

Conversion of Methanol on Rutile TiO₂ (110) and
Tungsten Oxide Clusters: 2. The Role of Defects and
Electron Transfer in Bifunctional Oxidic
Photocatalysts

Supplementary Information

Lars Mohrhusen, Jessica Kräuter and Katharina Al-Shamery*

Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Carl-von-Ossietzky Strasse 9-11, D-
26129 Oldenburg, Germany

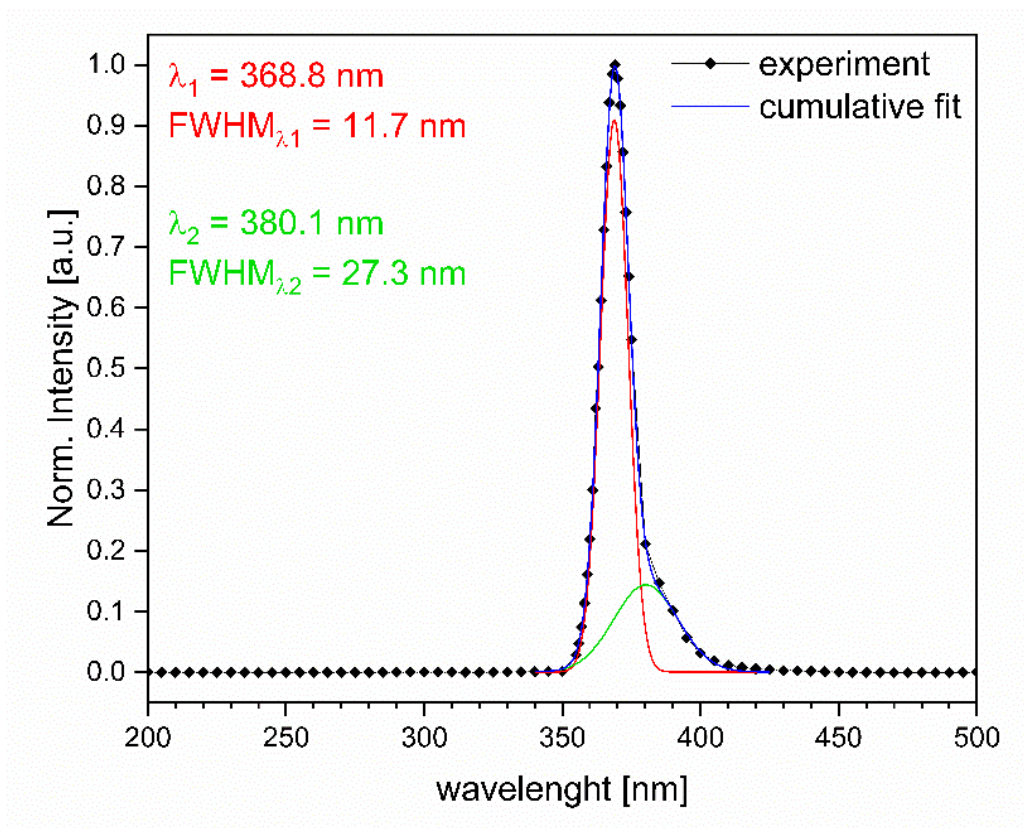


Figure S1. Spectroscopic characterization of the used UV irradiation system, based on a commercial Seoul Viosys UV-LED (CUN6AF4A, nominal wavelength 365 nm, 2.75 W). The data were collected by using the LED as the light source in a Shimadzu UV-120-02 spectrophotometer. The spectrum was fitted using two Gauss functions in Origin2019.

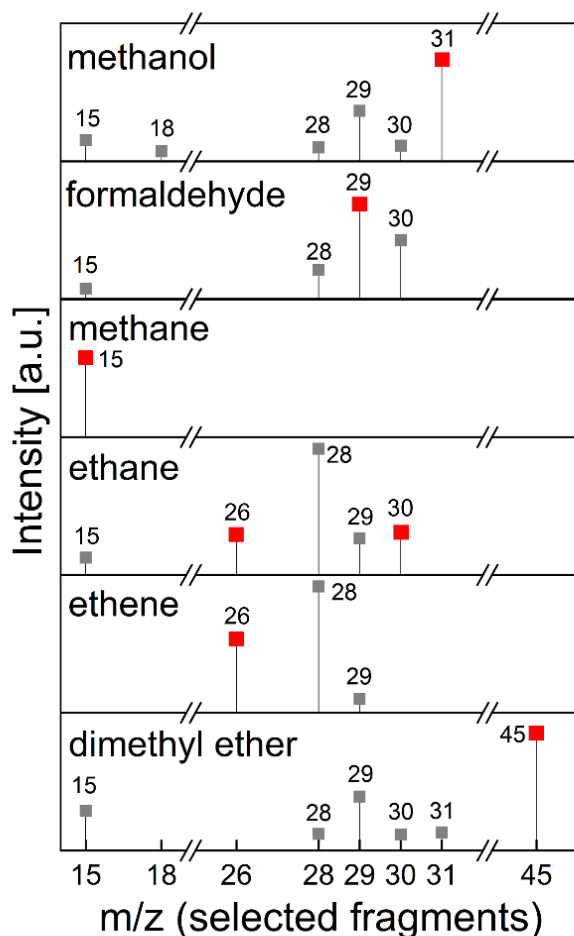


Figure S2. Fragmentation pattern of methanol and observed reaction products extracted from NIST WebBook.¹ Only selected m/z fragments, which are included in the TPR spectra, are shown for better clarity. Fragments with an intensity below 1% are neglected. Also, we have selected certain fragments (shown in red), which allow simple attribution to methanol or reaction products. For full fragmentation patterns, we refer to the NIST WebBook. However, we also have used additional fragments to double-check the drawn conclusions. Note, that the actual fragmentation may differ depending on the ionization conditions as well as the quadrupole analyzer. We have especially noticed that for methanol and formaldehyde, the $m/z = 28$ fragment is much more pronounced than expected from the NIST database.

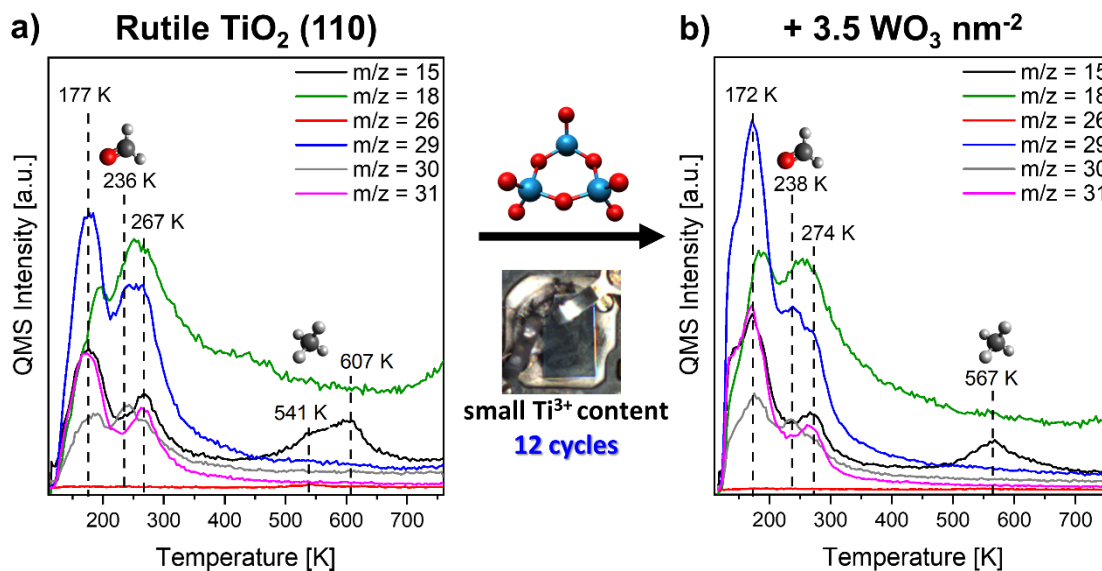


Figure S3: Temperature programmed reaction spectra after UV irradiation (30 minutes, nominal wavelength 365 nm, photon flux $> 1.5 \cdot 10^{16} \text{ s}^{-1} \text{ cm}^{-2}$) of a saturation coverage of methanol with preadsorption of 75 L O₂ at 110 K. Left, obtained from the clean rutile TiO₂ (110) surface and right obtained from the same surface after deposition of 3.5 WO₃ nm⁻² flashed to 880 K before adsorption of oxygen and methanol at 110 K. A rutile sample with a small concentration of bulk defects was used.

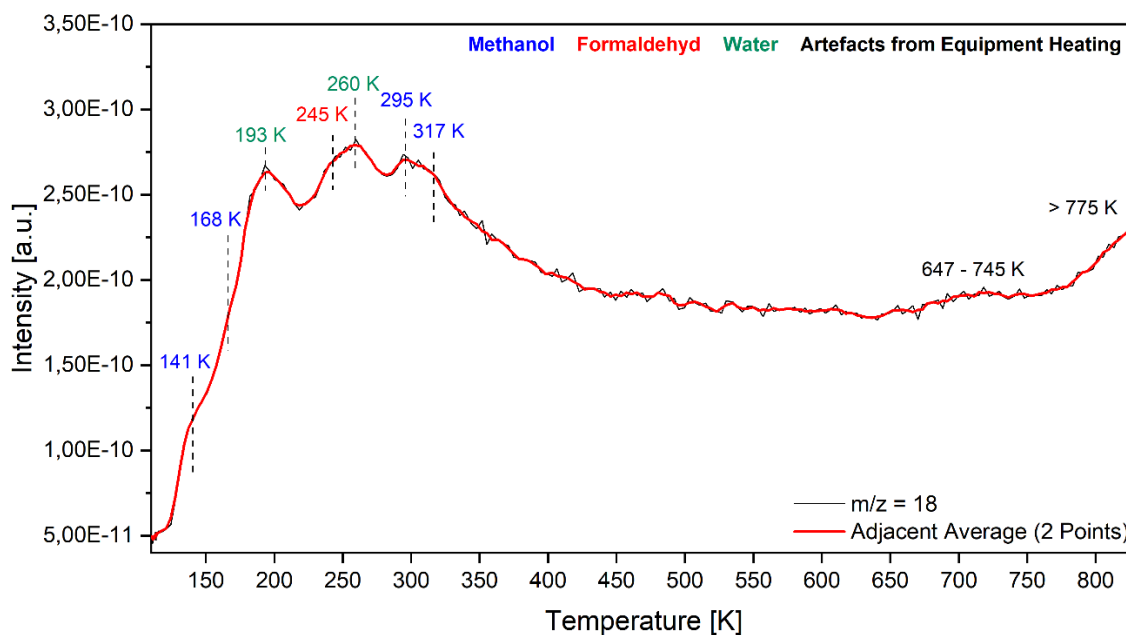


Figure S4: $m/z = 18$ trace obtained from a saturation coverage of methanol, preadsorbed oxygen (75L O₂ at 110 K) and subsequent UV irradiation. The sample with a large amount of Ti³⁺ defects was used (also given in figure 1a in the main text). The water desorption trace is a superposition of contributions from methanol, water formed from surface hydroxyls arising from methanol dissociation and water released during formaldehyde desorption.

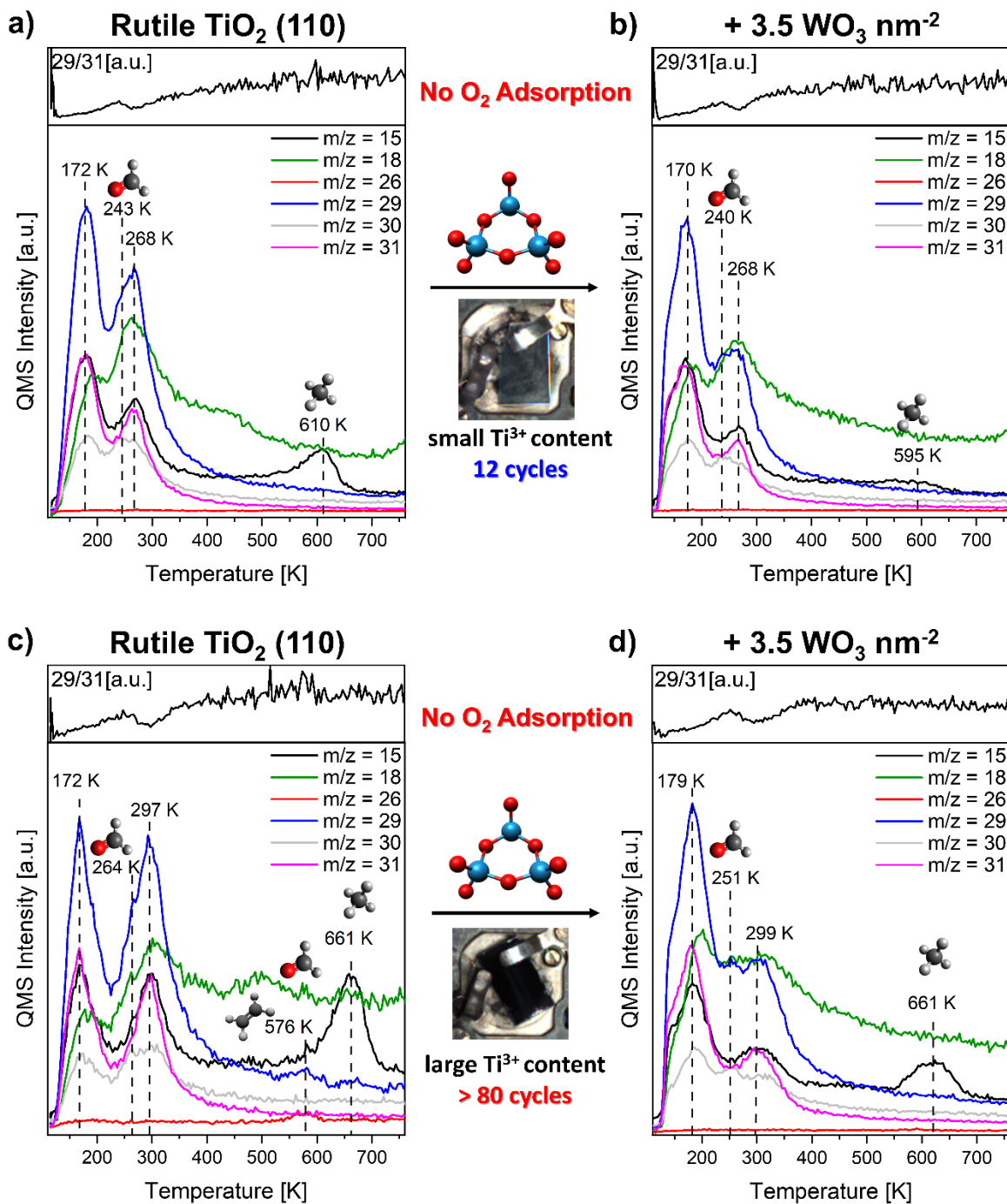


Figure S5: Temperature programmed reaction spectra after UV irradiation (30 minutes, nominal wavelength 365 nm, photon flux $> 1.5 \cdot 10^{16} \text{ s}^{-1} \text{ cm}^{-2}$) of a saturation coverage of methanol **without** preadsorption of oxygen. a and c were obtained from the clean rutile TiO₂ (110) surface, b and d were obtained from the same surfaces after deposition of 3.5 WO₃ nm⁻² flashed to 880 K before adsorption of methanol at 110 K. For all experiments, the ratio of m/z = 29 and 31 is given in the top box. Positive peaks within this ratio trace the desorption of formaldehyde.

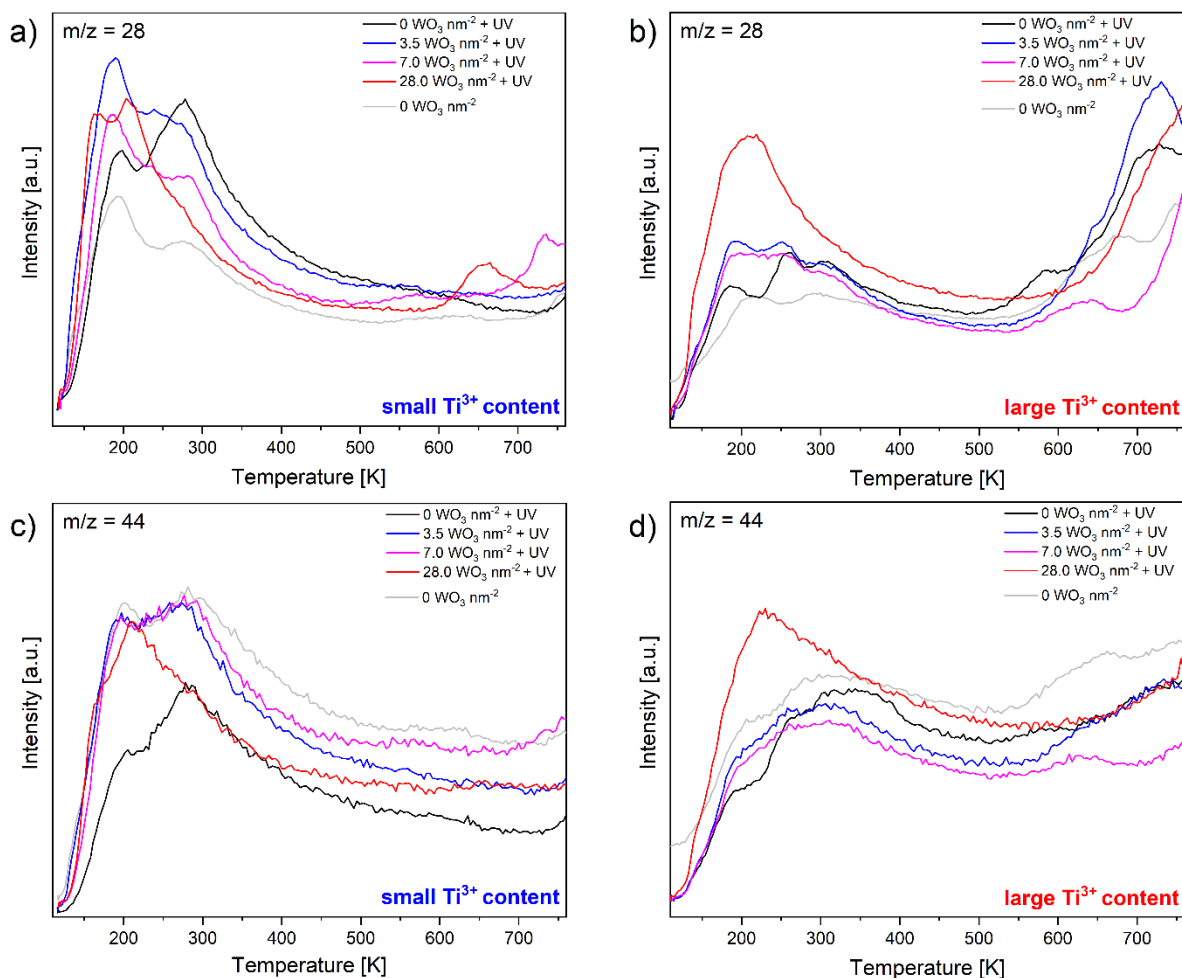


Figure S6: TPRS traces after adsorption of 75 L O₂ and 1 ML methanol and subsequent UV irradiation for $m/z = 28$ (a and b) and $m/z = 44$ (c and d) for large and small Ti³⁺ contents.

One should note that no dominant CO or CO₂ formation was observed for the thermal or photocatalytic reactions, as all intense peaks can be assigned either to other desorption products or to CO and/or CO₂ present and/or formed in the chamber background due to the intense sample heating. However, we cannot fully rule out the total oxidation of methanol under the used conditions.

For the photochemical experiments, the desorption of CO formed during UV irradiation would be expected at 135 K^{2,3}, while CO₂ desorption formed under UV light is expected at 137 K and 166 K.⁴ No such desorption signal were found in our experiments. Also, CO₂ activation appears thermodynamically unfavorable on tungsten oxide clusters based on recent DFT and CCSD(T) studies.⁵ Hence, we conclude, that total oxidation is of minor importance for the photochemical reaction.

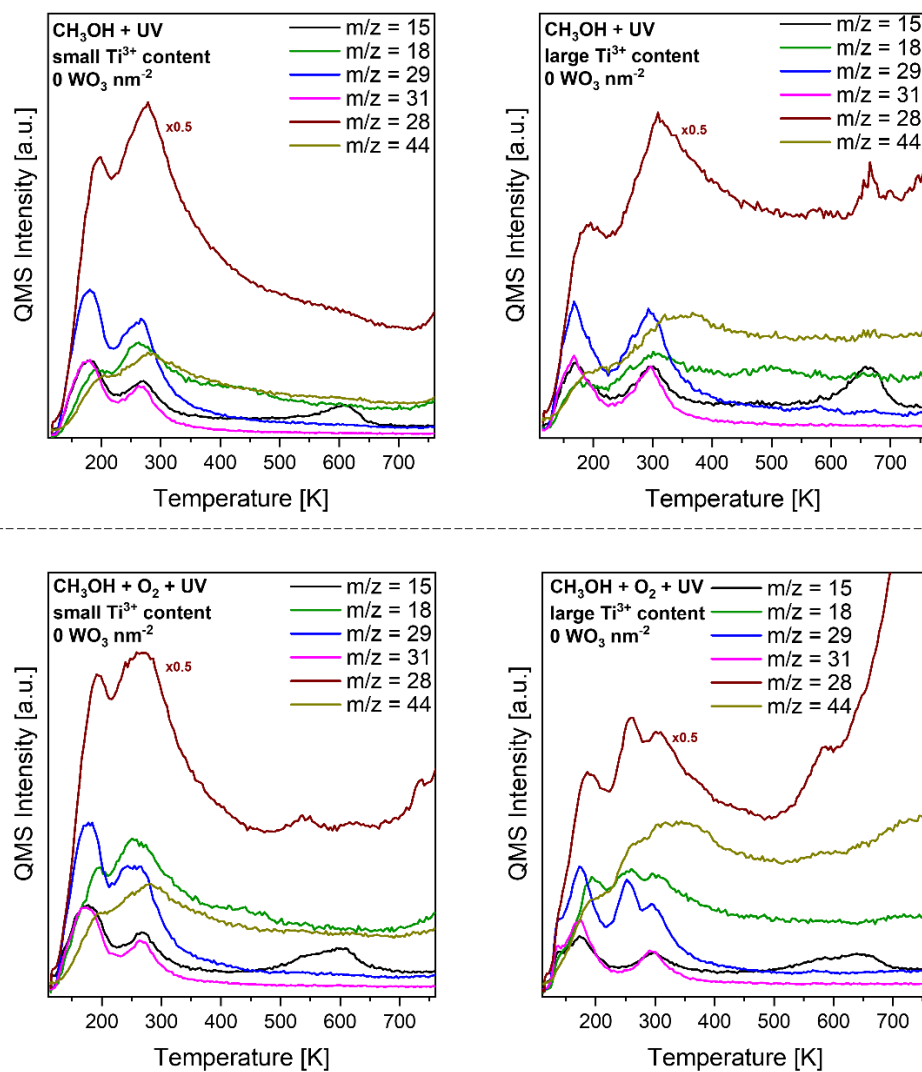


Figure S7: TPRS spectra including $m/z = 28$ and 44 obtained after UV irradiation of a saturation coverage of methanol on pristine TiO_2 with small (left) and large (right) Ti^{3+} density as well as the absence (top) and presence (bottom) of preadsorbed oxygen. One should note that $m/z = 28$ is a strong fragment in product molecules such as methanol, formaldehyde, ethene, ethane.

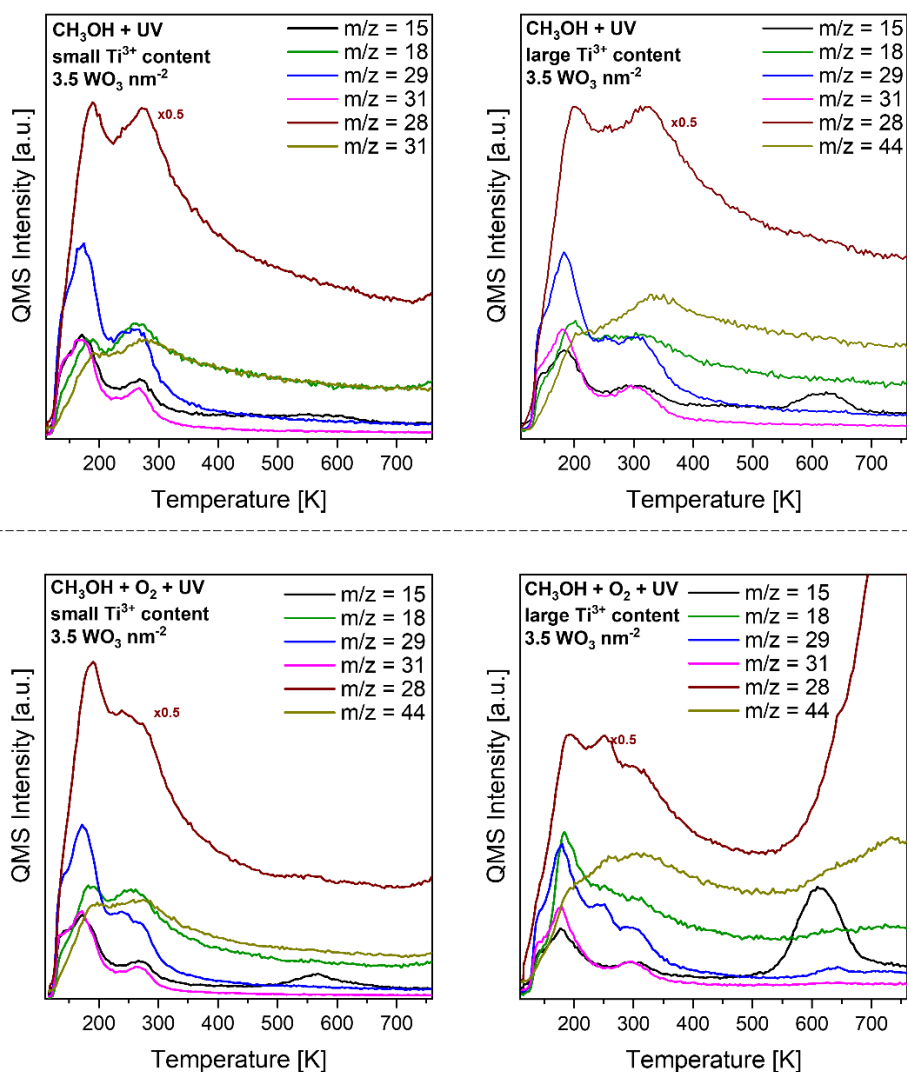


Figure S8: TPRS spectra including $m/z = 28$ and 44 obtained after UV irradiation of a saturation coverage of methanol on pristine TiO_2 with small (left) and large (right) Ti^{3+} density as well as the absence (top) and presence (bottom) of preadsorbed oxygen. Here, tungsten oxide clusters ($3.5 \text{ WO}_3 \text{ nm}^{-2}$) were deposited before use in experiments. One should note that $m/z = 28$ is a strong fragment in product molecules such as methanol, formaldehyde, ethene, ethane.

References

- (1) NIST Mass Spectrometry Data Center; Wallace, W. E. Mass Spectra. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; P.J. Linstrom, Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg MD, 2018. (Accessed February 2019)
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