

Conversion of Methanol on Rutile  $\text{TiO}_2(110)$  and  
Tungsten Oxide Clusters: 1. Population of Defect-  
Dependent Thermal Reaction Pathways

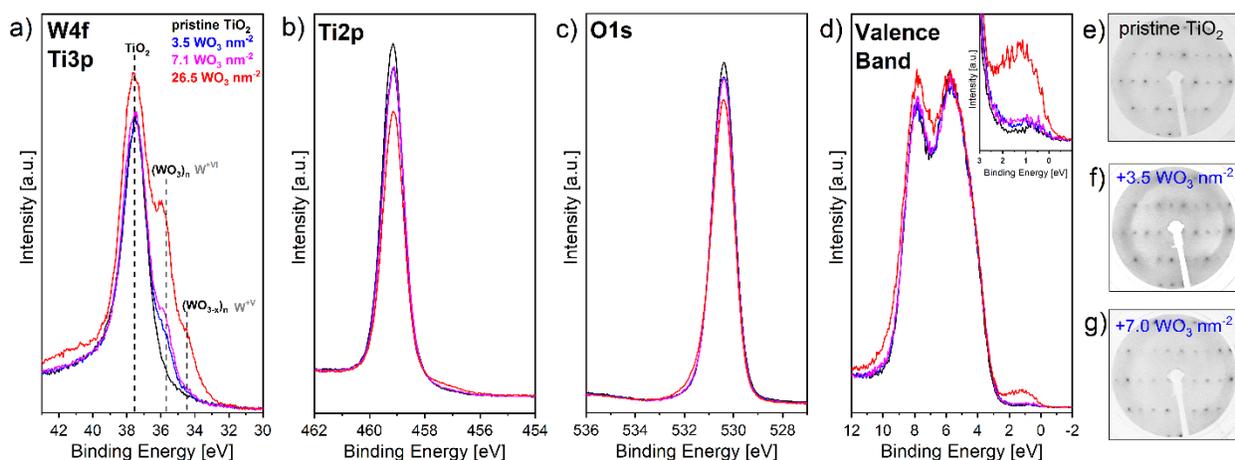
*Supplementary Information*

*Lars Mohrhusen\* and Katharina Al-Shamery*

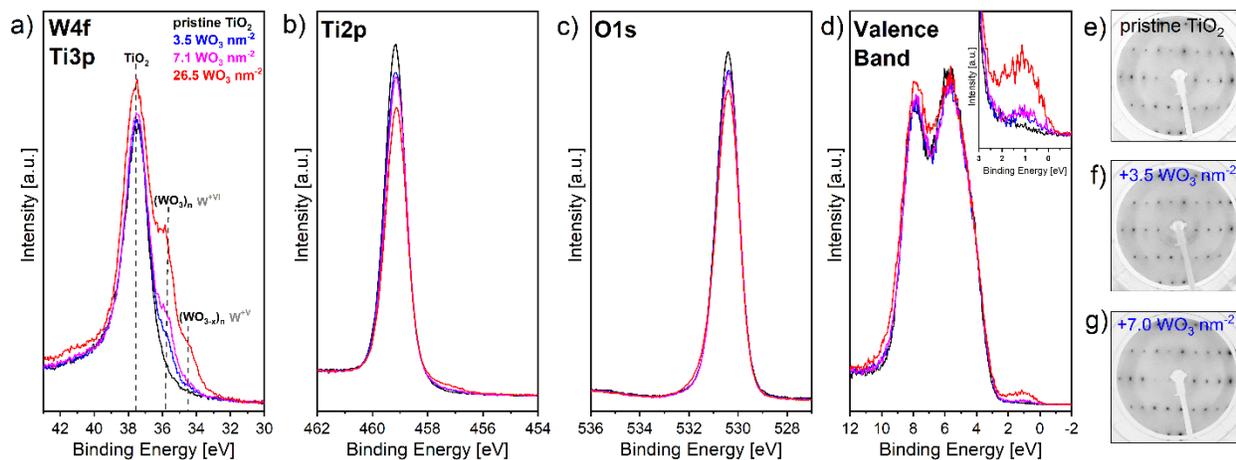
Institute of Chemistry, Carl-von-Ossietzky University of Oldenburg, Carl-von-Ossietzky Strasse 9-11, D-  
26129 Oldenburg, Germany

## Overview on Surface Characterization

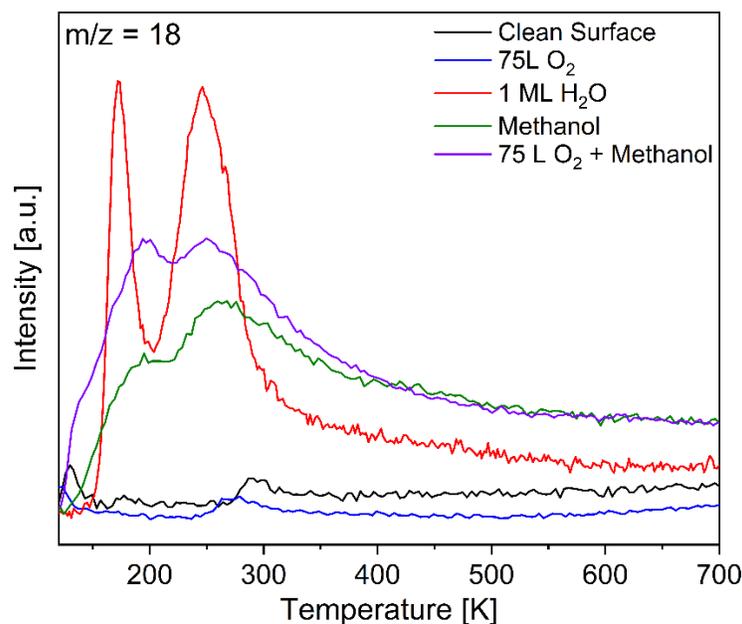
All XPS spectra were obtained from analogously prepared samples using a ThermoFisher ESCALAB 250Xi system (monochromatic Al K $\alpha$  radiation, 10 eV pass energy (except Valence Band spectra (here, 40 eV)), 10 Scans, 100 ms dwell time and step size of 0.05 eV). To exclude spectral shifts due to charging or work function changes, all data were calibrated to the O1s of Rutile TiO<sub>2</sub> (530.4 eV).<sup>1</sup> The major amount of the data presented in figure S1 and S2 is published in a separate paper focusing on the electronic interaction of Ti<sup>3+</sup> interstitials and tungsten oxide clusters as a function of defect density, cluster coverage and temperature.<sup>2</sup> For both figures S1 and S2, we have adapted central results with permission from “L. Mohrhusen, M. Grebien and K. Al-Shamery: Electron Transfer in Oxide-Oxide Cocatalysts: Interaction of Tungsten Oxide Clusters with Ti<sup>3+</sup> States in Rutile TiO<sub>2</sub>, *J. Phys. Chem. C*, **124**, 43, 23661-23673 (2020)” Copyright 2020 American Chemical Society.



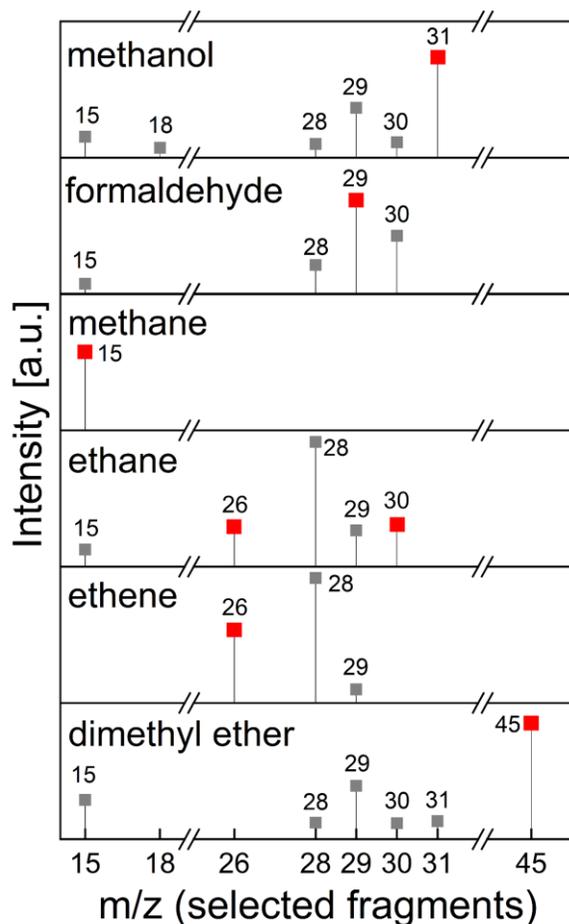
**Figure S1.** Overview on tungsten oxide clusters on a Rutile TiO<sub>2</sub> (110) sample with a large amount of Ti<sup>3+</sup>. a) W4f region which is overlapped by a Ti3p signal. Here, two types of tungsten oxide clusters can be distinguished: Stoichiometric (WO<sub>3</sub>)<sub>n</sub> clusters peaking at 35.8 eV and substoichiometric (WO<sub>3-x</sub>)<sub>n</sub> clusters at 34.5 eV. It is noteworthy, that substoichiometric clusters are only present for high coverages (26.5 WO<sub>3</sub> nm<sup>-2</sup>). b) Ti2p<sub>3/2</sub> region. Around 457.3 eV, the generation of Ti<sup>3+</sup> can be seen. c) O1s region. No signs for a significant surface hydroxylation from the chamber background (expected around 534 eV) were observed. d) Valence Band spectra evidencing the population of in-bandgap-states by generation of Ti<sup>3+</sup> and reduced tungsten oxide clusters. e-g) LEED patterns obtained with tungsten oxide cluster coverages as indicated (169 eV). The 1x1 reconstruction of the rutile surface can be observed in all three cases but slightly blurs with increasing cluster coverage.



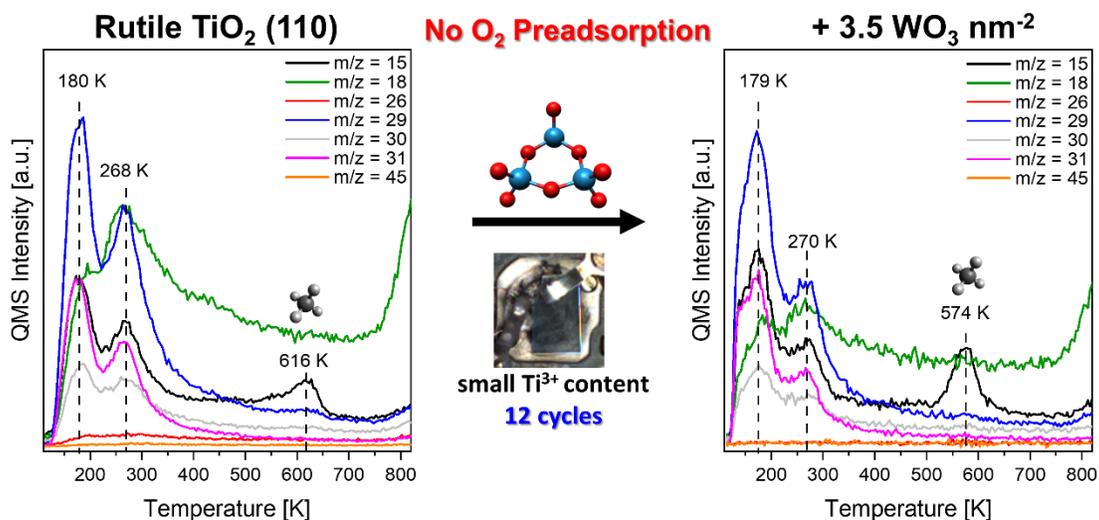
**Figure S2.** Overview on tungsten oxide clusters on a Rutile TiO<sub>2</sub> (110) sample with a small amount of Ti<sup>3+</sup>. Similar results as shown in figure S1 were obtained. a) W4f/Ti3p region. b) Ti2p<sub>3/2</sub> signal. c) O1s region. d) Valence Band. e-g) LEED patterns recorded at 169 eV.



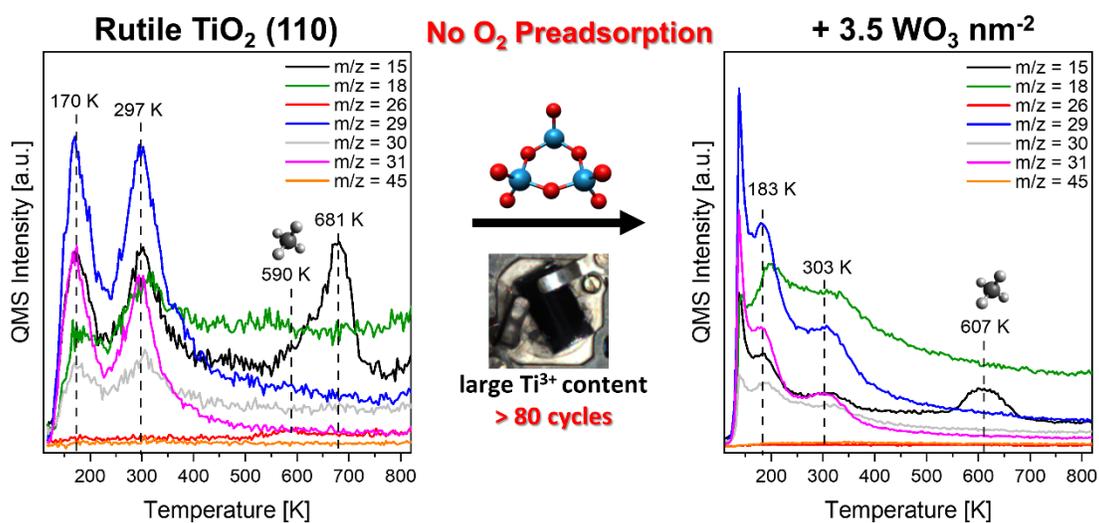
**Figure S3.** m/z = 18 traces recorded in different TPRS experiments using a Rutile TiO<sub>2</sub> (110) sample with a small amount of bulk defects. In comparison to the adsorption of a bilayer of water (blue) and saturation doses of methanol without (green) and with preadsorption of 75 L O<sub>2</sub> (purple), no relevant desorption features are observed for the clean surface (black) and after adsorption of 75 L O<sub>2</sub> at 110 K (blue). Hence, surface hydroxylation from water adsorption from the chamber background does not appear as a relevant issue for our experiments.



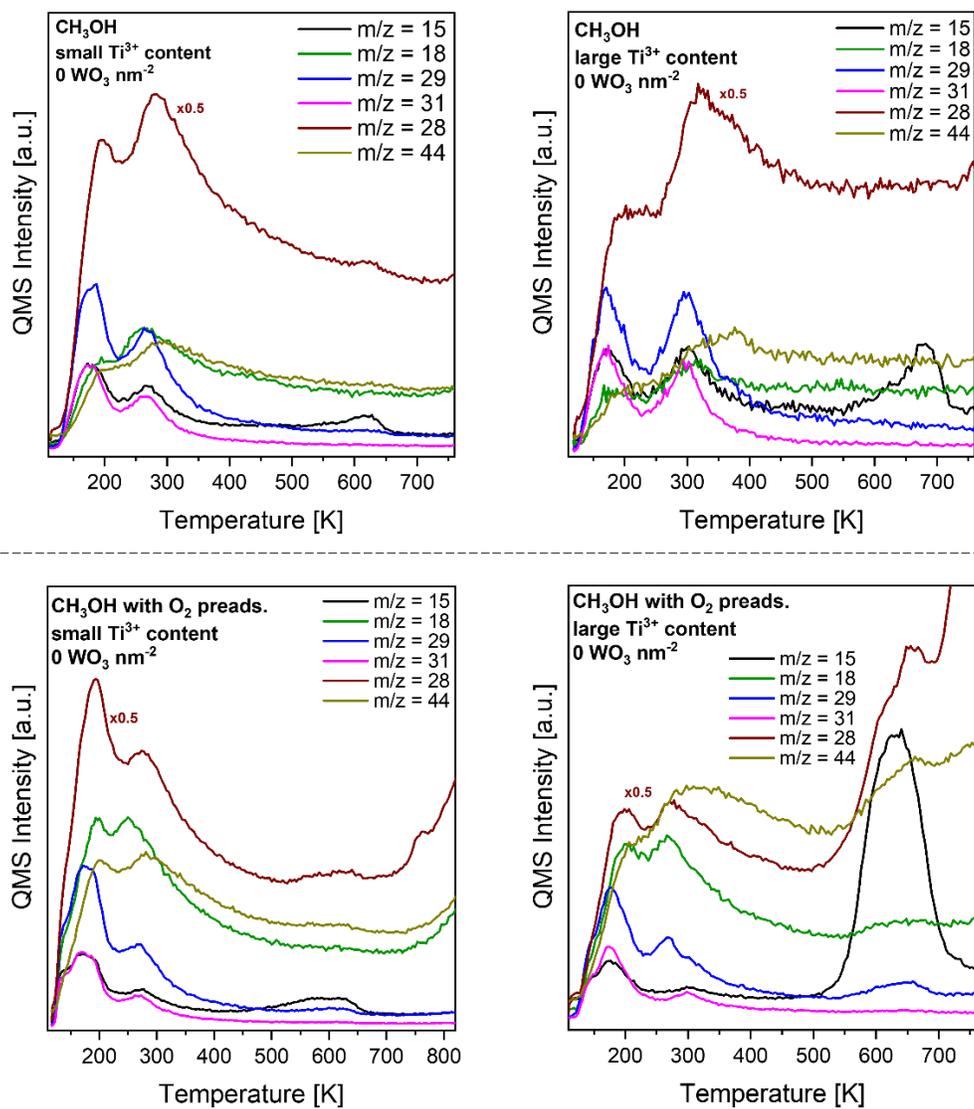
**Figure S4.** Fragmentation pattern of methanol and observed reaction products extracted from NIST WebBook.<sup>3</sup> Only selected  $m/z$  fragments, which are also included in the TPD spectra, are shown for better clarity. Fragments with an intensity below 1% are neglected. Also, we have selected 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.



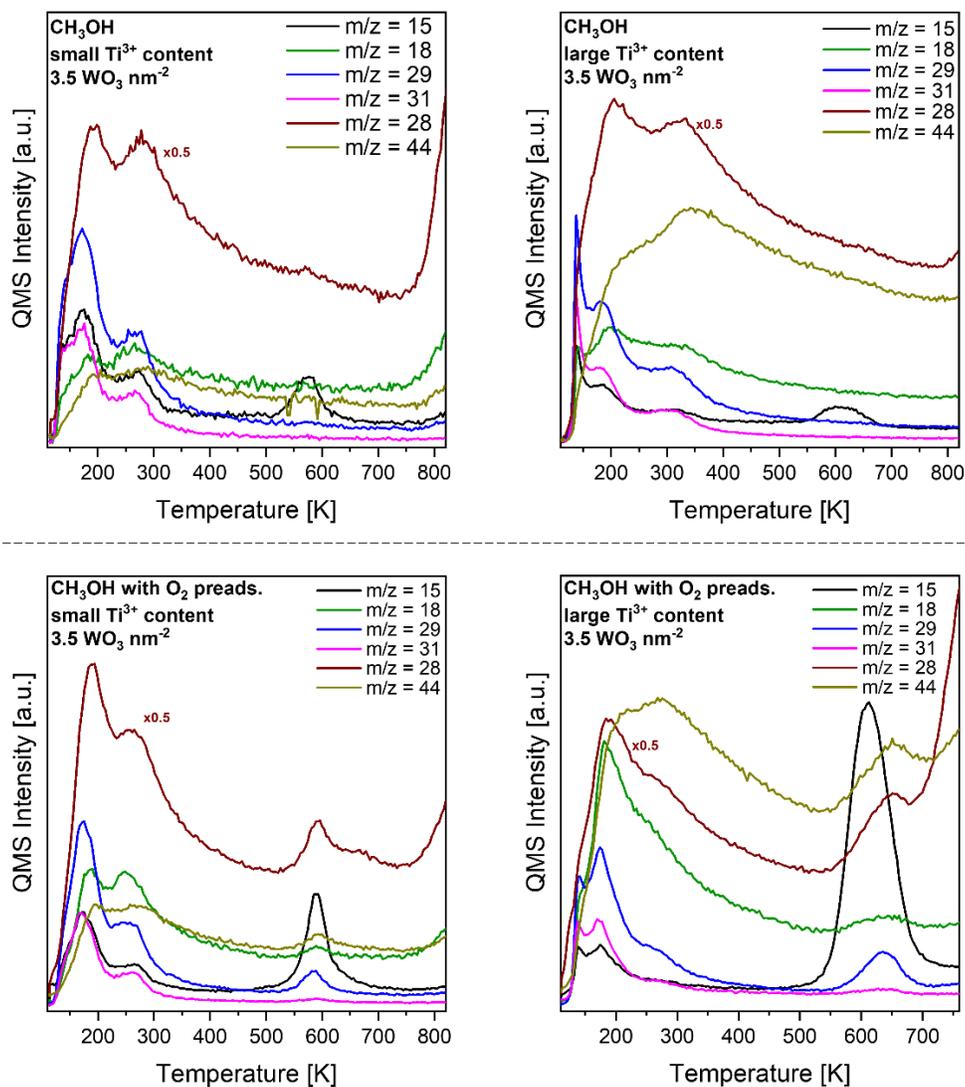
**Figure S5.** Temperature programmed reaction spectra (TPRS) of a saturation coverage of methanol, left, obtained from the pristine rutile TiO<sub>2</sub> (110) surface and right obtained from the same surface after deposition of 3.5 WO<sub>3</sub> nm<sup>-2</sup> flashed to 880 K before adsorption of methanol at 110 K. A rutile sample with a small amount of Ti<sup>3+</sup> was used.



**Figure S6.** Temperature programmed reaction spectra (TPRS) of a saturation coverage of methanol, left, obtained from the pristine rutile TiO<sub>2</sub> (110) surface and right obtained from the same surface after deposition of 3.5 WO<sub>3</sub> nm<sup>-2</sup> flashed to 880 K before adsorption of methanol at 110 K. A rutile sample with a large amount of Ti<sup>3+</sup> was used.



**Figure S7.** TPRS spectra including  $m/z = 28$  and  $44$  obtained after adsorption of a saturation coverage of methanol on pristine  $\text{TiO}_2$  with small (left) and large (right)  $\text{Ti}^{3+}$  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. Therefore, total oxidation is not considered to be dominant for our experiments.



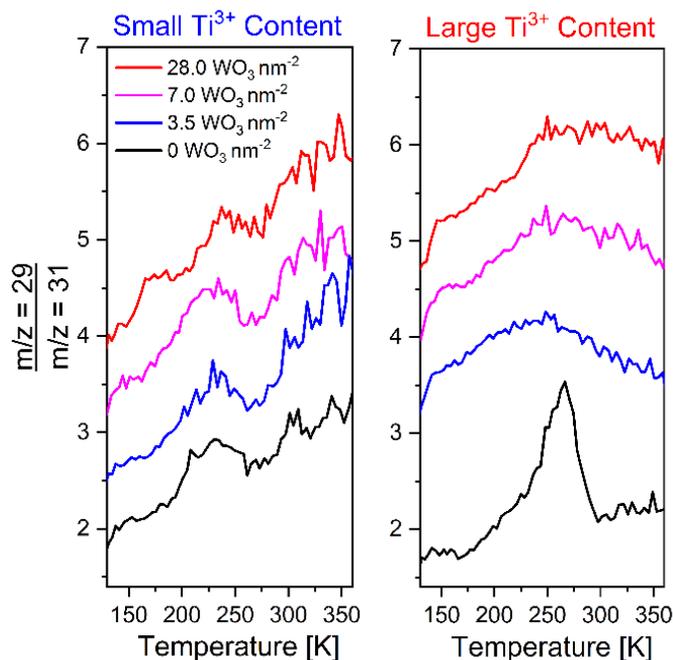
**Figure S8.** TPRS spectra including  $m/z = 28$  and  $44$  obtained after adsorption of a saturation coverage of methanol on  $\text{TiO}_2$  with small (left) and large (right)  $\text{Ti}^{3+}$  density as well as the absence (top) and presence (bottom) of preadsorbed oxygen. Here, tungsten oxide 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. Although a certain  $\text{CO}_2$  formation may appear especially for high  $\text{Ti}^{3+}$  density, total oxidation is not considered to be dominant for our experiments.

**Table S1.** Thermal high temperature formation of methane, monitored by the integral area of the  $m/z = 15$  peak. The percentage change is given compared to the value of pristine  $\text{TiO}_2$  ( $0.0 \text{ WO}_3 \text{ nm}^{-2}$ ).

	HT methane formation 400 – 700 K				HT Methane formation 450 – 700 K			
	Small $\text{Ti}^{3+}$ content				Large $\text{Ti}^{3+}$ content			
Coverage	Area [a.u.]		Peak	FWHM	Area [a.u.]		Peak	FWHM
$0.0 \text{ WO}_3 \text{ nm}^{-2}$	4.38		580 K	123 K	47.29		633 K	106 K
$3.5 \text{ WO}_3 \text{ nm}^{-2}$	8.36	+91%	589 K	51 K	57.53	+22%	609 K	75 K
$7.0 \text{ WO}_3 \text{ nm}^{-2}$	8.51	+94%	590 K	59 K	44.84	-5%	614 K	82 K
$28.0 \text{ WO}_3 \text{ nm}^{-2}$	3.79	-22%	528 K	137 K	6.07	-87%	612 K	104 K

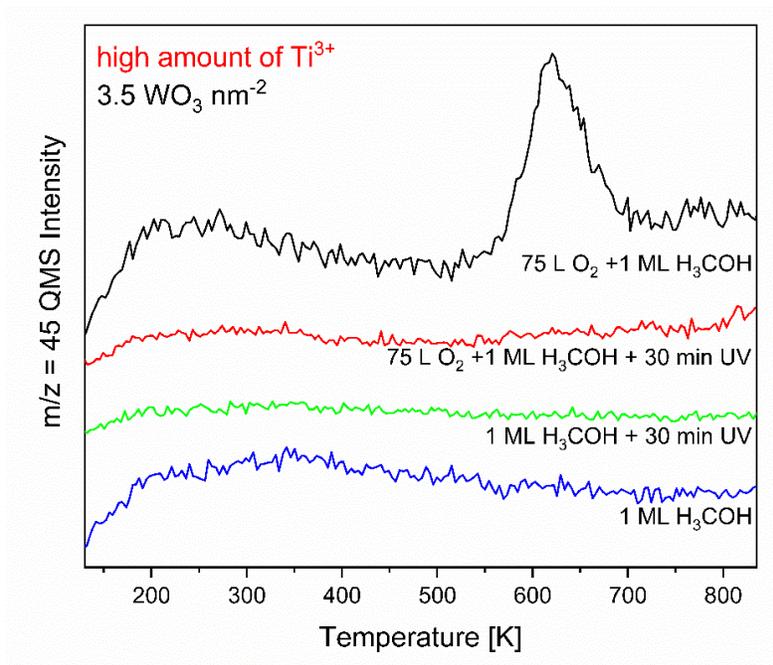
**Table S2.** Low and high temperature formation of formaldehyde, monitored by the integral area of peaks in the  $m/z = 29$  to  $m/z = 31$  ratio. The percentage change is given compared to the value of pristine  $\text{TiO}_2$  ( $0.0 \text{ WO}_3 \text{ nm}^{-2}$ ).

	LT [a.u.] 170 – 320 K		HT [a.u.] 500 – 750 K		Total	
Coverage	High $\text{Ti}^{3+}$ content					
$0.0 \text{ WO}_3 \text{ nm}^{-2}$	72.8		68.8		141.6	
$3.5 \text{ WO}_3 \text{ nm}^{-2}$	41.6	-43%	114.2	+66%	155.8	+10%
$7.0 \text{ WO}_3 \text{ nm}^{-2}$	58.3	-20%	103.5	+51%	161.8	+14%
$28.0 \text{ WO}_3 \text{ nm}^{-2}$	42.2	-42%		-100%	42.2	-70%
Coverage	Low $\text{Ti}^{3+}$ content					
$0.0 \text{ WO}_3 \text{ nm}^{-2}$	20.4		41.2		61.6	
$3.5 \text{ WO}_3 \text{ nm}^{-2}$	21.6	+6%	95.6	+132%	117.2	+90%
$7.0 \text{ WO}_3 \text{ nm}^{-2}$	23.2	+14%	96.4	+134%	119.6	+94%
$28.0 \text{ WO}_3 \text{ nm}^{-2}$	17.5	-14%		-100%	17.5	-72%



**Figure S9.** Ratio of  $m/z = 29$  and  $31$  TPRS traces as obtained from a saturation coverage of methanol with oxygen preadsorption ( $75 \text{ L O}_2$  at  $120 \text{ K}$ ). Positive signals in the  $m/z = 29$  to  $31$  ration are indicating formation of formaldehyde.

One should note that especially for large amounts of  $\text{Ti}^{3+}$ , the LT formaldehyde desorption appears as a very broad feature. As the integration of such features using an appropriate baseline correction is challenging, this may systematically affect the results for these data. However our discussion anyway focusses mainly on the high-temperature formaldehyde formation and therefore is not significantly affected.



**Figure S10.** TPR spectra ( $m/z = 45$ , dimethyl ether) obtained from  $3.5 \text{ WO}_3 \text{ nm}^{-2}$  deposited on  $\text{TiO}_2$  with a high  $\text{Ti}^{3+}$  density. If indicated, the sample was irradiated with UV light (365 nm,  $\text{be} > 1.5 \cdot 10^{16} \text{ s}^{-1} \text{ cm}^{-2}$ , 30 min) before the TPRS measurement. The formation of dimethyl ether at 617 K was exclusively observed for 1 ML methanol with oxygen preadoption.

## References

- (1) Diebold, U.; Madey, T. E.  $\text{TiO}_2$  by XPS. *Surf. Sci. Spectra* **1996**, 4 (3), 227–231. <https://doi.org/10.1116/1.1247794>.
- (2) Mohrhusen, L.; Grebien, M.; Al-Shamery, K. Electron Transfer in Oxide–Oxide Cocatalysts: Interaction of Tungsten Oxide Clusters with  $\text{Ti}^{3+}$  States in Rutile  $\text{TiO}_2$ . *J. Phys. Chem. C* **2020**, 124 (43), 23661–23673. <https://doi.org/10.1021/acs.jpcc.0c06591>.
- (3) 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).