

## Supporting Information

*for*

### Stepwise photocatalytic dissociation of methanol and water on TiO<sub>2</sub>(110)

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*and*

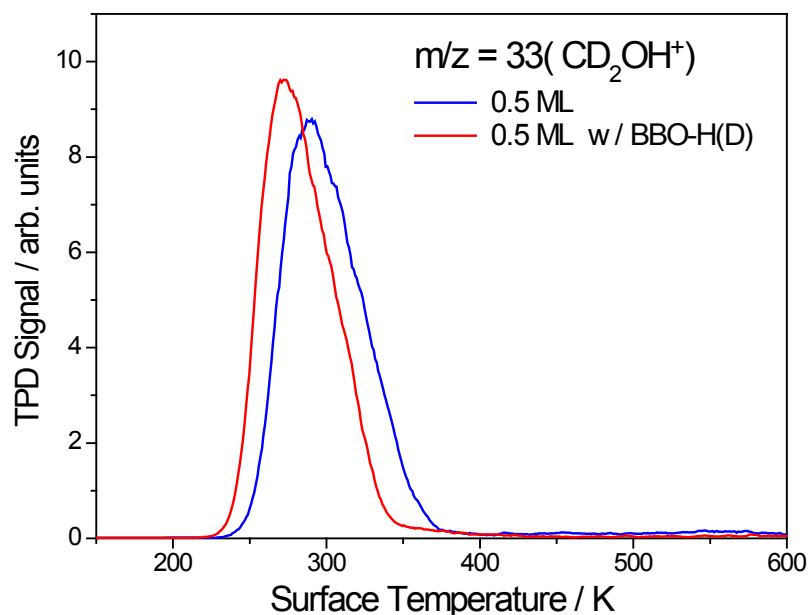
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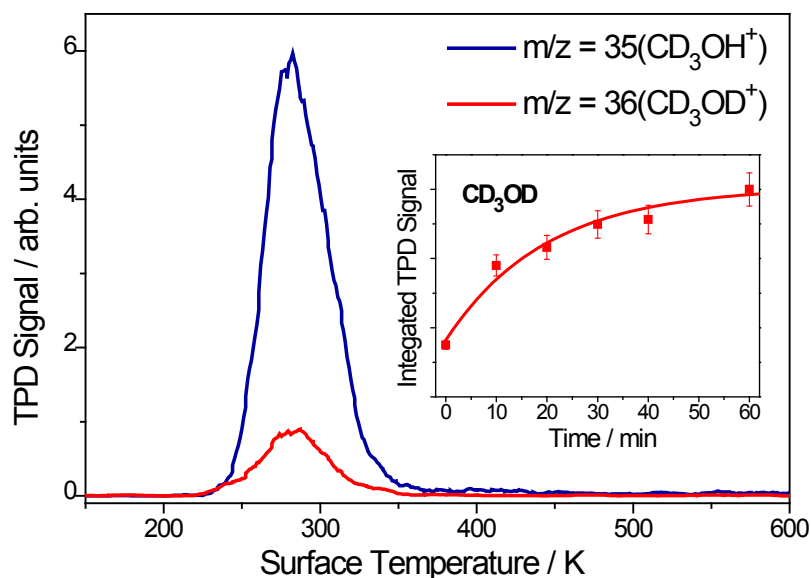
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**Effect of BBO-H(D) on the CD<sub>3</sub>OH TPD spectra.** From the experimental results, especially the TPD spectra of the water isotopologues, we have learned that all the dissociated H or D atoms from CD<sub>3</sub>OH go to the neighboring bridge-bonded oxygen (BBO) rows on the TiO<sub>2</sub>(110) surface. Here we investigate the shifting edge of the TPD peak for CD<sub>3</sub>OH (Figure 3A in the main text). The TPD spectra of CD<sub>3</sub>OH seem to show that those CD<sub>3</sub>OH molecules that desorb at higher temperature are specifically depleted after laser irradiation. In order to understand this observation, we carried out an experiment to investigate how the binding of H or D atoms to the BBO sites affected the TPD of CD<sub>3</sub>OH. In this experiment, we first prepared a large coverage of H or D atoms on the BBO sites by photocatalyzed dissociation of CD<sub>3</sub>OH (0.5 ML) by laser irradiation of the surface for 30 minutes at 100 K, followed by a TPD measurement as the sample was heated to 400 K. At this point, all the undissociated CD<sub>3</sub>OH molecules and the CD<sub>2</sub>O products were desorbed, leaving only H or D atoms, which must be bound to oxygen atoms on the BBO rows. Then we cooled the surface again to 100 K and adsorbed 0.5 ML of CD<sub>3</sub>OH and made the TPD measurement again. The results, presented in Figure S1, show that the CD<sub>3</sub>OH TPD peak with the presence of BBO-H(D) is shifted by about 20 K to lower temperature in comparison with the original CD<sub>3</sub>OH TPD peak (solid blue curve) before laser irradiation. Therefore, the shift of the CD<sub>3</sub>OH TPD peak toward lower temperatures after laser irradiation is caused by the presence of the H and D atoms on the BBO rows.



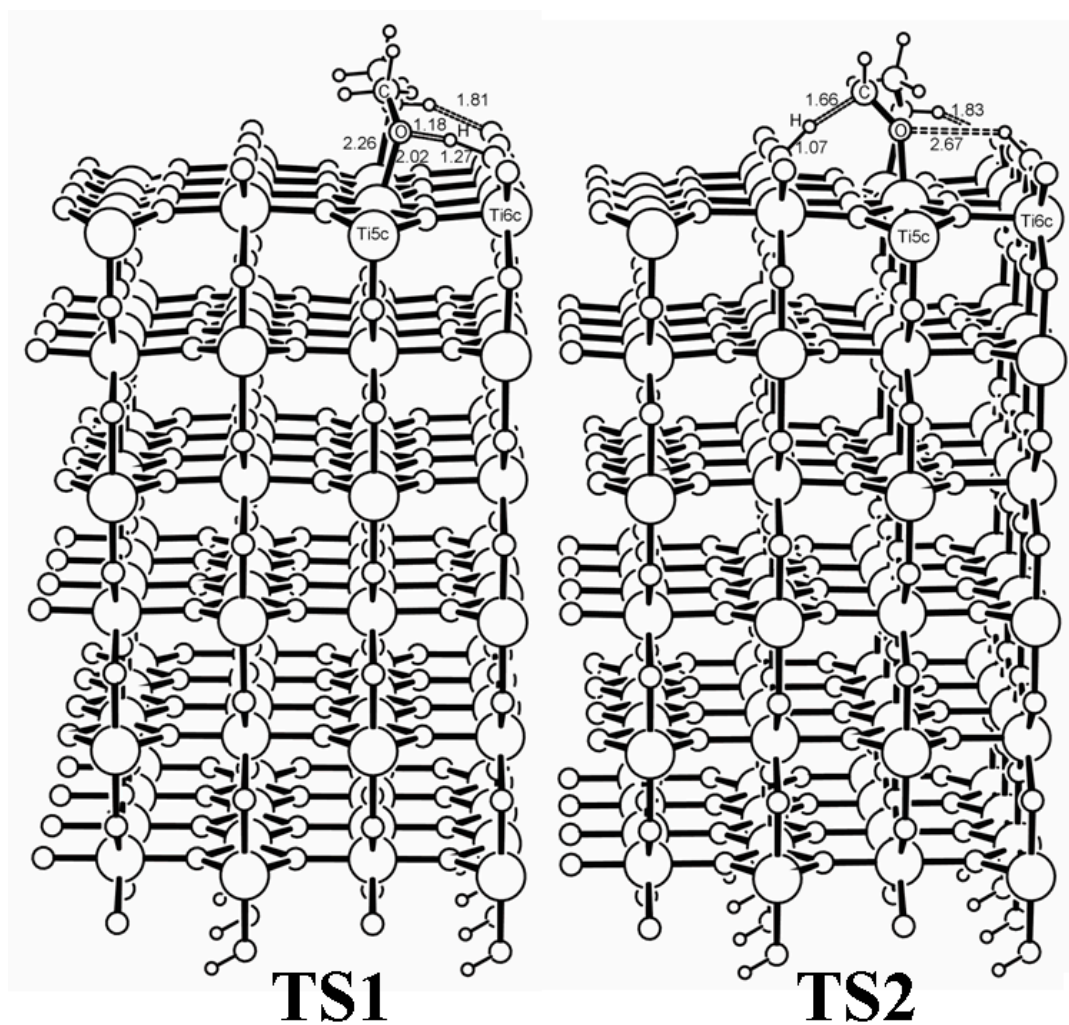
**Figure S1.** TPD signals for methanol, collected at  $m/z = 33$  ( $\text{CD}_2\text{OH}^+$ ), with and without the presence of pre-formed BBO-H(D).

**TPD spectra for  $\text{CD}_3\text{OD}$  versus  $\text{CD}_3\text{OH}$ .** TPD signals resulting from photocatalysis of  $\text{CD}_3\text{OH}$  on the  $\text{TiO}_2(110)$  surface were also observed at parent mass-to-charge ratios ( $m/z$ ) of 35( $\text{CD}_3\text{OH}^+$ ) and 36( $\text{CD}_3\text{OD}^+$ ). Figure S2 shows the TPD spectra at  $m/z = 35$  and 36 after a laser irradiation time of 30 minutes. The TPD signal at  $m/z = 36$  ( $\text{CD}_3\text{OD}^+$ ) is about 16.4% of that at  $m/z = 35$  ( $\text{CD}_3\text{OH}^+$ ). The TPD signal at  $m/z = 36$  increases as the laser irradiation time increases and is anti-correlated with the TPD signal at  $m/z = 35$ , similar to the formaldehyde signal (Figure 4 in main text). The photoinduced  $\text{CD}_3\text{OD}$  signal is likely the result of recombination of  $\text{CD}_3\text{O}$  intermediate products on the  $\text{Ti}_{5c}$  sites with D atoms on the BBO sites. This implies that the intermediate species of  $\text{CD}_3\text{O}$  on  $\text{Ti}_{5c}$  is present in the photocatalytic dissociation of methanol. This observation thus supports the stepwise dissociation mechanism inferred in this work.

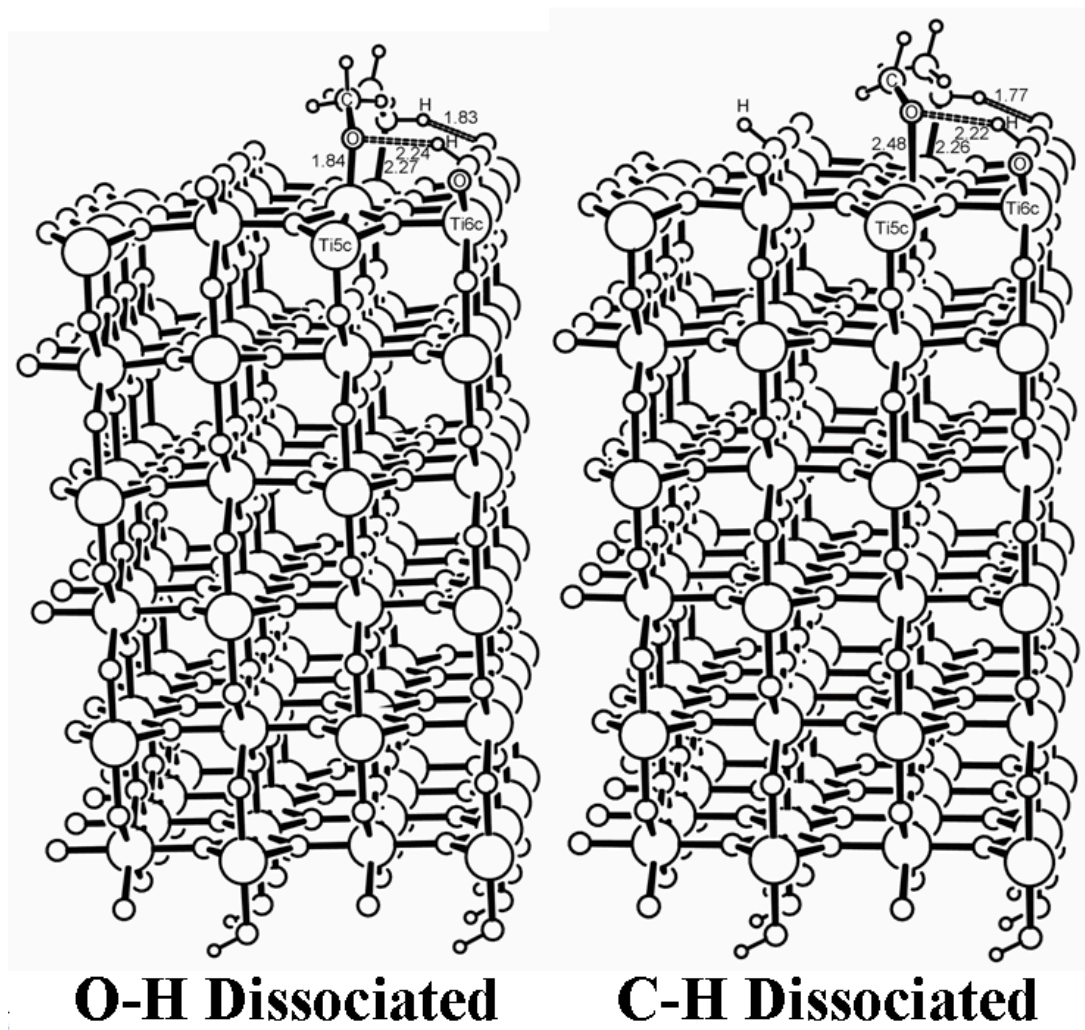


**Figure S2.** TPD spectra collected at  $m/z = 35(\text{CD}_3\text{OH}^+)$  and  $36(\text{CD}_3\text{OD}^+)$  from the photocatalysis of  $\text{CD}_3\text{OH}/\text{TiO}_2(110)$  with a laser irradiation time of 30 min. The inset graph shows the integrated TPD signal for  $\text{CD}_3\text{OD}$ , collected at  $m/z = 36$ , as a function of irradiation time. The integrated signal for  $\text{CD}_3\text{OH}$  decreases with irradiation time, as shown in Figure 4 in the main text.

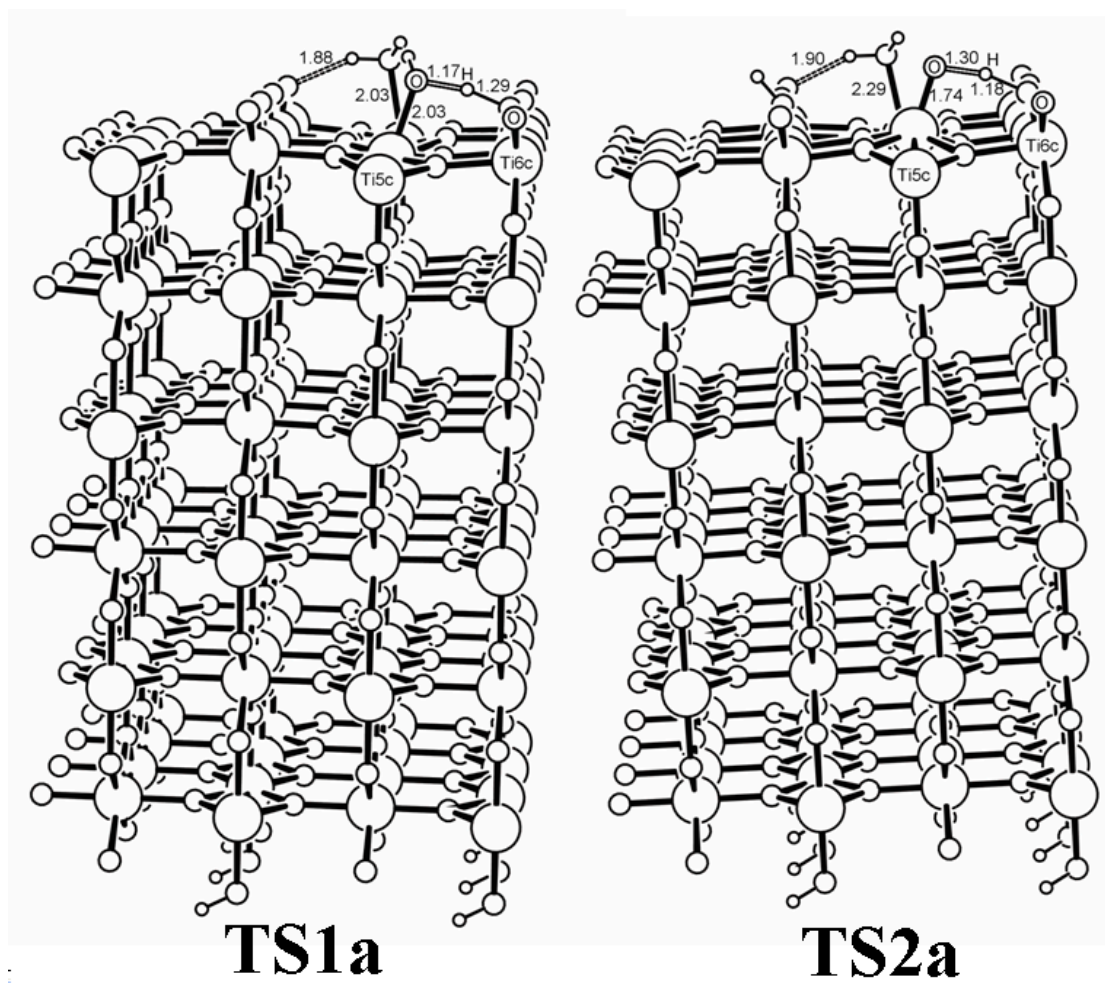
**Optimized structures from theory.** The optimized  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  adsorbed structures are shown in Figure 2 in the main text. The optimized transition states and dissociated structures for stepwise dissociation of  $\text{CH}_3\text{OH}$  are shown in Figures S3 and S4, respectively. The analogous optimized transition states and dissociated structures for stepwise dissociation of  $\text{H}_2\text{O}$  are shown in Figures S6 and S7, respectively.



**Figure S3.** Transition state structures for O-H and C-H dissociation of CH<sub>3</sub>OH on a TiO<sub>2</sub>(110) surface.

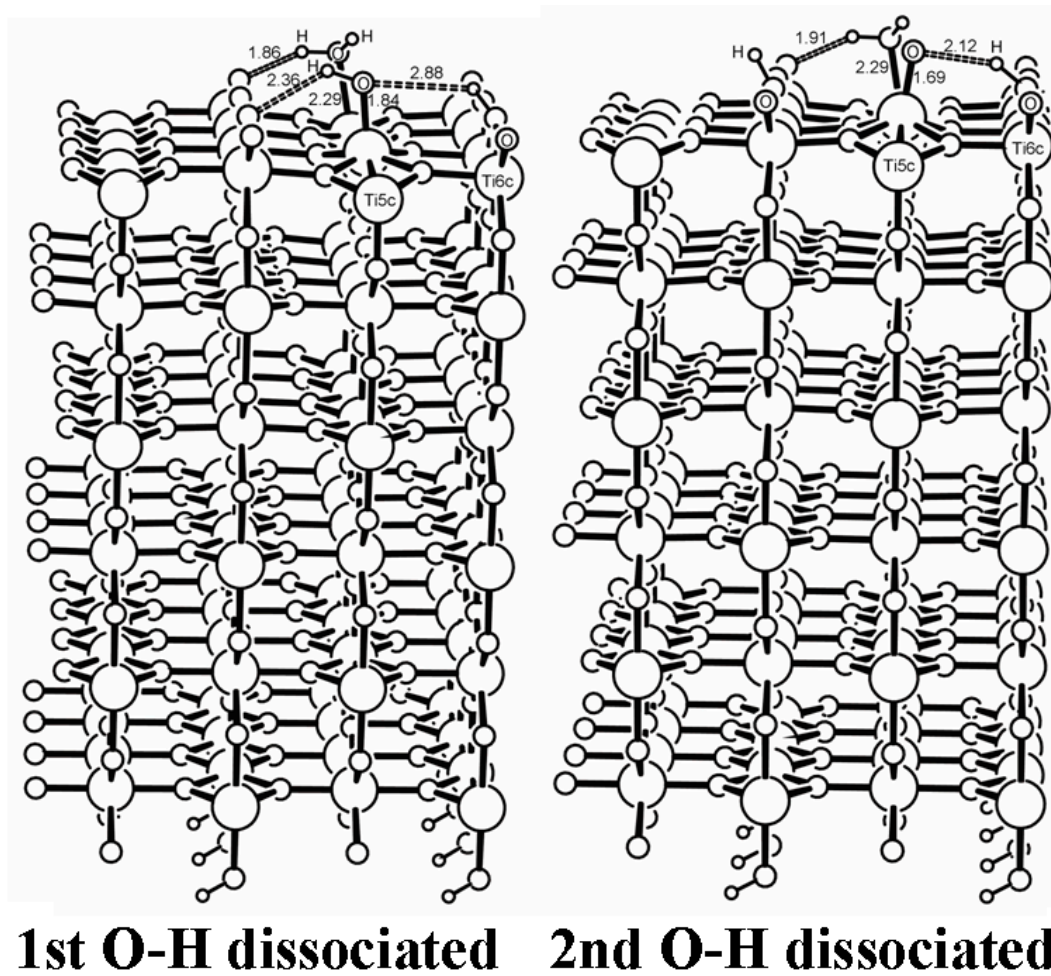


**Figure S4.** Optimized structures for products following the first (O-H) and second (C-H) dissociation steps for  $\text{CH}_3\text{OH}$  on a  $\text{TiO}_2(110)$  surface.



**Figure S5.** Transition state structures for the first and second O-H dissociation steps for H<sub>2</sub>O on a TiO<sub>2</sub>(110) surface.





**Figure S6.** Optimized structures for products following the first and second O-H dissociation steps for  $\text{H}_2\text{O}$  on a  $\text{TiO}_2(110)$  surface.