

## Surface Chemistry

International Edition: DOI: 10.1002/anie.201509021  
German Edition: DOI: 10.1002/ange.201509021Methanol Conversion into Dimethyl Ether on the Anatase TiO<sub>2</sub>(001) SurfaceFeng Xiong<sup>+</sup>, Yan-Yan Yu<sup>+</sup>, Zongfang Wu, Guanghui Sun, Liangbing Ding, Yuekang Jin, Xue-Qing Gong,\* and Weixin Huang\*

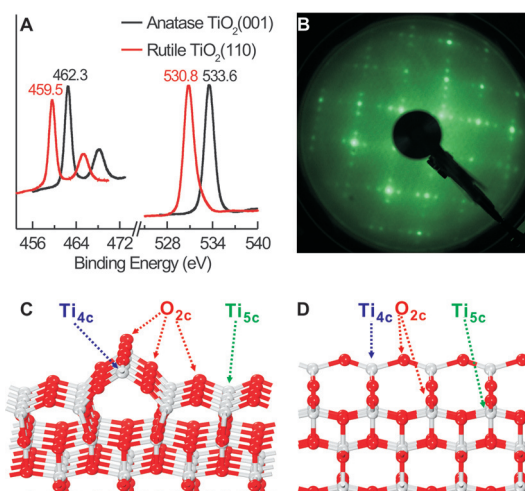
**Abstract:** Exploring reactions of methanol on TiO<sub>2</sub> surfaces is of great importance in both C1 chemistry and photocatalysis. Reported herein is a combined experimental and theoretical calculation study of methanol adsorption and reaction on a mineral anatase TiO<sub>2</sub>(001)-(1 × 4) surface. The methanol-to-dimethyl ether (DME) reaction was unambiguously identified to occur by the dehydration coupling of methoxy species at the fourfold-coordinated Ti<sup>4+</sup> sites (Ti<sub>4c</sub>), and for the first time confirms the predicted higher reactivity of this facet compared to other reported TiO<sub>2</sub> facets. Surface chemistry of methanol on the anatase TiO<sub>2</sub>(001)-(1 × 4) surface is seldom affected by co-chemisorbed water. These results not only greatly deepen the fundamental understanding of elementary surface reactions of methanol on TiO<sub>2</sub> surfaces but also show that TiO<sub>2</sub> with a high density of Ti<sub>4c</sub> sites is a potentially active and selective catalyst for the important methanol-to-DME reaction.

The conversion reactions of methanol are among the most important reactions in C1 chemistry, wherein the dehydration of methanol into dimethyl ether (DME) catalyzed by solid acids, including γ-Al<sub>2</sub>O<sub>3</sub>, zeolite, hetero-polyacid, and composite oxides, receives increasing interest because DME has emerged as a star molecule in energy and environmental chemistry, and plays an alternative role to methanol.<sup>[1–4]</sup> As a representative and versatile oxide catalyst, TiO<sub>2</sub> has been explored as catalysts for methanol conversion.<sup>[5,6]</sup> The photocatalytic conversion of methanol over TiO<sub>2</sub> has been a hot topic in photocatalysis.<sup>[7]</sup> These reports have motivated fundamental studies of methanol adsorption and reaction on TiO<sub>2</sub> surfaces that mostly employed TiO<sub>2</sub> single crystals as a model surfaces.<sup>[8–18]</sup>

Among various types of TiO<sub>2</sub> facets anatase TiO<sub>2</sub>(001) is of particular interest. Several theoretical calculations sug-

gested the anatase TiO<sub>2</sub>(001) surface to be very reactive,<sup>[19–23]</sup> however, this reactivity has not been experimentally proved. Meanwhile, experimental studies of its surface structure and reactivity are very limited, with most reports on anatase TiO<sub>2</sub>(001) thin films<sup>[24–27]</sup> and a few on mineral anatase TiO<sub>2</sub>(001) surfaces.<sup>[25,28]</sup> Herein we report a combinational thermal desorption spectra (TDS), X-ray photoelectron spectroscopy (XPS), and density-function theory (DFT) calculation study of methanol adsorption and reaction on a mineral anatase TiO<sub>2</sub>(001) surface. The methanol-to-DME reaction was unambiguously identified to occur by the dehydration coupling of a methoxy species (CH<sub>3</sub>O) at the fourfold-coordinated Ti<sup>4+</sup> sites (Ti<sub>4c</sub>) of the anatase TiO<sub>2</sub>(001)-(1 × 4) surface, and thus, for the first time confirmed the predicted higher reactivity of this facet than other reported TiO<sub>2</sub> facets.

Experiments were performed in a Leybold stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 1.2 × 10<sup>−10</sup> mbar.<sup>[16]</sup> Prior to experiments, an anatase TiO<sub>2</sub>(001) single crystal (5 × 5 × 0.5 mm<sup>3</sup>), purchased from MaTeck, was cleaned by repeated cycles of Ar ion sputtering, oxidation at 800 K, and annealing at 900 K. Figure 1A shows the Ti 2p and O 1s XPS spectra of a clean anatase TiO<sub>2</sub>(001) surface, giving the Ti 2p<sub>3/2</sub> and O 1s binding energies respectively at 462.3 and 533.6 eV, which are both 2.8 eV higher than the corresponding Ti 2p<sub>3/2</sub> and O 1s binding energies of a clean rutile TiO<sub>2</sub>(110) surface. This difference could be attributed to



**Figure 1.** A) Ti 2p and O 1s XPS spectra of clean anatase TiO<sub>2</sub>(001) and rutile TiO<sub>2</sub>(110) surfaces. B) LEED pattern of a clean anatase TiO<sub>2</sub>(001) surface ( $E_p = 170$  eV). C, D) Front view and side view of the proposed model of the anatase TiO<sub>2</sub>(001)-(1 × 4) surface.

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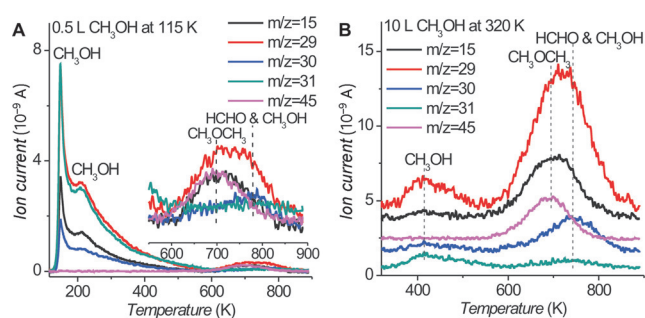
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the fact that the rutile  $\text{TiO}_2(110)$  surface is more easily reduced than the anatase  $\text{TiO}_2(001)$  surface and thus exhibits a better conductivity.<sup>[25]</sup> However, the XPS spectra of the clean anatase  $\text{TiO}_2(001)$  surface remained unchanged upon X-ray irradiation during XPS measurements (see Figure S1 in the Supporting Information), suggesting the absence of a differential charge effect and a continuous charge accumulation. We thus calibrated the binding energies of measured XPS spectra by setting the Ti  $2p_{3/2}$  binding energy to 459.5 eV to facilitate their assignments. The low-energy electron diffraction (LEED) pattern of a clean anatase  $\text{TiO}_2(001)$  surface (Figure 1B) shows a sharp  $(1 \times 4)$  reconstructed pattern. This pattern demonstrates the formation of a reconstructed anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface upon treatment, and the proposed structure is schematically illustrated in Figures 1C and D.<sup>[24,25]</sup> The  $\text{Ti}^{4+}$  cations on the ridge and terrace of the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface are respectively  $\text{Ti}_{4c}$  and fivefold-coordinated  $\text{Ti}^{4+}$  ( $\text{Ti}_{5c}$ ), whereas the surface O anions are all twofold-coordinated ( $\text{O}_{2c}$ ).

Figure 2 shows TDS spectra of 0.5 L  $\text{CH}_3\text{OH}$  exposed at 115 K and 10 L  $\text{CH}_3\text{OH}$  exposed at 320 K on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface. Corresponding TDS spectra of various  $\text{CH}_3\text{OH}$  exposures are shown in Figures S2 and S3.

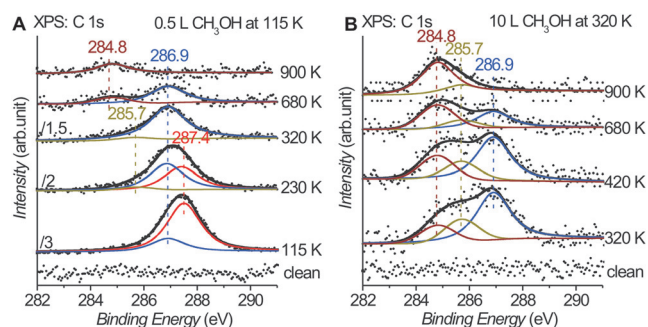


**Figure 2.** TDS spectra of 0.5 L  $\text{CH}_3\text{OH}$  exposed at 115 K (A) and 10 L  $\text{CH}_3\text{OH}$  exposed at 320 K (B) on the clean anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface. The inset in Figure 2A shows the zoom-in TDS spectra between 550 and 900 K.

$\text{CH}_3\text{OH}$  desorption peaks at 150, 210, and 415 K can be respectively assigned to the desorption of  $\text{CH}_3\text{OH}(\text{a})$  multilayer, the desorption of  $\text{CH}_3\text{OH}(\text{a})$  monolayer, and the recombinative desorption of adsorbed methoxy species [ $\text{CH}_3\text{O}(\text{a})$ ]. Similar results were previously reported for  $\text{CH}_3\text{OH}$  adsorption on other  $\text{TiO}_2$  single-crystal surfaces.<sup>[11–18]</sup> Simultaneously desorption peaks of HCHO, inferred by the higher intensity of the  $m/z = 30$  signal relative to the  $m/z = 31$  signal, and  $\text{CH}_3\text{OH}$  were also observed at 780 K after 0.5 L  $\text{CH}_3\text{OH}$  exposure at 115 K, and both features grow and shift to 750 K after 10 L  $\text{CH}_3\text{OH}$  exposure at 320 K. Such features were not observed for  $\text{CH}_3\text{OH}$  adsorption on vacuum-annealed rutile  $\text{TiO}_2(110)$ ,<sup>[12–16]</sup>  $\text{TiO}_2(001)$ ,<sup>[11]</sup> or  $\text{TiO}_2(011)-(2 \times 1)$  surfaces,<sup>[18]</sup> but were observed on anatase  $\text{TiO}_2(101)$ ,<sup>[17]</sup> faceted rutile  $\text{TiO}_2(001)-[011]$ ,<sup>[11]</sup> and oxidized rutile  $\text{TiO}_2(110)$  surfaces,<sup>[12,15]</sup> and attributed to the disproportionation reaction between two  $\text{CH}_3\text{O}(\text{a})$  species. Thus  $\text{CH}_3\text{O}(\text{a})$ , with a high thermal stability, forms upon  $\text{CH}_3\text{OH}$  adsorption on

the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface and its formation is enhanced at elevated temperatures. Of particular interest is the observation of obvious and simultaneous desorption peaks of the  $m/z = 45$ , 15, and 29 signals at 700 K. After careful examination of all likely products (see Figure S4), the desorption peaks of these signals at 700 K were identified to arise from the desorption of DME. The amount of desorbed DME is larger after 10 L  $\text{CH}_3\text{OH}$  exposure, at 320 K, than after 0.5 L  $\text{CH}_3\text{OH}$  exposure at 115 K. The production of DME from methanol adsorption has not been observed on other reported  $\text{TiO}_2$  single-crystal surfaces,<sup>[12–18]</sup> except on a seriously restructured rutile  $\text{TiO}_2(001)-[114]$  faceted surface.<sup>[11]</sup> It is noteworthy that the observed products from  $\text{CH}_3\text{OH}$  adsorption and reaction on our anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface are quite similar to those on anatase  $\text{TiO}_2$  powders,<sup>[29,30]</sup> suggesting that the surface sites having similar structures to those on anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface should dominate the surface chemistry of methanol on anatase  $\text{TiO}_2$  powders.

The surface species formed upon  $\text{CH}_3\text{OH}$  adsorption and reaction on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface were examined with XPS. Figure 3 shows C 1s XPS spectra of



**Figure 3.** C 1s XPS spectra of 0.5 L  $\text{CH}_3\text{OH}$  exposed at 115 K (A) and 10 L  $\text{CH}_3\text{OH}$  exposed at 320 K (B) on the clean anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface followed by annealing at the indicated temperatures. The scatter data and solid lines represent original data and fitted results, respectively.

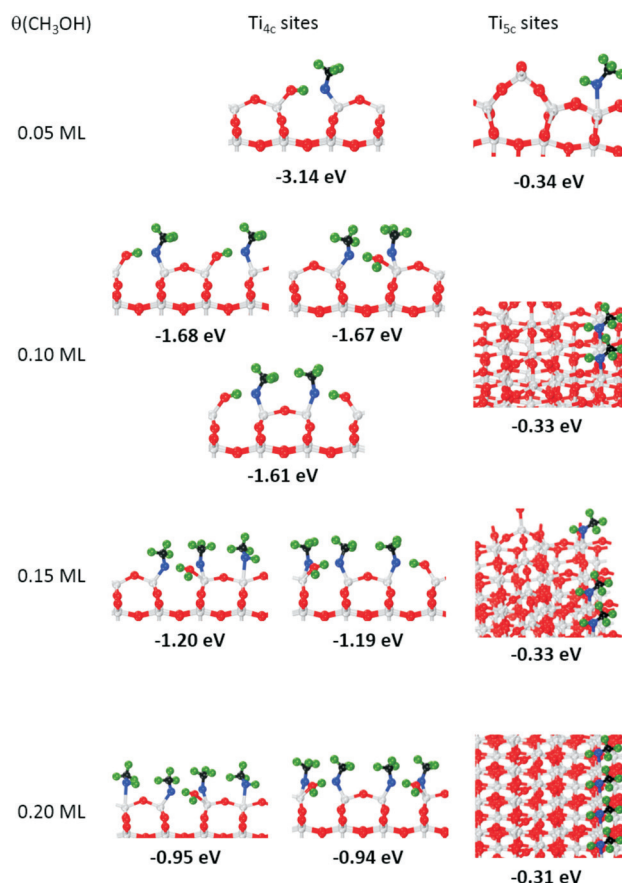
0.5 L  $\text{CH}_3\text{OH}$  exposed at 115 K and 10 L  $\text{CH}_3\text{OH}$  exposed at 320 K on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface followed by annealing at indicated temperatures. As shown in Figure 3A, 0.5 L of  $\text{CH}_3\text{OH}$  exposed at 115 K gives a C 1s spectrum with a dominant component at 287.4 eV and a shoulder at 286.9 eV, which can be assigned to adsorbed  $\text{CH}_3\text{OH}(\text{a})$  and  $\text{CH}_3\text{O}(\text{a})$ , respectively.<sup>[16]</sup> Upon annealing, the  $\text{CH}_3\text{OH}(\text{a})$  component reduces at 230 K and disappears at 320 K. The  $\text{CH}_3\text{O}(\text{a})$  component keeps increasing until 320 K and then reduces at 680 K and disappears at 900 K. A weak component at 285.7 eV, assigned to a  $\text{CH}_x$  species<sup>[31]</sup> (see Figure S5), emerges at 320 K and slightly grows at 680 K and disappears at 900 K. And a carbon component at 284.8 eV appears at 680 K and grows at 900 K. As shown in Figure 3B, 10 L  $\text{CH}_3\text{OH}$  exposed at 320 K gives a C 1s spectrum consisting of  $\text{CH}_3\text{O}(\text{a})$ ,  $\text{CH}_x$ , and carbon components. Upon annealing, the  $\text{CH}_3\text{O}(\text{a})$  component keeps decreasing and disappears at 900 K, as does the  $\text{CH}_x$  component. However, the carbon

component keeps growing. The tiny  $\text{CH}_x$  component observed at 900 K should arise from the decomposition of  $\text{CH}_3\text{OH}$  in the residual gases of our UHV chamber because of the relatively large  $\text{CH}_3\text{OH}$  exposure during the XPS measurements. It is noteworthy that X-ray radiation during the XPS measurements does not affect the surface reactions of  $\text{CH}_3\text{O}(\text{a})$  (see Figure S6). C 1s XPS spectra of various  $\text{CH}_3\text{OH}$  exposures at 115 K (see Figure S7) and 320 K (see Figure S8) demonstrate that the decomposition of  $\text{CH}_3\text{OH}$  into  $\text{CH}_3\text{O}(\text{a})$  and carbon is preferred at very low coverages at 115 K, and the molecular adsorption gradually dominates with the coverage increasing while  $\text{CH}_3\text{OH}$  always decomposes into  $\text{CH}_3\text{O}(\text{a})$ ,  $\text{CH}_x$ , and carbon at 320 K.

The above XPS and TDS results of  $\text{CH}_3\text{OH}$  adsorption and reaction on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface demonstrate the unprecedented complex surface reactions of  $\text{CH}_3\text{OH}$  on  $\text{TiO}_2$  single-crystal surfaces.  $\text{CH}_3\text{OH}$  can decompose into  $\text{CH}_3\text{O}(\text{a})$ , adsorbed  $\text{CH}_x$  species, and carbon at temperatures as low as 115 K. Upon heating,  $\text{CH}_3\text{O}(\text{a})$  can undergo the recombination reaction to produce  $\text{CH}_3\text{OH}$  at 415 K, the dehydration coupling reaction to produce important  $\text{CH}_3\text{OCH}_3$  at 700 K, the disproportionation reaction to produce  $\text{CH}_3\text{OH}$  and  $\text{HCHO}$  at 750–780 K, and decomposition into carbon. These results unambiguously prove the higher catalytic activity of the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface relative to other reported  $\text{TiO}_2$  single crystal surfaces, as predicted by previous theoretical calculations.<sup>[19–23]</sup>

The dominant surface reaction between 420 and 680 K after  $\text{CH}_3\text{OH}$  exposure at 320 K is the dehydration coupling reaction of  $\text{CH}_3\text{O}(\text{a})$  to produce DME (Figure 2B). Estimated from the peak intensity decrease between the corresponding C 1s XPS spectra of the surfaces annealed at 420 and 680 K (Figure 3B), about 55 % of  $\text{CH}_3\text{O}(\text{a})$  on the surface underwent the dehydration coupling reaction. The production of DME and  $\text{CH}_3\text{OH}/\text{HCHO}$  are clearly controlled by the bimolecular surface reactions of  $\text{CH}_3\text{O}(\text{a})$ . Therefore, by leading-edge analysis of second-order desorption spectra employing the fragments at  $m/z = 45$  (exclusively arising from DME) and  $m/z = 30$  (exclusively arising from  $\text{CH}_3\text{OH}$  and  $\text{HCHO}$ ), shown in Figure 2A, the surface reaction barriers of the dehydration coupling reaction of  $\text{CH}_3\text{O}(\text{a})$  to produce  $\text{CH}_3\text{OCH}_3$  and the disproportionation reaction of  $\text{CH}_3\text{O}(\text{a})$  to produce  $\text{CH}_3\text{OH}$  and  $\text{HCHO}$  on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface were estimated to be about  $99 \text{ kJ mol}^{-1}$  (1.03 eV) and  $142 \text{ kJ mol}^{-1}$  (1.43 eV), respectively.

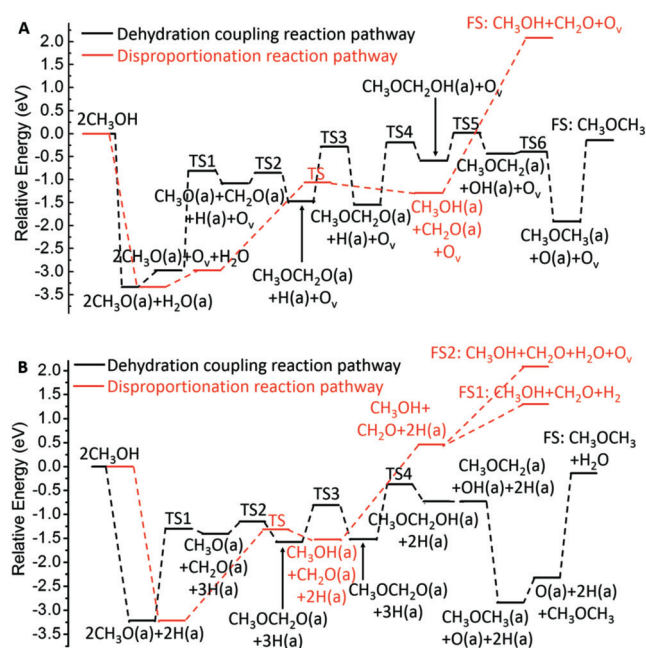
DFT calculations were performed to understand the adsorption and surface reactions of  $\text{CH}_3\text{OH}$  on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface. Figure 4 shows the most stable calculated adsorption configurations of  $\text{CH}_3\text{OH}$  at the  $\text{Ti}_{4c}$  and  $\text{Ti}_{5c}$  sites with different coverage with respect to the total number of surface Ti sites. At the  $\text{Ti}_{4c}$  sites,  $\text{CH}_3\text{OH}$  dissociates with the most stable configuration, thus giving an adsorption energy as large as  $-3.14 \text{ eV}$  at a 0.05 ML coverage, and no stable configuration of molecularly adsorbed  $\text{CH}_3\text{OH}(\text{a})$  could be identified. Three configurations of dissociative adsorption are similarly stable at a 0.1 ML coverage, and configurations of dissociative adsorption and mixed dissociative and molecular adsorption become similarly stable at higher coverages. The dissociation of  $\text{CH}_3\text{OH}$  at



**Figure 4.** The most stable, calculated adsorption configurations with average adsorption energies for  $\text{CH}_3\text{OH}$  at the  $\text{Ti}_{4c}$  and  $\text{Ti}_{5c}$  sites of the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface. The grey, red, blue, black, and green spheres represent Ti, O of  $\text{TiO}_2$ , O of  $\text{CH}_3\text{OH}$ , C, and H atoms, respectively.

the  $\text{Ti}_{4c}$  sites was found to result in the breaking of  $\text{Ti}_{4c}\text{--O}$  bonds. The average adsorption energy of  $\text{CH}_3\text{OH}$  at the  $\text{Ti}_{4c}$  sites decreases with the  $\text{CH}_3\text{OH}$  coverage. At the  $\text{Ti}_{5c}$  sites, the molecular adsorption of  $\text{CH}_3\text{OH}$  is always more stable and the average adsorption energy does not vary much with the coverage. Stable configurations of dissociative adsorption of  $\text{CH}_3\text{OH}$  at the  $\text{Ti}_{5c}$  sites could be identified (see Figure S9) but the average adsorption energy is much lower than that of molecular adsorption. It is noteworthy that in our structural model the  $\text{CH}_3\text{OH}$  coverages calculated with respect to the individual  $\text{Ti}_{4c}$  and  $\text{Ti}_{5c}$  sites are as 5 and 1.25 times that calculated with respect to the total number of the  $\text{Ti}_{4c}$  and  $\text{Ti}_{5c}$  sites, respectively. On the basis of these calculation results,  $\text{Ti}_{4c}$  on the ridge is much more reactive than  $\text{Ti}_{5c}$  on the terrace, and  $\text{CH}_3\text{OH}$  preferentially dissociates at the  $\text{Ti}_{4c}$  sites, but molecularly adsorbs at the  $\text{Ti}_{5c}$  sites. Thus  $\text{CH}_3\text{O}(\text{a})$  experimentally observed in our XPS results are located at the  $\text{Ti}_{4c}$  sites.

The reaction pathways and energy profiles of the observed bimolecular dehydration coupling reaction and disproportionation reaction of  $\text{CH}_3\text{O}(\text{a})$  were explored by DFT calculations at a 0.1 ML  $\text{CH}_3\text{OH}$  coverage. Two separate  $\text{CH}_3\text{O}(\text{a})$  species, in the configuration with an average adsorption



**Figure 5.** Calculated energy profiles of the bimolecular dehydration coupling reaction and disproportionation reaction of  $\text{CH}_3\text{O}(\text{a})$  at the  $\text{Ti}_{4c}$  sites of the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface (0.1 ML  $\text{CH}_3\text{OH}$  coverage): A) the configuration with an average adsorption energy of  $-1.67$  eV and B) the configuration with an average adsorption energy of  $-1.61$  eV.

energy of  $-1.68$  eV, were found not to undergo the bimolecular surface reaction. With the configuration consisting of an average  $\text{CH}_3\text{OH}$  adsorption energy of  $-1.67$  eV (see Figure 5A and Figure S10), surface reactions are initiated by the desorption of  $\text{H}_2\text{O}(\text{a})$  formed by dissociative  $\text{CH}_3\text{OH}$  adsorption, and simultaneously a surface oxygen vacancy is created. The desorption of molecularly chemisorbed  $\text{H}_2\text{O}(\text{a})$  from the surface was experimentally observed in the water TDS spectra following  $\text{CH}_3\text{OH}$  exposures at 115 K (see Figure S2). During the dehydration coupling reaction to produce DME, one  $\text{CH}_3\text{O}(\text{a})$  firstly dehydrogenates to produce  $\text{CH}_2\text{O}(\text{a})$  with a barrier of 2.16 eV, and then  $\text{CH}_2\text{O}(\text{a})$  facily couples with the other  $\text{CH}_3\text{O}(\text{a})$  to form  $\text{CH}_3\text{OCH}_2\text{O}(\text{a})$  which subsequently undergoes a series of low-barrier surface reactions to form  $\text{CH}_3\text{OCH}_3(\text{a})$ .  $\text{CH}_3\text{OCH}_3(\text{a})$  desorbs from the surface with a barrier of 1.77 eV, thus producing gaseous DME and recovering the original surface. During the disproportionation reaction, two  $\text{CH}_3\text{O}(\text{a})$  species undergo a H-transfer reaction to form  $\text{CH}_3\text{OH}(\text{a})$  and  $\text{CH}_2\text{O}(\text{a})$  with a barrier of 1.91 eV, and their desorption to produce the final products needs to overcome a large barrier of 3.37 eV because of the creation of an oxygen vacancy.

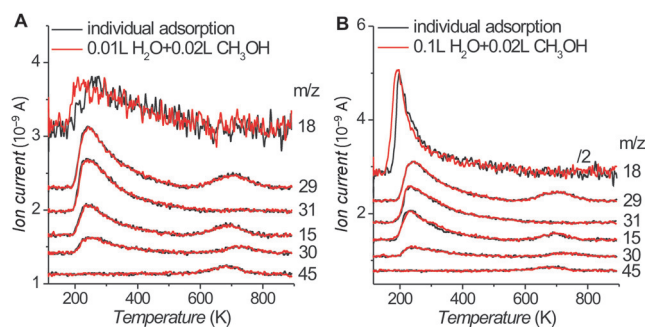
During the dehydration coupling reaction to produce DME from the configuration with an average  $\text{CH}_3\text{OH}$  adsorption energy of  $-1.61$  eV (see Figure 5B and Figure S11), one  $\text{CH}_3\text{O}(\text{a})$  firstly dehydrogenates to produce  $\text{CH}_2\text{O}(\text{a})$  with a barrier of 1.95 eV, and then  $\text{CH}_2\text{O}(\text{a})$  facily couples with the other  $\text{CH}_3\text{O}(\text{a})$  to form  $\text{CH}_3\text{OCH}_2\text{O}(\text{a})$ , which subsequently undergoes a series of low-barrier surface reactions to form  $\text{CH}_3\text{OCH}_3(\text{a})$ . And  $\text{CH}_3\text{OCH}_3(\text{a})$  facily

desorbs from the surface to produce gaseous DME, and the remaining two H(a), in the form of a hydroxy group, and an O atom react to produce gaseous  $\text{H}_2\text{O}$  with a barrier of 2.18 eV, thus recovering the original surface. For the disproportionation reaction, two  $\text{CH}_3\text{O}(\text{a})$  species undergo a H-transfer reaction to form  $\text{CH}_3\text{OH}(\text{a})$  and  $\text{CH}_2\text{O}(\text{a})$  with a barrier of 1.9 eV, and they desorb to produce the  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$  with a barrier of 1.99 eV, and the remaining two H(a) atoms, in the form of hydroxy groups, preferentially recombine to produce gaseous  $\text{H}_2$ , thus recovering the original surface.

The above DFT calculation results demonstrate that the bimolecular dehydration coupling reaction and disproportionation reaction of  $\text{CH}_3\text{O}(\text{a})$  at the  $\text{Ti}_{4c}$  sites both involve elementary surface reactions with activation energies of about 2 eV, but their very high thermal stability allow the occurrence of both reactions, as experimentally observed. The dehydration coupling reaction of methanol to DME is slightly exothermic while the disproportionation reaction to formaldehyde is more endothermic. Meanwhile, the disproportionation reaction pathways involve a step with a barrier of 3.37 eV. These DFT calculation results qualitatively agree with our experimental observations that DME, the product of the dehydration coupling reaction with an activation energy of 1.03 eV, is produced at lower temperatures than  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{O}$ , which are the products of the disproportionation reaction having an activation energy of 1.43 eV. Therefore,  $\text{TiO}_2$  which exposes a high density of  $\text{Ti}_{4c}$  sites can be expected to be an active and selective catalyst for the important methanol-to-DME reaction.

Water adsorption has been demonstrated to affect the adsorption and surface reaction of methanol on  $\text{TiO}_2$  single-crystal surfaces.<sup>[8,9]</sup> In the TDS spectra of water adsorption on a clean anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface at 115 K (see Figure S12), four water desorption features evolve with the increasing water exposure: hydroxy group recombination peak at about 400 K, desorption peak of  $\text{H}_2\text{O}(\text{a})$  chemisorbed at Ti sites at 270 K, desorption peak of  $\text{H}_2\text{O}(\text{a})$  chemisorbed at O sites at 195 K, and multilayer water desorption peak at 170 K. Similar water TDS results were observed for water adsorption on the rutile  $\text{TiO}_2(110)$  surface with surface bridging bonded oxygen vacancies where water dissociation occurred.<sup>[32]</sup> For water adsorption on stoichiometric rutile  $\text{TiO}_2(110)$  and anatase  $\text{TiO}_2(101)$  surfaces,<sup>[32,33]</sup> only desorption peaks of  $\text{H}_2\text{O}(\text{a})$  on Ti sites,  $\text{H}_2\text{O}(\text{a})$  on O sites, and multilayer water were observed. Thus the TDS results demonstrate the water dissociation on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface at 115 K, thus agreeing with previous synchrotron radiation-excited core-level photoelectron spectroscopy results.<sup>[34]</sup> DFT calculations were performed for water adsorption on a clean anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface with different water coverages (see Figures S13 and S14). At the  $\text{Ti}_{4c}$  sites,  $\text{H}_2\text{O}$  preferentially dissociates at low coverage and both dissociatively and molecularly adsorb at large coverage. At the  $\text{Ti}_{5c}$  sites, the molecular adsorption of  $\text{H}_2\text{O}$  is always preferred. The calculated adsorption energies of  $\text{H}_2\text{O}$  on the clean anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface are also similar to those of methanol. Similar DFT calculation results were previously reported for water and methanol adsorption on an anatase  $\text{TiO}_2(001)-(1 \times 1)$  surface.<sup>[21]</sup>

Figure 6 shows TDS spectra of the adsorption of 0.02 L  $\text{CH}_3\text{OH}$  on anatase  $\text{TiO}_2(001)-(1 \times 4)$  surfaces pre-exposed to 0.01 L and 0.1 L  $\text{H}_2\text{O}$  at 115 K. The anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface preadsorbed with 0.01 L  $\text{H}_2\text{O}$  at 115 K has hydroxy groups at the  $\text{Ti}_{4c}$  sites and  $\text{H}_2\text{O}(\text{a})$  chemisorbed at the  $\text{Ti}_{5c}$



**Figure 6.** TDS spectra of 0.02 L  $\text{CH}_3\text{OH}$  exposed on anatase  $\text{TiO}_2(001)-(1 \times 4)$  surfaces precovered by 0.01 L (A) and 0.1 L (B)  $\text{H}_2\text{O}$  at 115 K. Corresponding TDS spectra of individual  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  exposures are also included.

sites, whereas that preadsorbed with 0.1 L  $\text{H}_2\text{O}$  at 115 K has hydroxy groups at the  $\text{Ti}_{4c}$  sites,  $\text{H}_2\text{O}(\text{a})$  chemisorbed at the  $\text{Ti}_{5c}$  sites, and  $\text{H}_2\text{O}(\text{a})$  chemisorbed at the O sites. The desorption traces of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ , and  $\text{HCHO}$  are identical to those following the corresponding individual methanol adsorption on the clean surface. The desorption peaks of molecularly adsorbed water appear at slightly lower temperatures and are slightly stronger than those following corresponding individual water adsorption on clean surface. Meanwhile, the TDS spectra of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OCH}_3$ ,  $\text{HCHO}$ , and  $\text{H}_2\text{O}$ , after 0.02 L methanol adsorption on a 0.1 L water-precovered surface, are identical to those after 0.1 L water adsorption on 0.02 L methanol-precovered surface (see Figure S15). Therefore, co-chemisorbed water has little influence on the surface chemistry adsorption and surface reactions of methanol on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface, while co-adsorbed methanol exerts repulsive interactions on molecularly adsorbed water. The enhanced desorption peaks of molecularly adsorbed water for coadsorption of methanol and water over individual water adsorption suggest the transformation of some hydroxy groups, formed by water dissociation at the  $\text{Ti}_{4c}$  sites, into molecularly adsorbed water. Similar results were also observed for coadsorption of methanol and water on the rutile  $\text{TiO}_2(110)$  surface and  $\text{CH}_3\text{OH}$  adsorption on hydroxylated rutile and anatase  $\text{TiO}_2$  powders.<sup>[12,30,35–38]</sup>

In summary, our results of combined experimental and theoretical calculation studies unambiguously demonstrate that methanol facilely dissociates at the  $\text{Ti}_{4c}$  sites of the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface to form strongly adsorbed methoxy groups. These methoxy groups undergo the dehydration coupling reaction to produce DME. The chemisorption and surface reactions of methanol on the anatase  $\text{TiO}_2(001)-(1 \times 4)$  surface is not affected by co-chemisorbed water. These results not only greatly deepen the fundamental understanding of methanol chemistry and  $\text{TiO}_2$  catalysis but

also predict  $\text{TiO}_2$  exposing a high density of  $\text{Ti}_{4c}$  sites as potentially active and selective catalysts for the important methanol-to-DME reaction.

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