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# Conversion of methanol on rutile TiO<sub>2</sub> (110) and tungsten oxide clusters: 1. population of defect-dependent thermal reaction pathways†

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Tungsten oxide clusters deposited on rutile TiO<sub>2</sub> (110) single crystals were used as a model system for heterogeneous oxide-oxide bifunctional catalysts. The population of different thermal reaction routes in methanol conversion in the presence of preadsorbed oxygen was probed under UHV conditions. By temperature programmed reaction spectroscopy, we have identified three thermal reaction channels, namely the deoxygenation under formation of methane, the partial oxidation forming formaldehyde and the condensation route under desorption of ethane and dimethyl ether. The specific local reaction environment at the oxidic surface was found to be key for the population of the different reaction channels as exhibited by the introduction of Lewis acidic and basic sites (especially (WO<sub>3</sub>)<sub>n</sub> clusters) and available charge carriers such as Ti<sup>3+</sup>. Especially the amount of bulk Ti<sup>3+</sup> interstitials, that can partially transfer charge towards the tungsten oxide clusters at the TiO<sub>2</sub> surface, was found to be a key parameter that enables a relatively high methanol conversion in thermal reactions. It turned out that the deoxygenation is by far the most dominant reaction followed by the partial oxidation. The condensation is observed only in low amounts under special conditions, but is an interesting example for reactivity at defect sites.

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## 1. Introduction

Transition metal oxides, often as mixed compounds, are widely used as non-toxic and well accessible heterogeneous (photo-) catalysts. However, there is little understanding of underlying processes at bifunctional oxide-oxide catalysts. In order to understand key parameters ruling the catalytic activity of such systems, UHV studies on tungsten oxide clusters (WO<sub>3</sub>)<sub>n</sub> deposited on rutile TiO<sub>2</sub> (110) surfaces are presented in this work as a model study. Supported (WO<sub>3</sub>)<sub>n</sub> clusters appear as relevant candidates for thermal and photochemical reactions due to

their relatively high Lewis acidity at the W<sup>6+</sup> centers, combined with the presence of strong Brønsted bases in form of the terminal W=O<sub>t</sub> groups.<sup>1,2</sup> Such clusters have been subject to experimental and theoretical studies of dehydration, dehydrogenation and condensation reactions of alcohols,<sup>3–6</sup> partial oxidations,<sup>2</sup> aldehyde and ketone polymerization<sup>7–9</sup> as well as the decomposition of toxic compounds such as organophosphates.<sup>10</sup>

To study the conversion of alcohols on such systems, we follow the reaction of methanol as a test molecule. Methanol is an important compound in the chemical industry and therefore an interesting model reactant for catalytic conversion.<sup>11,12</sup> The chemistry of methanol and other alcohols on stoichiometric rutile TiO<sub>2</sub> (110) was already in the focus of several studies, especially by the groups of Henderson and Dohnálek.<sup>13–23</sup> In addition, from reports of the group of Madix and our own work it is known that the chemistry of methanol is sensitive to the presence of defects, such as oxygen vacancies or Ti<sup>3+</sup> interstitials.<sup>24–26</sup> Therefore, methanol is a perfect probe molecule for testing the conversion in different reaction pathways involving reduced transition metal oxide centers. In detail, methanol is hardly converted to any products on the defect free stoichiometric rutile TiO<sub>2</sub> (110) surface by simple thermal reactions. In contrast, at least two additional thermal reaction pathways will be populated, if bulk and surface defects are

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† Electronic supplementary information (ESI) available: Overview on surface characterization including XPS and LEED data for tungsten oxide clusters at rutile TiO<sub>2</sub> with a small (Fig. S1) and large (Fig. S2) Ti<sup>3+</sup> density; Fig. S3: additional *m/z* = 18 traces; Fig. S4: fragmentation pattern obtained from NIST database of methanol and possible reaction products; Fig. S5 and S6: additional TPR spectra for methanol on TiO<sub>2</sub> with and without tungsten oxide clusters in the absence of additional oxygen; Fig. S7 and S8: additional TPR spectra for *m/z* = 28 and 44 obtained from methanol on TiO<sub>2</sub> with (S7) and without (S8) tungsten oxide clusters; Tables S1 and S2: semi-quantitative analysis changes of the thermal methane (Table S1) and formaldehyde (Table S2) formation; Fig. S9: ratio of *m/z* = 29 and 31 for the LT formaldehyde formation; Fig. S10: additional TPR spectra for *m/z* = 45 (dimethyl ether). See DOI: 10.1039/d1cp01175h



present: the deoxygenation pathway forming mainly methane and, in the presence of oxygen, the partial oxidation to formaldehyde. In consensus with earlier studies,<sup>22,24,25,27</sup> we have recently shown in a temperature programmed reaction spectroscopy (TPRS) and Fourier-transformation infrared reflection-absorption spectroscopy (FT-IRRAS) based study, that the methane formation proceeds *via* a methoxy intermediate, while formaldehyde desorbs from a dioxomethylene-like structure at the surface.<sup>26</sup>

While the chemistry of alcohols on pristine TiO<sub>2</sub> is in the focus of a number of studies, alcohol conversion at tungsten oxide clusters on top of rutile TiO<sub>2</sub> surfaces has not been studied so intensively in comparison. However, several parameters relevant for alcohol conversion at tungsten oxide clusters on rutile TiO<sub>2</sub> (110) have been investigated, predominantly by the group of Dohnálek. This includes effects by the aliphatic chain,<sup>4,28</sup> binding to supports and cluster deactivation thereby,<sup>5,6,29</sup> as well as the impact of altered Lewis acidic sites on activation barriers.<sup>3</sup> Nevertheless, in case of rutile TiO<sub>2</sub>, point defects such as Ti<sup>3+</sup> interstitials drastically influence chemical reactions, such as O<sub>2</sub> activation,<sup>30–32</sup> C–C coupling<sup>33–35</sup> or alcohol (photo-) conversion.<sup>24–26,36,37</sup> Therefore it is surprising, that the role of defects in oxide-oxide systems involving tungsten oxide at TiO<sub>2</sub> has not been addressed before. That is one aim of this work.

Recently, we demonstrated that Ti<sup>3+</sup> point defects can induce a temperature dependent charge transfer between (WO<sub>3</sub>)<sub>n</sub> clusters and an underlying rutile TiO<sub>2</sub> (110) substrate.<sup>38</sup> As surface charges are known to have a substantial impact on the chemical reactivity we present a systematic study of thermal methanol conversion with oxygen as a function of the Ti<sup>3+</sup> content as well as the (WO<sub>3</sub>)<sub>n</sub> cluster coverage as a model system to understand the conversion of alcohols on defect rich oxide-oxide systems.

## 2. Experimental

All results were obtained using a home-built UHV chamber (base pressure below 10<sup>−10</sup> mbar) equipped with a commercial low energy electron diffraction (LEED) setup (OCI Vacuum Microengineering, BDL800IR-LMX-ISIJ), a quadrupole mass spectrometer equipped with a Feulner-cup for temperature programmed reaction spectroscopy (TPRS) (Pfeiffer Vacuum Prisma TM QMA 200) and an argon ion source. Moreover, the system allows adsorption of high purity compounds *via* a directional pinhole doser or chamber backfilling *via* a leak valve. In this work, oxygen (Air liquide, 99.999%), argon (Air liquide, 99.999%) and methanol (Fisher Scientific, 99.99% (HPLC grade)) were used. Methanol was cleaned before use by at least five freeze-pump-thaw cycles. The deposition of tungsten oxide clusters from WO<sub>3</sub> powder (Sigma Aldrich, purity 99.995%) was done at room temperature in an individual evaporation chamber (allowing *in vacuo* sample transfer at a base pressure below 10<sup>−9</sup> mbar) using a Focus EFM3 electron beam evaporator equipped with a molybdenum crucible with an alumina inset with identical devices and conditions as described elsewhere.<sup>38</sup> Since the sample preparation was

identically conducted using the same conditions, devices, parameters and evaporating materials, the detailed surface characterization with respect to thermal and coverage effects involving charge transfer with Ti<sup>3+</sup> point defects may be directly transferred to the experiments within this work. For clarity, we present a collection of central aspects in the ESI<sup>†</sup> (Fig. S1 and S2). After deposition and before use in TPRS experiments, the clusters were initially heated to 880 K (2 K s<sup>−1</sup>, keeping 880 K for 1 minute) to remove possible residual adsorbates from the cluster evaporation process.

We have used a home-built sample holder,<sup>39</sup> which can be transferred *in vacuo* to a liquid nitrogen cooled stage, allowing experiments between 110 K and 900 K. The sample temperature was measured *via* a K-type thermocouple (CHAL-005, Omega Engineering, approx. error 0.75%) glued inside a tiny hole at the side of the sample (Ceramabond 569, Aremco). For all experiments, rutile TiO<sub>2</sub> (110) single crystals (10 × 10 × 1 mm<sup>3</sup>, Surface Net GmbH) were used, which were initially cleaned by sonification in isopropanol before use.

Clean (110)(1 × 1) reconstructed surfaces were produced by repeated cycles of argon ion bombardment (20 minutes at 300 K, 1 keV, 2 μA cm<sup>−2</sup> at 5 × 10<sup>−5</sup> mbar argon background pressure) and subsequent annealing at 880 K for 15 minutes in UHV. This procedure leads to a partial reduction of the titania sample. Hence, this will be called one “reduction cycle” in the following. One should note, that a certain amount of argon (typically <0.9 at% based on X-ray photoelectron spectroscopy (XPS)) is present in titania surfaces from this very common sample preparation protocol.<sup>40</sup> The surface quality was frequently checked by LEED. All TPR spectra were recorded using a temperature ramp of 2 K s<sup>−1</sup>. Based on earlier recorded XPS data<sup>38</sup> and comparison of different *m/z* = 18 TPRS traces, we exclude a relevant impact of surface hydroxylation prior to adsorption of methanol by water adsorption from the chamber background (ESI,† Fig S3).

## 3. Results

In the following, we present the conversion of methanol with oxygen preadsorption (75 L O<sub>2</sub> at 110 K) in thermal reactions. All experiments were performed as a function of the tungsten oxide cluster coverage as well as the amount of bulk Ti<sup>3+</sup> interstitials. To clearly differentiate between the TiO<sub>2</sub> surfaces with and without tungsten oxide clusters, we shall refer to the “pristine TiO<sub>2</sub>” surface in the following for absence of tungsten oxide, even if (sub-)surface defects of course are already a variation compared to stoichiometric TiO<sub>2</sub>.

In order to produce mixed oxide systems, tungsten oxide clusters can be prepared by evaporation of bulk WO<sub>3</sub> for example from effusion cells at temperatures around 1120–1300 K. By this way, (WO<sub>3</sub>)<sub>n</sub> clusters with *n* = 1, 2, 3, ... are formed, with *n* = 3 being the dominant compound.<sup>41–45</sup> In our case, an electron beam evaporator is used to deposit such clusters onto the rutile (110) surface. We have characterized the surface of such a model system for a bifunctional oxidic



catalyst by means of mainly XPS but also LEED and probe molecule temperature-programmed desorption (TPD) spectroscopy in a recently published report.<sup>38</sup> Here, we use the identical devices under the same conditions with comparable materials as this paper is the second in a series of three consecutive papers.<sup>37,38</sup> Therefore, in this case, the surface characterization may be directly transferred from our previously published results. Since we do not want to reproduce all details here, we will give a brief overview and refer to central aspects in the original publication<sup>38</sup> and the ESI† (Fig. S1 and S2):

1. Oxidation state of the produced clusters: stoichiometric  $(\text{WO}_3)_n$  clusters are the dominant compound in the oxide vapor, but in addition substoichiometric, oxygen deficient  $(\text{WO}_{3-x})_n$  clusters with  $0 < x < 1$  are produced. By electron transfer from these clusters towards the  $\text{TiO}_2$  substrate, the first layer of clusters becomes reoxidized under formation of  $\text{Ti}^{3+}$  sites in the near subsurface. Hence, coverages up to  $7.1 \text{ WO}_3 \text{ nm}^{-2}$  lead to a layer of stoichiometric  $(\text{WO}_3)_n$  clusters in direct interaction with the surface possibly *via* Ti-O-W like features. On  $\text{TiO}_2$ , substoichiometric  $(\text{WO}_{3-x})_n$  clusters were only observed for coverages above  $7.1 \text{ WO}_3 \text{ nm}^{-2}$ .

2. Accessibility of  $\text{Ti}_{5c}$  sites: the amount of accessible five-fold coordinated  $\text{Ti}_{5c}$  sites is decreased with increasing cluster coverage, but a significant part is still available at higher coverage based on water and CO TPD. Thus, the clusters appear as an unordered, open layer growing in a three-dimensional motif.

3. Equilibrium-like  $\text{Ti}^{3+}$  content: the  $\text{Ti}^{3+}$  content reaches an equilibrium around 6–7%  $\text{Ti}^{3+}/\text{Ti}^{4+}$  based on Ti2p XPS for deposition of a monolayer of clusters (up to  $7.1 \text{ WO}_3 \text{ nm}^{-2}$ ) roughly independent of the initial  $\text{Ti}^{3+}$  content. Thus,  $\text{Ti}^{3+}$  formed by electron transfer from substoichiometric clusters stays in the near subsurface in case of low bulk  $\text{Ti}^{3+}$  density, while such states partially disappear into the bulk likely by diffusion in case of high  $\text{Ti}^{3+}$  bulk content.

4. High-temperature accumulation of  $\text{Ti}^{3+}$  and electron transfer towards the clusters: in temperature dependent experiments using X-ray photoelectron spectroscopy (XPS), the clusters appeared very stable on  $\text{TiO}_2$  up to 900 K. However, for titania samples with a large amount of bulk  $\text{Ti}^{3+}$ , an accumulation of  $\text{Ti}^{3+}$  interstitials near the surface was observed between 500 and 800 K. By the appearance of a new W4f species in this temperature range, we have suggested the possible formation of an anionic  $[(\text{WO}_3)_n]^{2-}$ -like species by electron transfer from  $\text{Ti}^{3+}$  in these cases. This is also in line with several predictions from DFT-based studies.<sup>1,8,46,47</sup>

### 3.1 Defect-dependent thermal conversion of methanol

At this point, the thermal chemistry of methanol at a mixed oxide-oxide catalyst consisting of tungsten oxide clusters at rutile  $\text{TiO}_2$  shall be presented. To examine the impact of defects, all experiments were carried out using  $\text{TiO}_2$  substrates with a small (light blue, 10–15 reduction cycles,  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio < 4.2%) and large  $\text{Ti}^{3+}$  content (dark blue, > 80 reduction cycles,  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio > 7.5%). While we have not measured XPS here, we calculated the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio from Ti2p spectrum deconvolution of samples that were analogously prepared with a similar number of reduction cycles under the same conditions in our group.<sup>38</sup>

The TPR spectra obtained after preadsorption of 75 L  $\text{O}_2$  and a saturation coverage of methanol at 110 K are shown in Fig. 1, left for the pristine rutile  $\text{TiO}_2$  (110) surface with a small amount of bulk  $\text{Ti}^{3+}$ , right for a cluster coverage of  $3.5 \text{ WO}_3 \text{ nm}^{-2}$  on top.

For the pristine titania surface, four relevant desorption features can be observed at 144 K, 177 K, 263 K and in the range of 571–624 K. In accordance with earlier publications, we attribute all three low temperature features (144 K, 177 K and 263 K) to the molecular desorption of unconverted methanol. With respect to the fragmentation pattern<sup>48</sup> (Fig. S4 in the ESI†),

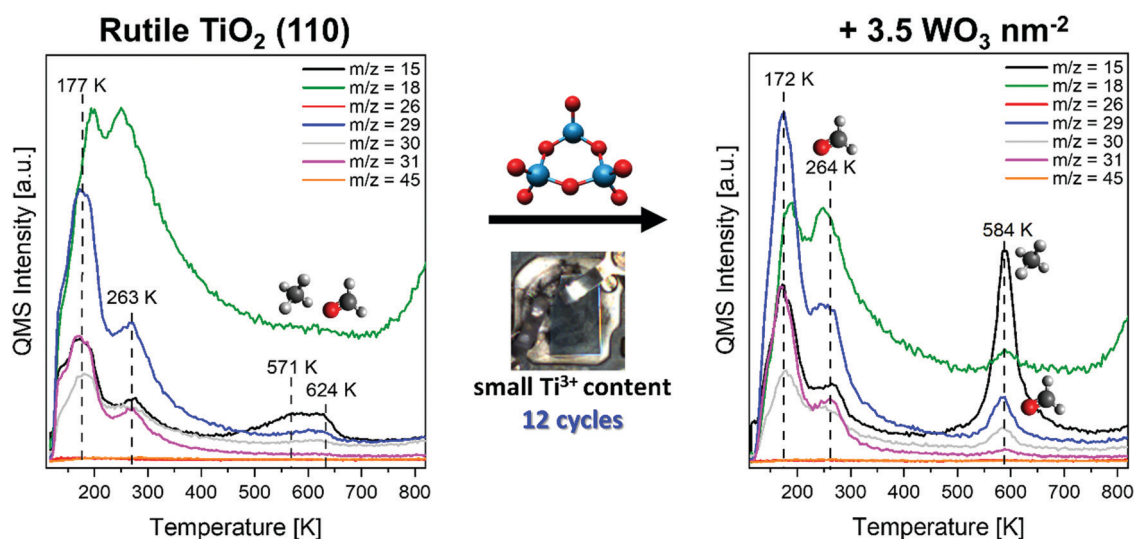


Fig. 1 Temperature programmed reaction spectra (TPRS) of a saturation coverage of methanol with preadsorption of 75 L  $\text{O}_2$  at 110 K. Left, obtained from the pristine rutile  $\text{TiO}_2$  (110) surface. Right, obtained from the same surface after deposition of  $3.5 \text{ WO}_3 \text{ nm}^{-2}$  flashed to 880 K before adsorption of methanol and oxygen at 110 K. A rutile sample with a small amount of  $\text{Ti}^{3+}$  was used.



**Table 1** List of selected  $m/z$  traces according to Fig. 1 and 2. Major and minor contributors are given with the respective fragments. Characteristic traces that can be used to identify the respective molecule are labeled in bold letters. Anyway, it is usually necessary to review more than one  $m/z$  trace to surely identify the desorbing compound. Moreover, interference with other traces due to the natural isotopic distribution (especially  $^{13}\text{C}$  which accounts for approximately 1% of the overall amount of carbon) is mostly neglected for the table for clarity. The concordant fragmentation patterns are to be found in Fig. S4 (ESI)<sup>48</sup>

$m/z$	Major contributor	Fragments	Minor contributor	Fragments
15	<b>Methane</b>	$\text{CH}_3, (^{13}\text{CH}_2)$	Ethane	$\text{CH}_3, (^{13}\text{CH}_2)$
	Methanol	$\text{CH}_3, (^{13}\text{CH}_2)$	Formaldehyde	$^{13}\text{CH}_2$
	Dimethyl ether	$\text{CH}_3, (^{13}\text{CH}_2)$		
18	<b>Water</b>	$\text{H}_2\text{O}$	Methanol	$\text{H}_2\text{O}^a$
26	<b>Ethene</b>	$\text{HCCH}, \text{H}_2\text{CC}$	—	—
	<b>Ethane</b>	$\text{HCCH}, \text{H}_2\text{CC}$		
29	Methanol	HCO	Ethene	$\text{H}_2^{13}\text{CCH}_2$
	<b>Formaldehyde</b>	HCO		
	Ethane	$\text{H}_3\text{CCH}_2, (\text{H}_2^{13}\text{CCH}_2)$		
	Dimethyl ether	HCO		
30	Formaldehyde	$\text{H}_2\text{CO}$	Dimethyl ether	$\text{H}_2\text{CO}$
	Methanol	$\text{H}_2\text{CO}, \text{HCOH}$		
31	<b>Ethane</b>	$\text{H}_3\text{CCH}_3$		
	<b>Methanol</b>	$\text{H}_3\text{CO}, (\text{H}_2\text{COH})$	Dimethyl ether	$\text{H}_3\text{CO}$
45	<b>Dimethyl ether</b>	$\text{H}_2\text{COCH}_3$	—	—

<sup>a</sup>  $\text{H}_2\text{O}$  is not a direct fragment of methanol, but can be detected in traces likely arising from recombination in the mass spectrometer.

we consequently observe signals at these temperatures in  $m/z = 15, 29, 30$  and  $31$ , but not in  $26$  or  $45$  (Table 1).

Especially the low temperature desorption signals are already well discussed in the literature,<sup>16,24,26</sup> so we can easily assign them to methanol desorption from  $\text{Ti}_{5c}$  centers peaking at 263 K, methanol desorption from bridging oxygen atoms adsorbed *via* hydrogen bonds at 177 K and weak multilayer desorption at 144 K. One should note, that recombination of dissociated methanol (methoxy fragments) with the corresponding surface hydroxyl groups also contributes to the desorption of methanol at 263 K. The coverage shown here is the lowest coverage, that exhibits a saturated species at 177 K and hence first little shoulders for the multilayer desorption. In this situation, all adsorption sites at the surface ( $\text{Ti}_{5c}$  and  $\text{O}_{br}$  sites) are covered by methanol. Despite the fact, that traces of a methanol multilayer may be present, we shall call this a saturation coverage of methanol in the following. Thus, we will not further discuss this little shoulder, as it is assigned to methanol multilayer desorption at similar temperatures (141–145 K) in all cases of appearance. While in the low temperature regime no significant methanol conversion can be observed, desorption of methane and formaldehyde is detected in small amounts in two overlapping features at 571 K and 624 K ( $m/z = 15$  and  $29, 30$  respectively, while signals in  $m/z = 31$  are absent). This is in accordance with results from earlier reports.<sup>26</sup>

Since the desorption of water is the most important way to remove hydrogen from the surface yielding the reactive

methoxy-species, we further emphasize the  $m/z = 18$  trace. This turned out to be a superposition of different contributions. First, methanol itself can contribute to the  $m/z = 18$  fragment according to the fragmentation pattern (Table 1 and Fig. S4 in the ESI<sup>†</sup>). More important, water can be formed from surface hydroxyls arising from OH dissociation under formation of methoxy fragments. This water desorbs in well-known desorption features around 180 K (water hydrogen bonded to  $\text{O}_{br}$ ) and 265 K (desorption from  $\text{Ti}_{5c}$  sites). Accordingly, the desorption features around 175 K (arising from methanol) are shifted in comparison to the  $m/z = 18$  trace (water). In addition, water is released during the formation of formaldehyde due to the necessary C–H dissociation (for example around 585 K after  $(\text{WO}_3)_n$  cluster deposition). Finally, at the high-temperature end of our experiments, frequently also water desorption from parts of our equipment due to partial heatup may occur (*e.g.* Fig. 1 above 750 K). It is noteworthy that surface hydroxylation from water adsorption from the chamber background does not appear as a relevant issue based on earlier XPS experiments<sup>38</sup> and comparison of different  $m/z = 18$  TPRS traces (ESI<sup>†</sup>, Fig. S3).

After the deposition of  $3.5 \text{ WO}_3 \text{ nm}^{-2}$  at this low reduced titania surface, we still observe the desorption of unreacted methanol from  $\text{Ti}_{5c}$  at 264 K as well as from bridging oxygen atoms at 172 K. The desorption temperatures appear roughly unchanged for both features. However, methanol desorption from the bridging oxygen atoms of the tungsten oxide clusters may appear at a similar temperature as for bridging oxygens at titania. But, compared to pristine  $\text{TiO}_2$ , more methanol is converted to other products, especially for the high-temperature reactions: here, the two features observed on pristine  $\text{TiO}_2$  are replaced by a more intense formation of methane ( $m/z = 15$ , dominant) and formaldehyde ( $m/z = 29$  and  $30$ , less than methane) exhibiting a relatively narrow desorption feature at 584 K. One should note, that this is significantly shifted to lower temperatures especially compared to the second high temperature desorption feature peaking at 624 K on pure  $\text{TiO}_2$ . A very weak signal for  $m/z = 31$  at this temperature indicates, that a little fraction of methanol also desorbs during this reaction.

In brief, the  $\text{TiO}_2$  substrate appears more reactive after cluster deposition, similar to a higher reduced one. This suits well with our earlier finding, that  $\text{Ti}^{3+}$  sites are generated by deposition of tungsten oxide and subsequent charge transfer from substoichiometric tungsten oxide clusters towards the  $\text{TiO}_2$  crystal.<sup>38</sup> We will discuss this at a later point in more detail.

The titania surface with a high defect density appears much more reactive. In Fig. 2, left side, TPR spectra are shown recorded after adsorption of oxygen followed by a saturation coverage of methanol on a  $\text{TiO}_2$  substrate with a high  $\text{Ti}^{3+}$  density. Additional to the typical desorption features of unreacted methanol from bridging oxygens (177 K) and  $\text{Ti}_{5c}$  sites (here 295 K), a significant amount of formaldehyde is formed mainly in a low-temperature reaction peaking at 263 K (no signal at  $m/z = 15$  and  $31$ ) as well as to some extent in a high-temperature reaction around 640 K (signals at  $m/z = 30$  and  $29$ , but not at  $31$ ). However, the dominant product is



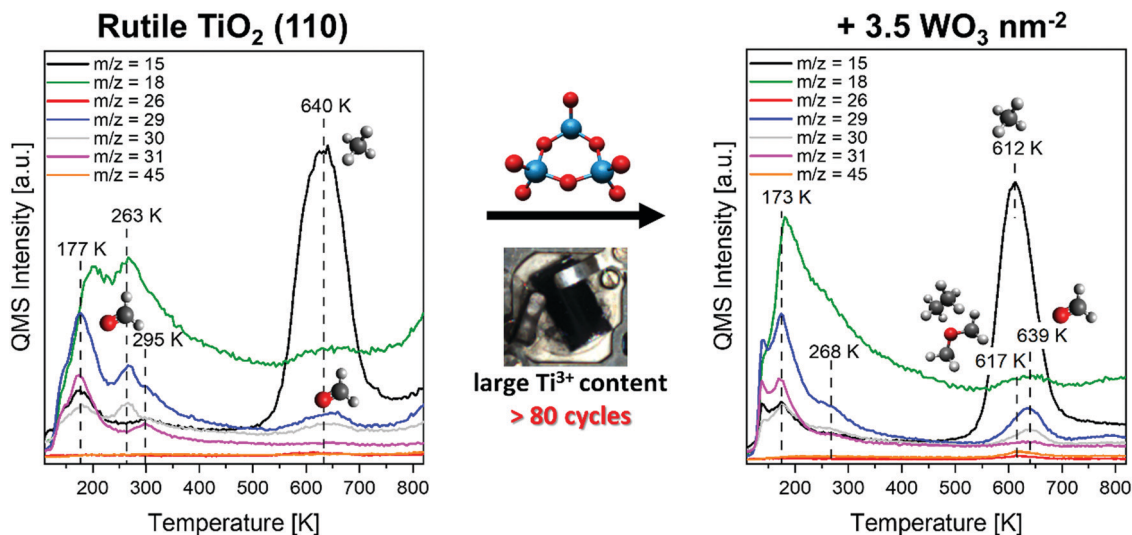


Fig. 2 Temperature programmed reaction spectra (TPRS) of a saturation coverage of methanol with preadsorption of 75 L O<sub>2</sub> at 110 K. Left, obtained from the pristine rutile TiO<sub>2</sub> (110) surface and right obtained from the same surface after deposition of 3.5 WO<sub>3</sub> nm<sup>-2</sup> flashed to 880 K before adsorption of methanol and oxygen at 110 K. A rutile sample with a large concentration of defects was used.

methane formed in a deoxygenation reaction at the same temperature ( $m/z = 15$ ). This is in agreement with a recent publication of our group demonstrating the defect dependent formation of methane from a methoxy-intermediate, while a dioxomethylene-like species was suggested for the formaldehyde formation.<sup>26</sup> In contrast, here the desorption of methanol from Ti<sub>5c</sub> is somewhat shifted in temperature from 263 K to 295 K (+32 K). However, as the position of the onset of multi-layer desorption (144 K) as well as desorption from bridging oxygens (177 K) is almost the same for low and highly reduced TiO<sub>2</sub>, we exclude an error of the thermocouple readout and suggest, that due to the high defect density, the desorption energy for methanol from Ti<sub>5c</sub> may be increased in this case.

After deposition of 3.5 WO<sub>3</sub> nm<sup>-2</sup> on this surface, the TPR spectra still exhibit the three desorption features of unreacted methanol as described above. It is noteworthy, that the desorption of methanol from Ti<sub>5c</sub> sites is shifted back to 268 K, which is close to the value for low reduced TiO<sub>2</sub>. Again, the presence of tungsten oxide clusters has a bigger impact on the high-temperature (HT) reaction. Here, still methane is the dominant product ( $m/z = 15$ ), but the desorption peak is narrowed (FWHM: -24 K), while the peak temperature is shifted significantly to 612 K (-28 K compared to highly reduced TiO<sub>2</sub>). Besides, an enhanced formation of formaldehyde at 639 K ( $m/z = 29$  and 30, not 31) was detected, again accompanied by the desorption of traces of methanol ( $m/z = 31$ ) while the low temperature formation of formaldehyde is slightly reduced.

Remarkably, this relatively rich chemistry was exclusively observed in case of oxygen preadsorption (here, 75 L O<sub>2</sub> at 110 K). For comparison, the corresponding TPRS spectra in absence of additional oxygen are given in the ESI,<sup>†</sup> Fig. S5 and S6. There, the overall methanol conversion appears much less. Similar molecular desorption features (around 180 K and 265–300 K) were

observed in absence of additional oxygen, but no partial oxidation or condensation products were recorded. The formation of methane in a deoxygenation reaction is observed, but drastically diminished in absence of oxygen which is in accordance with our earlier results.<sup>26</sup> Although a certain CO<sub>2</sub> formation is detected throughout our experiments especially for tungsten oxide on reduced TiO<sub>2</sub>, total oxidation does not appear dominant and is therefore neglected. The TPRS spectra including  $m/z = 28$  and 44 are given in the ESI,<sup>†</sup> Fig. S7 and S8.

## 4. Analysis and discussion

### 4.1 Trends in product distributions: population of deoxygenation, partial oxidation and condensation routes

In the following, we shall analyze and discuss the trends for three different reaction pathways (deoxygenation, partial oxidation and condensation) of methanol in coadsorption with oxygen in more detail. To be correct, we want to point out that a large amount of methanol desorbs unconverted in our experiments. Anyway, significant amounts of products were observed, predominantly methane from the deoxygenation reaction. Deposition of 3.5–7.0 WO<sub>3</sub> nm<sup>-2</sup> on highly reduced TiO<sub>2</sub> leads to the most reactive surfaces shown here (ESI:<sup>†</sup> Tables S1 and S2). This coverage is in line with other publications reporting the highest catalytic activity for coverages around 7 W nm<sup>-2</sup>.<sup>49</sup> Interestingly, cluster coverages significantly higher than the monolayer coverage of 7.1 WO<sub>3</sub> nm<sup>-2</sup> do not show a relevant catalytic activity which is indicative that the direct interaction of tungsten oxide clusters and the TiO<sub>2</sub> surface is crucial in this case. The product distribution is dependent on the detailed environment of precursor species such as the methoxy fragment. Especially Ti<sup>3+</sup> sites as well as Lewis acid or Brønsted base sites can significantly affect the adsorbates



and steer the product distribution. In this work, all reaction pathways required the presence of oxygen (partial oxidation and condensation) or were at least significantly enhanced (deoxygenation) by oxygen preadsorption (see for comparison Fig. 1, 2 and Fig. S5, S6 in the ESI<sup>†</sup>). One reason for this behavior may be the boosted OH dissociation forming methoxy species, which can be confirmed in this work based on the water desorption from the surface. This is in line with earlier reports based on FT-IRRAS or TPRS experiments consenting that the methoxy-fragments appears much more reactive than molecular methanol.<sup>13,24,26</sup> Since no particular desorption feature for molecular oxygen ( $m/z = 16, 32$ ) can be identified in our TPR spectra, we conclude, that oxygen dissociates at the surface. Furthermore, we cannot rule out that oxygen also reacts with the tungsten oxide clusters, especially for the case of highly reduced TiO<sub>2</sub> in which the clusters may exhibit an enriched electron density.<sup>38,47</sup>

**4.1.1 Deoxygenation: methane.** First, we shall focus on methane, that appears as the most important valuable product. The formation of methane clearly dominates the methanol conversion in the presence of coadsorbed oxygen. We estimate that this product appears in amounts approximately one order of magnitude larger than the other ones. For methane, we follow the  $m/z = 15$  trace in the region above 400 K (Fig. 3). This appears suitable, because methane is the dominant component contributing to this  $m/z$  trace in this interval. One should note, that the desorption of other products accompanies the methane formation. However, formaldehyde does not exhibit

relevant contributions in the used  $m/z$  traces (see Table 1 and Fig. S4 in the ESI<sup>†</sup>). Also, a small amount of methanol desorbs in the high-temperature regime. In case of the desorption of dimethyl ether and ethane, which appears exclusively for 3.5–7.0 WO<sub>3</sub> nm<sup>-2</sup> on highly reduced TiO<sub>2</sub>, both byproducts interfere with the  $m/z = 15$  trace. Anyway, as all of them (methanol, ethane and dimethyl ether) are only formed in small amounts (roughly a few percent of the amount of methane), while the  $m/z = 15$  fragment is not the most intense one for these other molecules, we neglect this at this point. Hence, we believe that our approach yields acceptable trends.

Fig. 3 gives an overview on the methane desorption. For TiO<sub>2</sub> with a small Ti<sup>3+</sup> content, the methane yield can be significantly increased by the deposition of tungsten oxide clusters. This is in line with the formation of Ti<sup>3+</sup> by charge transfer from the clusters.<sup>38</sup> However, higher amounts of tungsten oxide (especially above 7 WO<sub>3</sub> nm<sup>-2</sup>) decrease the methane yield in comparison to small WO<sub>3</sub> coverages. In case of high Ti<sup>3+</sup> contents, the methane yield is drastically larger. The highest methane formation can be found for 3.5 WO<sub>3</sub> nm<sup>-2</sup>, whereas higher coverages slightly decrease the yield again. Notably, by the presence of tungsten oxide clusters, the high-temperature deoxygenation reaction forming methane is substantially shifted with respect to the reaction temperature (approx. –30 K) for TiO<sub>2</sub> with a large amount of Ti<sup>3+</sup> and significantly narrowed. Hence, we attribute Ti<sup>3+</sup> sites to be the dominant species responsible for the deoxygenation reaction. In presence of (WO<sub>3</sub>)<sub>n</sub>, the Ti<sup>3+</sup> centers appear more localized and pinned to

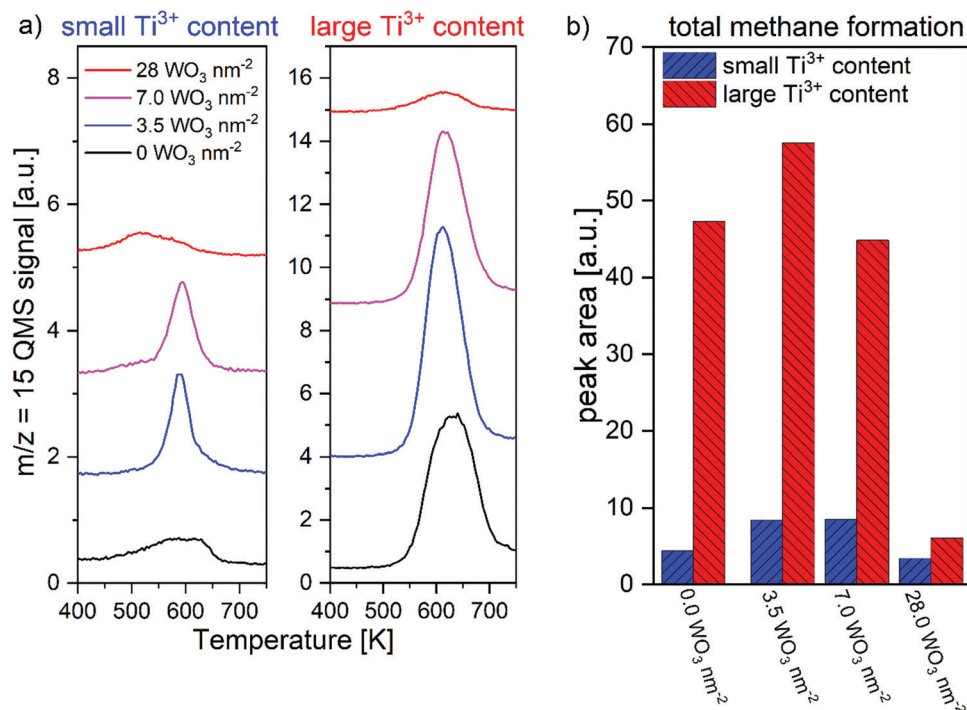


Fig. 3 Formation of methane at elevated temperatures as a function of cluster coverage and Ti<sup>3+</sup> content. (a) Methane formation as observed in the  $m/z = 15$  trace obtained from TPRS experiments. Note that the traces for small Ti<sup>3+</sup> contents (left) are differently scaled for better visibility (by a factor of two in comparison to the traces for large Ti<sup>3+</sup> content). (b) Integral peak area obtained from a. Blue columns correspond to small Ti<sup>3+</sup> content, red columns to large Ti<sup>3+</sup> contents. More details are given in the ESI<sup>†</sup> Table S1.



the  $(\text{WO}_3)_n$  cluster, leading also to a higher charge density near the surface.<sup>38</sup> So, the desorption features are shifted to lower temperatures and appear more narrow. This is in line with an earlier finding of Dohnálek and coworkers, highlighting that the alkene formation temperature on transition metal oxide surfaces decreases with increasing available electron density, in their case supplied by +I effects of the aliphatic chain.<sup>19</sup>

**4.1.2 Partial oxidation: formaldehyde.** As the second important reaction product of methanol with oxygen, we have further monitored the formation of formaldehyde in the low (LT = 170–320 K) and high temperature regime (HT = 500–750 K). One should note that formaldehyde appears as a side product, but is still produced in fair amounts. For formaldehyde, we follow the ratio of  $m/z = 29$  to  $m/z = 31$ , that is in principle proportional to the sum of the methanol and formaldehyde partial pressures divided by the methanol partial pressure, and therefore can be used as a measure of the formaldehyde yield (Fig. 4a and Fig. S9 in the ESI†). To precisely calculate absolute amounts of formaldehyde, it would have been necessary to record the detailed fragmentation pattern for all involved molecules together with a temperature-dependent residual gas analysis. Furthermore, we have additionally calculated the actual fragmentation of methanol from the multilayer desorption signals for  $m/z = 29$  and 31 (key fragments for formaldehyde and methanol) and thereby tried to correct the  $m/z = 29$  trace with respect to methanol signals. These data support our trends for the high-temperature reactions (as already apparent from the raw spectra), but did not gain acceptable results for the desorption features below 300 K due to the complex spectra and background correction

problems. For this reason we prefer the semi-quantitative approach to show trends for the partial oxidation route. Again, this is possible under the assumption, that no other molecules contribute significantly either to the  $m/z = 29$  nor  $m/z = 31$  trace. Methane does not exhibit relevant fragments (Fig. S4, ESI†), but ethane and dimethyl ether contribute to the  $m/z = 29$  and 31 traces in case of 3.5–7.0  $\text{WO}_3 \text{ nm}^{-2}$  on highly reduced  $\text{TiO}_2$ . Again, this is neglected here, because the overall amount of both compounds is relatively small and both fragments ( $m/z = 29$  and 31) are not intense in the fragmentation pattern of ethane and dimethyl ether (Fig. S4, ESI†). Similar is true for ethene, which in principle exhibits a weak  $m/z = 29$  fragment due to the natural carbon isotope distribution. However, since no signs for a significant ethene formation were observed, this does not appear relevant at this point.

One can easily see that the formation of formaldehyde in a HT reaction is evidently increased for 3.5  $\text{WO}_3 \text{ nm}^{-2}$  and 7.0  $\text{WO}_3 \text{ nm}^{-2}$  compared to pristine  $\text{TiO}_2$ . Simultaneously, the LT formaldehyde yield drops (for highly reduced  $\text{TiO}_2$ ) or stays roughly constant (for low reduced  $\text{TiO}_2$ ). One should note, that especially for low reduced  $\text{TiO}_2$  this LT formation appears as a broad weak peak in the  $m/z = 29$  to  $m/z = 31$  ratio (Fig. S9 in the ESI†). The overall formaldehyde yield is higher for titania with a large  $\text{Ti}^{3+}$  content, but in that case the enhancement by tungsten oxide clusters is not so pronounced (see Table S2 in the ESI† for a detailed calculation of the relative changes). This portends the importance of  $\text{Ti}^{3+}$  for the thermal production of formaldehyde, because the deposition of tungsten oxide clusters up to 7.1  $\text{WO}_3 \text{ nm}^{-2}$  regulates the amount of surface-near  $\text{Ti}^{3+}$  to an equilibrium-like  $\text{Ti}^{3+}/\text{Ti}^{4+}$  value of 6–7% as we

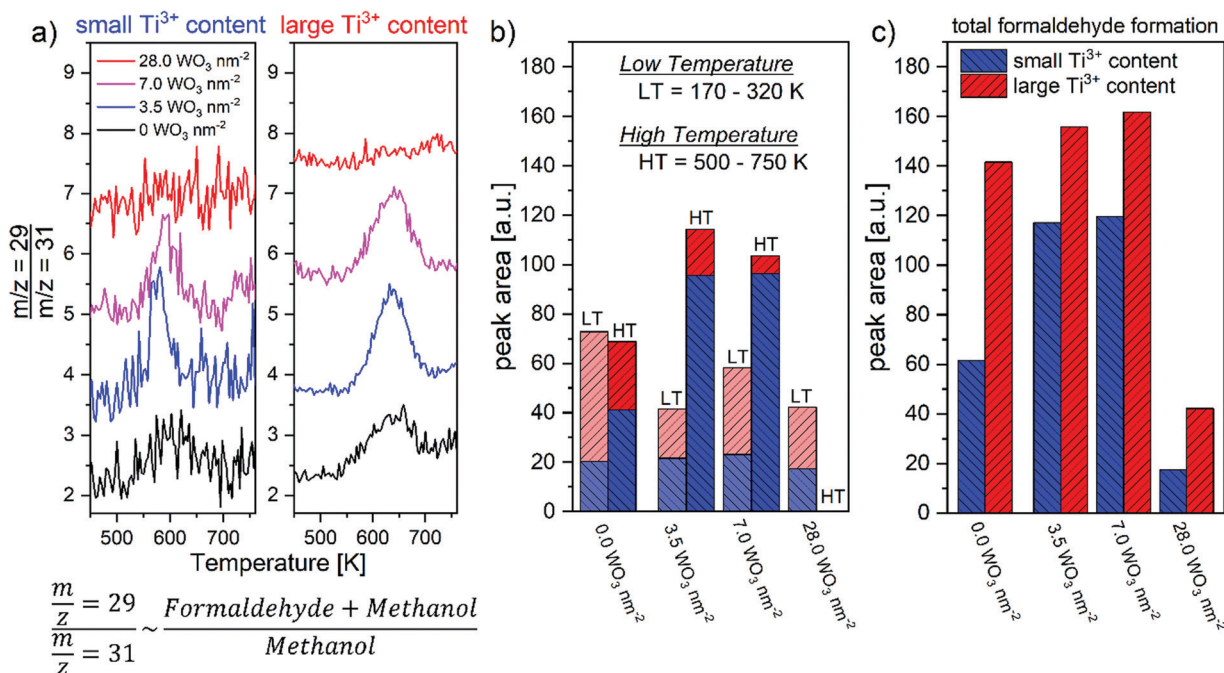


Fig. 4 Thermal formation of formaldehyde as a function of cluster coverage and bulk  $\text{Ti}^{3+}$  content. (a) Ratio of  $m/z = 29$  and  $m/z = 31$  TPRS spectra for the high temperature regime (500–750 K). (b) and (c) Integral area of the low and high temperature peaks shown in a and Fig. S9 in the ESI.† Note, that the peak area is a measure of the formaldehyde yield.



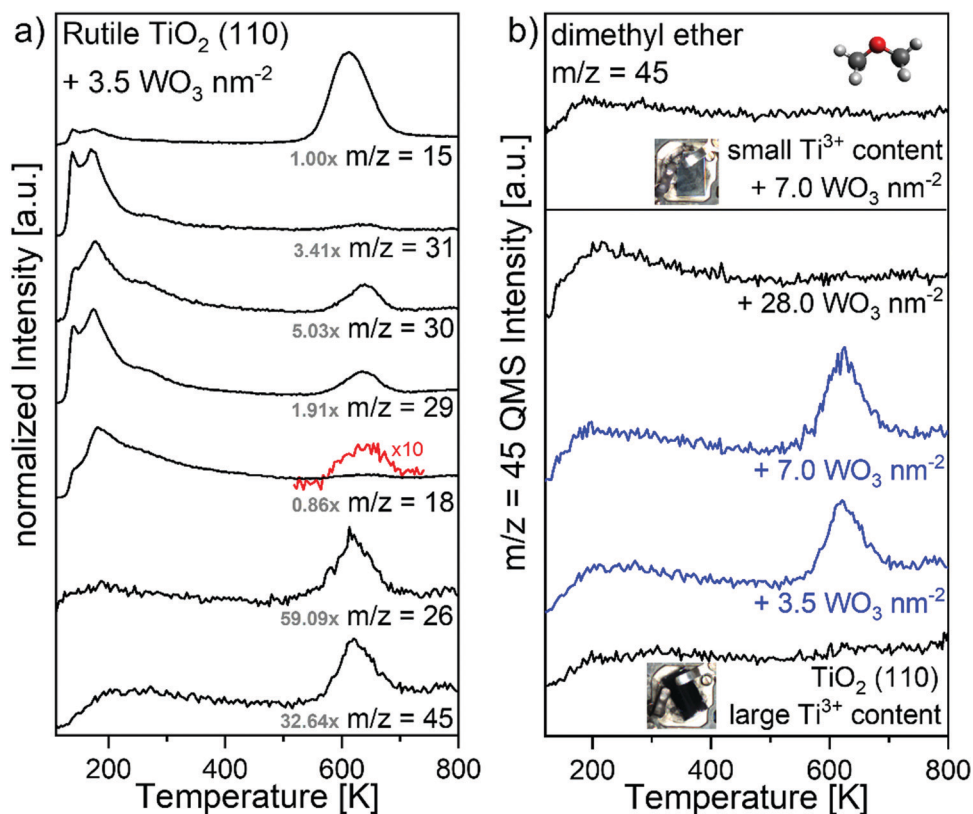
have shown recently.<sup>38</sup> Consequently, the oxide-oxide catalyst from an initially low reduced titania support acts like a stronger reduced simple titania surface. Interestingly, only the high temperature partial oxidation yield is enhanced by the cluster deposition, not the low temperature reaction. Furthermore, the partial oxidation obviously needs a certain amount of available  $Ti_{5c}$  sites in the cluster neighborhood, because high coverages ( $28 \text{ WO}_3 \text{ nm}^{-2}$ ) do not show a high temperature formaldehyde formation independent of the bulk  $Ti^{3+}$  density. Hence, we suggest, that the partial oxidation of methanol at higher temperatures proceeds at  $TiO_2$  adsorption sites, that are affected by the presence of the tungsten oxide clusters nearby as well as by subsurface  $Ti^{3+}$ .

Moreover, the role of the tungsten oxide clusters in this reaction is interesting. For the formation of formaldehyde, a C–H bond has to be broken under abstraction of one H atom. As water desorption accompanies the formaldehyde desorption even at higher temperatures, it is likely, that the C–H dissociation itself induces the formaldehyde desorption. Therefore, we rule out, that the high temperature formaldehyde results from a molecular precursor formed at lower temperatures, but forms under direct release at higher temperatures. However, still Lewis base sites are required to accomplish the hydrogen abstraction. Since the  $W(=O)_2$  sites are particularly strongly polarized moieties with a huge basicity, the hydrogen

abstraction by such groups appears as the key step that steers the product composition. The basicity of these groups is likely increased by the presence of electronic charge density supplied by defect sites.

**4.1.3 Condensation: ethane and dimethyl ether.** We also want to focus on the desorption of two other byproducts: the desorption of dimethyl ether ( $m/z = 15, 29, 45$ ) and ethane ( $m/z = 15, 26, 29, 30$ , not 31) peaking at 617 K. While the formation of dimethyl ether was already assigned to the chemistry of free tungsten oxide clusters by Rousseau, Dixon and Dohnálek,<sup>28</sup> namely by coupling of two alkoxy-fragments at one common tungsten center, our results point out that  $Ti^{3+}$  sites indeed have an impact on this reaction revealing a more rich chemistry. The most obvious difference in comparison to the earlier reports is that the condensation here is accompanied by the formation of ethane as a reductive C–C coupling product, which was not reported previously. Both products appeared in relatively low amounts and are therefore not discussed because of commercial interest in a potential production route for, *e.g.* the chemical industry, but for scientific reasons.

For better clarity, we refer to Fig. 5a. Here, the same TPR spectra as in Fig. 2, right side are shown, but now normalized to its maximum each. Thus, the desorption peaks in  $m/z = 45$  and 26 become evident. Together with the similar peak shape and



**Fig. 5** (a) Temperature programmed reaction spectra obtained from a saturation coverage of methanol with preadsorption of 75 L  $O_2$  at 110 K on  $3.5 \text{ WO}_3 \text{ nm}^{-2}$  on a highly reduced  $TiO_2$  surface as in Fig. 2. All spectra have been normalized to their maximum for better clarity, the normalization factor is given with respect to the  $m/z = 15$  trace. (b)  $m/z = 45$  traces (attributed to desorption of dimethyl ether) after adsorption of a saturation coverage of methanol with 75 L  $O_2$  preadsorption at 110 K on different  $TiO_2$  substrates and tungsten oxide coverages.





the HT peak in the  $m/z = 18$  trace, which indicates the desorption of water, we can suggest the condensation of methanol forming dimethyl ether and ethane under water desorption. One should note, that as from the desorption peak maximum, the HT formation of formaldehyde (639 K) is not related to this condensation. Due to the overlapping desorption of formaldehyde and methane it is challenging to correctly assign the peak in the  $m/z = 26$  trace, because ethane and ethene both exhibit the  $m/z = 26$  and other common fragments. However, based on the asymmetry of the  $m/z = 29$  and 30 peaks with a small shoulder at 617 K, we assign the  $m/z = 26$  signal to ethane. By comparison with other  $m/z$  traces, we have additionally ruled out ethanol, formic acid and carbon dioxide ( $^{13}\text{CO}_2$ ) being the source of the  $m/z = 45$  fragment.

It is even more interesting, that the formation of ethane and dimethyl ether is sensitive to the cluster coverage as well as the bulk  $\text{Ti}^{3+}$  density (Fig. 5b). The described condensation reaction was only found for 3.5 and 7.0  $\text{WO}_3 \text{ nm}^{-2}$  deposited on the titania substrate with a high  $\text{Ti}^{3+}$  density, and remarkably here the condensation yield appears roughly equal for both cluster coverages (blue TPR spectra in Fig. 5b). For all other cluster coverages as well as in the absence of tungsten oxide clusters, no evidence for the formation of dimethyl ether around 600 K was found. This also implies, that this particular reaction at least partially takes place at the tungsten oxide clusters itself, but it proves that the interaction with the titania substrate is crucial. On titania with a small  $\text{Ti}^{3+}$  content, this condensation reaction was absent independent of the cluster coverage. We have also recognized, that the presence of oxygen is mandatory for the condensation. Additionally, UV irradiation (365 nm, 30 min,  $> 1.5 \times 10^{16} \text{ s}^{-1} \text{ cm}^{-2}$ ) quenched this reaction for 3.5 and 7.0  $\text{WO}_3 \text{ nm}^{-2}$  on highly reduced  $\text{TiO}_2$  (Fig. S10 in the ESI†). By UV irradiation, methoxy species are consumed for the photochemical formation of low temperature formaldehyde.<sup>37</sup> This suits earlier studies by the group of Henderson which gave evidence, that only methoxy species can be photo-oxidized on  $\text{TiO}_2$  (110), but not undissociated methanol.<sup>13</sup> Therefore, we suggest that methoxy intermediates are involved in this special condensation pathway under the simultaneous formation of dimethyl ether and ethane. In accordance, alkoxy species were identified by other groups to be the key intermediates in such reactions on supported and unsupported tungsten oxide clusters.<sup>3–5</sup> As the formation of dimethyl ether was previously assigned to the  $\text{O}=\text{W}=\text{O}$  moieties, one may suspect that defect sites such as  $\text{Ti}^{3+}$  can be accounted for the ethane formation. In this process,  $\text{Ti}^{3+}$  from the bulk may serve as oxygen acceptors and may react with the leftover oxygen to form  $\text{TiO}_x$  islands.<sup>30,32,50,51</sup> Besides the involvement of methoxy-intermediates adsorbed at the metal sites, it is challenging to derive more elementary reaction steps from our data. However, it is striking that the condensation yield is approximately equal for 3.5 and 7  $\text{WO}_3 \text{ nm}^{-2}$ . One possible hypothesis for this effect may be, that the reaction is not limited by the amount of tungsten oxide clusters but by the charge that is supplied by  $\text{Ti}^{3+}$  defects from the bulk. This suits the low overall yield for this reaction route, since the amount of defects can be roughly estimated in the same order of magnitude as the

approximate dimethyl ether yield. In a recent publication, we have shown a  $\text{Ti}^{3+}$  accumulation in the cluster neighborhood between 500 and 800 K on highly reduced  $\text{TiO}_2$  and postulated the formation of anionic tungsten oxide clusters ( $[(\text{WO}_3)_n]^{z-}$ -like) by electron transfer from  $\text{Ti}^{3+}$  towards the clusters.<sup>38</sup> Since DFT results<sup>47</sup> suggested that molecular oxygen can strongly interact with such partially anionic tungsten oxide clusters under formation of superoxide species ( $\text{O}_2^-$ ), which can act as strong bases in proton abstraction, one may also consider that species here.<sup>52</sup> In turn, the formation of that species is expected to be limited by the amount of available electron charge transferred from defect sites, suiting our finding for the dimethyl ether yield.

## 5. Conclusion

By a systematic TPRS based study we have elucidated the conversion of methanol as a model reactant in the presence of oxygen on rutile  $\text{TiO}_2$  (110) as a function of tungsten oxide cluster coverage as well as the amount of bulk  $\text{Ti}^{3+}$ . Three important thermal conversion routes (deoxygenation, partial oxidation and condensation) were found. The central findings are the following:

High bulk  $\text{Ti}^{3+}$  contents increase the thermal reactivity in the dominant deoxygenation reaction and the less pronounced partial oxidation. The deposition of tungsten oxide clusters (up to 7.1  $\text{WO}_3 \text{ nm}^{-2}$ ) on  $\text{TiO}_2$  substrates under concomitant generation of surface-near  $\text{Ti}^{3+}$  activates both of these reaction pathways. Especially the thermal partial oxidation forming formaldehyde (desorption around 640 K) is strongly enhanced on all  $\text{TiO}_2$  substrates, likely due to a more effective proton abstraction from C–H bonds. The deoxygenation of methanol producing methane is shifted to lower temperature by the presence of tungsten oxide clusters.

In contrast to earlier reports we have shown that the thermal condensation of methanol under the formation of dimethyl ether exhibits an impact of  $\text{Ti}^{3+}$  sites. Unlike those previous publications, ethane was identified as an additional product of this conversion route. As apparent from photochemical experiments, methoxy intermediates are involved in this reaction that proceed at tungsten oxide clusters which are directly interacting with a  $\text{Ti}^{3+}$  rich  $\text{TiO}_2$  (sub-)surface. Since a high  $\text{Ti}^{3+}$  content in the bulk is mandatory for this reaction, we suggest a reaction limitation by the available charge from defect sites under involvement of partially anionic clusters.

## Conflicts of interest

The authors declare no conflict of interest.

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