]

\[ \text{H}_3\text{O}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \]
Figure S2. a) Methoxy species prepared by reaction of methanol with O$_2$. b) The same area after 28 minutes of UV irradiation.
Figure S3: Alternative pathway for methanol + O\textsubscript{2} photoreaction. This reaction mechanism is feasible for non-reduced samples.

Identification of H atoms at the anatase (101) surface

Figure S4. Left: STM image of the anatase (101) surface exposed to atomic hydrogen. The bright spots are bridging hydroxyl groups. V\textsubscript{SAMPLE} = +0.8 V, I\textsubscript{T} = 0.2 nA. Right: The same surface imaged at an increased sample bias of +3.0 V. H atoms move when scanned at a positive sample bias above +2 V.
Hydrogen atoms are one of the products from the photocatalytic oxidation of the methoxy group to formaldehyde. These hydrogen atom are transferred to the surface during the reaction, forming so called bridging hydroxyl groups. In order to identify these hydroxyls in STM images (Figure 4d), we exposed a clean anatase (101) surface to atomic hydrogen (created by cracking H₂ at a hot W filament). The result in Figure S4 shows that the bridging hydroxyl groups appear as bright protrusions. The adsorbed species become unstable when the STM sample bias is increased above +2 V. We used this knowledge for identification of the adsorbed species shown in Figure 4d in the main text.
STM appearance of various species

Figure S5 shows the typical appearance of the discussed species when imaged by STM. The methanol, methoxy, and formaldehyde all appear as bright dimers centred above the Ti5c surface atoms (Figure S5a,b,c, respectively). This appearance is in agreement with the DFT calculations of the corresponding species (Figure S5d,e,f). These species differ in the apparent height; typical line profiles are shown in Figure S5g. The formaldehyde appear highest, followed by methanol and methoxy (lowest). The apparent height is, though, a rather weak tool for chemical assignment. It only allows to discern different species when they are present at the surface together.

**Figure S5**: (a-c) Experimental STM images of methanol, methoxy, and formaldehyde species, respectively. (d-f) Calculated constant current images of the same species; the sample bias corresponds to +1.5 V. (g) Experimental line profiles of these species measured along the direction marked in panel (a).
Calculations of C1s core-level shifts in XPS

We have performed calculations of the C1s core-level shift between the adsorbed methanol and methoxy groups according to the final-state scheme of ref 4. First we examined the rutile (110) surface to verify that our setup provides reasonable values, next we repeated the calculations for anatase. The resulting energy shifts are reported in table ST1 while the slab geometry is shown Figure S6. The calculations were performed using both standard PBE and PBE+U, and assuming the core electron to be either completely ejected, so that the system is positively charged, or promoted to the conduction band, so as to maintain charge neutrality. The core level shifts obtained with these different setups show slight variations, but the trend between rutile and anatase is apparent in all of them.

Table S1: Calculated final-state core-level shifts between CH$_3$OH and (CH$_3$O$^-$). The numbers denote the difference (in eV) between the slab with a core hole on the methanol and methoxy.
Additional TPD data in the high-coverage regime

**Table S2**: Cracking patterns of formaldehyde, methanol, and methyl formate

| m/z [a.u.] | formaldehyde | methanol | methyl formate |
|-----------|--------------|----------|---------------|
| 28        | 0.24         | 0.26     |               |
| 29        | 1.00         | 0.99     | 0.82          |
| 30        | 0.58         | 0.15     | 0.12          |
| 31        |              | 1.00     | 1.00          |
| 32        | 0.70         |          | 0.37          |
| 60        |              |          | 0.20          |

Table S2 shows TPD cracking patterns measured for our experimental settings. Formaldehyde and methanol data were measured by dosing 0.2 ML of the respective molecules on the anatase (101) surface and integrating TPD peaks of the relevant m/z signals. The cracking pattern of methyl formate was measured by dosing 0.67 ML methanol on the rutile (110) surface, illuminating it by UV light for 30 minutes and measuring TPD. Here we used the rutile (110) surface as a substrate, because the methyl formate peak does not overlap with methanol, as is the case on the anatase (101) surface.

Figure S7 shows TPD signals of 0.67 ML methanol dosed on the rutile (110) and anatase (101) surfaces after UV illumination for 30 minutes. The methyl formate (m/z=60) peak is higher on rutile, likely because this coverage provides the maximum photoactivity, while for anatase it is at the lower limit of coverages where the material is photoactive. For rutile Figure S7a), the methyl formate peak is well separate from the methanol signal and allows calibration of the cracking pattern (Table S2). For anatase (Figure. S7b), the methanol and formaldehyde peaks partially overlap. The data do not indicate production of formaldehyde, which was reported in previous studies. This is possibly due to higher UV doses used in this study.

![Figure S7: TPD spectra of a) rutile (110) surface, and b) anatase (101) surface after dosing 0.67 ML methanol at 100 K and 30 minutes UV illumination.](image-url)
Even though we did not detect any other reaction product than methyl formate, we note that we have detected water after the UV illumination, see Figure. S8. The amount of water is relatively high, and correlates with the amount of produced methyl formate, therefore it seems unlikely that it would originate solely from contamination of the sample from the background pressure. In principle, this water might be produced by dehydration of the methyl formate (producing dimethyl ether). Such a reaction has been reported on the anatase (001) surface.\(^8\) We did not measure the m/z signals that correspond to dimethyl ether. Alternatively, the water could originate from hydrogen atoms, which are produced in the photocatalytic reaction, and are transferred to the surface. These hydrogen atoms may react with surface O atoms of TiO\(_2\) surfaces and desorb as water,\(^9\) effectively reducing the surface. However, this scenario seems less likely because this reaction typically occurs at a temperature of ~500 K,\(^5\) while our TPD peak appears below room temperature.

**Figure S8:** TPD spectra of m/z = 18 (water) measured on the anatase (101) surface after exposing to different doses of methanol and 30 minutes of UV illumination. The inset shows the corresponding amount of water in monolayers. The values were obtained by integration of the m/z=18 peak up to 280 K (the shoulder above room temperature is attributed to desorption from the sample plate).
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