

Supporting Information

for

“Molecular Hydrogen Formation from Photocatalysis of Methanol on Anatase-TiO₂(101)”

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TPD spectra for CH₃OH TPD signals of CH₃OH on the A-TiO₂(101) surface as a function of coverage was observed at mass-to-charge ratios (m/z) of 31(CH₂OH⁺) depicted in Figure S1. The desorption features are similar to previous results.¹ Five desorption features peaked at 142 K, 188 K, 270 K, 410 K, and 650 K are observed with better resolution and higher desorption temperature than previous study. In spite of better resolution, compared to the case of CH₃OH on R-TiO₂(110),² the first layer peak and the second layer peak are overlapped with each other seriously, implying that the adsorption sites and structures of A-TiO₂(101) are more complicated than the case of R-TiO₂(110).

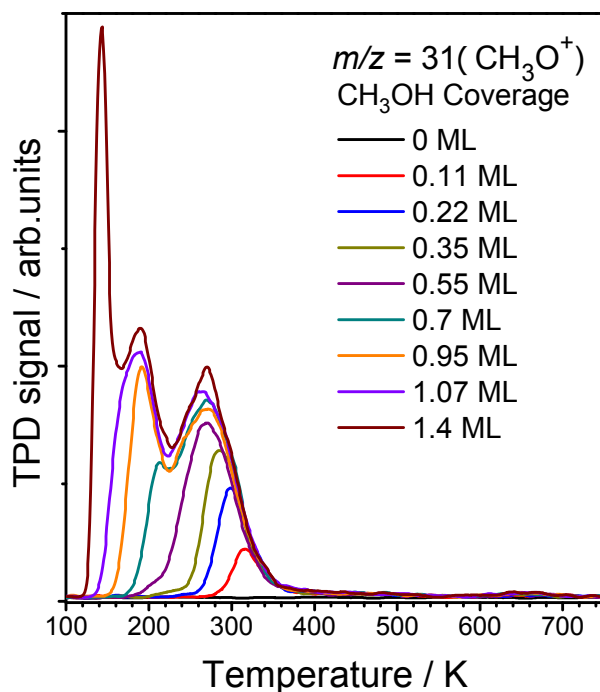
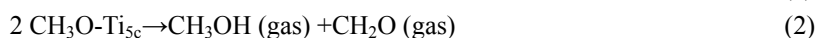


Figure S1. CH₃OH TPD spectra ($m/z = 31$) spectra from various exposures of CH₃OH on the A-TiO₂(101) surface at 100 K.

TPD spectra for $m/z = 30, 31, 32$ TPD signals of mass 30, 31 and 32 resulting from 0.38 ML CH₃OH on the A-TiO₂(101) surface have been collected. The area ratio of $m/z = 31$ and 32 at 270 K and 650 K peak in Figure S2, is the same, equal to 1.55, consistent with the cracking pattern of CH₃OH detected in our quadrupole mass spectroscopy. And this implies that the $m/z = 31$ and 32 650 K peak is from CH₃OH. Thus, this is likely due to CH₃O disproportionation at the five-coordinated Ti⁴⁺(Ti_{5c}) sites, as on the R-TiO₂(110) surface,³



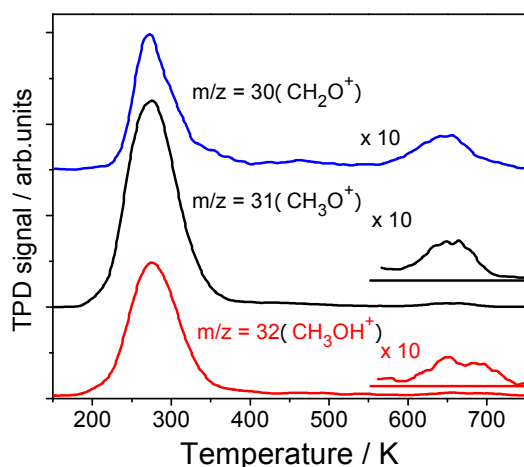


Figure S2. TPD spectra from a vacuum-annealed anatase (101) sample for a CH₃OH coverage of 0.38 ML ($m/z = 30, 31$, and 32).

TOF signals for $m/z = 15, 18, 30, 32$ Photo desorbed signals of CH₃ ($m/z = 15$), H₂O ($m/z = 18$), CH₂O ($m/z = 30$), CH₃OH ($m/z = 32$) and HCOOCH₃ ($m/z = 60$) were monitored during 10 min laser irradiation (by time-of-flight methods, as shown in Figure. S3), a big desorption signal of formaldehyde (CH₂O) was detected, as well as methyl radical (CH₃) and methanol (CH₃OH). However, CH₂O and CH₃ signals are much bigger than CH₃OH signal. Considering ionizer fragmentation patterns of CH₃OH, the CH₃ signal has two components: the parent ion signal of methyl radical (CH₃), and the ion-fragment signal of the parent CH₃OH molecule, as well as the CH₂O signal. No H₂O desorption signal was detected. As shown in the picture, the ratio of density flux of CH₂O and CH₃OH is 4:1, the electron-impact ionization cross section of CH₂O and CH₃OH at 70 eV is nearly the same. The desorption yield of CH₂O is 4 times of that of CH₃OH.

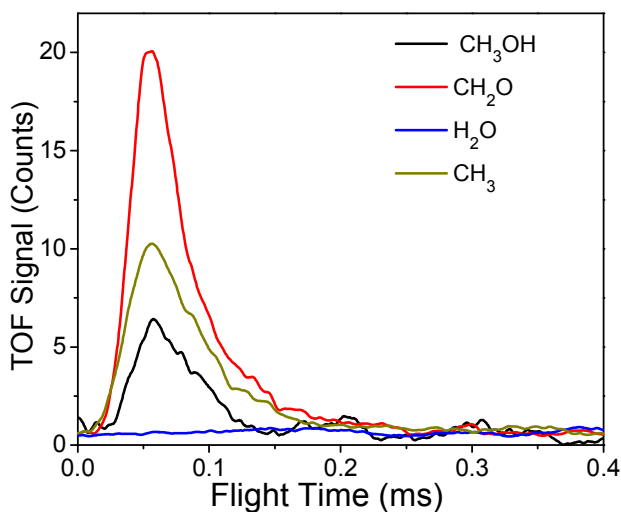


Figure S3. Time of flight signals of $m/z = 15$ (CH₃⁺), 18 (H₂O⁺), 30 (CH₂O⁺), and 32 (CH₃OH⁺) during 10 min 266 nm irradiation with a photon flux of 1.9×10^{17} photons cm⁻² s⁻¹.

Mass fragmentation pattern of CH₃OH Mass fragmentation pattern of CH₃OH was collected by our quadrupole mass detector; the cracking signal of CH₃OH to $m/z = 30$ is only 1/5 of the parent mass ion.

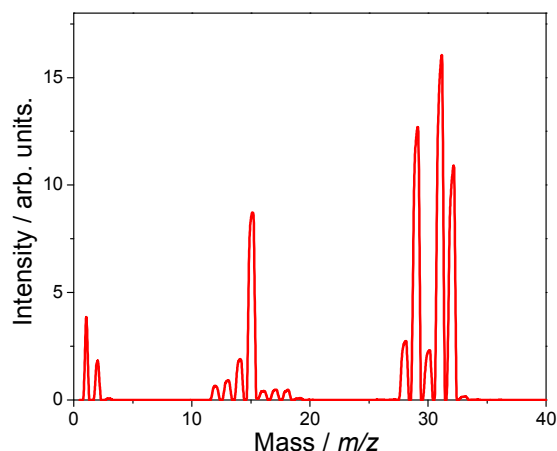


Figure S4. Mass fragmentation pattern of CH₃OH in the TOF mass detector in our surface photocatalysis apparatus.

TPD spectra for $m/z = 15$ TPD signals of $m/z = 15$ resulting from 0.38 ML CH₃OH on the A-TiO₂(101) surface as a function as irradiation time were collected. The 550 K peak has two components: one component is CH₃ radical desorption, and this part is about 0.03 ML, other one is the fragment of CH₃OH at 650 K. After irradiation, the 550 K shifted toward lower temperature and the peak width is narrowed, as the peak intensity is also increased after UV irradiation. The high temperature side of the 550 K CH₃ peak decreases rapidly in the first 1 min., which is due to the fast depletion of CH₃O-Ti_{5c} at 650 K.

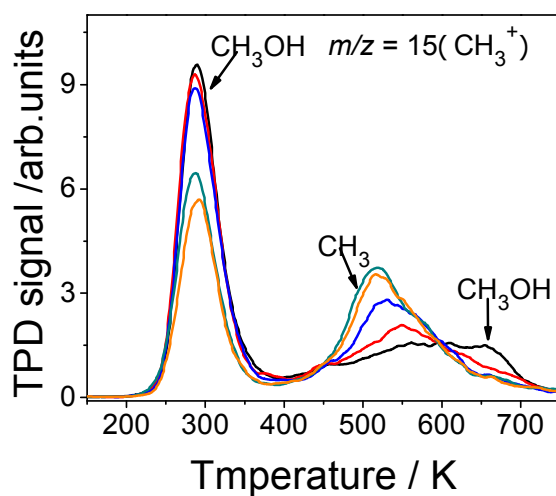


Figure S5. TPD spectra collected at $m/z = 15$, from the photocatalysis of CH₃OH/A-TiO₂(101) with a photon flux of 1.9×10^{17} photons cm⁻² s⁻¹.

Product yields for D₂O versus D₂ on rutile-TiO₂(110) Product yields of D₂O and D₂ on a 0.5 ML CD₃OD covered R-TiO₂(110) surface as a function of irradiation time were measure, as depicted in Figure S5. The rate of D₂O product formation as a function of laser irradiation time is quite different from that of D₂ product. The D₂O yield increases very fast first and then reaches a plateau. Since one oxygen defect is created for one D₂O molecule formed during TPD, it appears that BBO defects make D₂O formation more difficult. The D₂ yield, however, increases faster than that of D₂O as the number of BBO defects increases. Hence, more BBO defects created by D₂O recombinative desorption on the surface can make formation of D₂ easier than D₂O formation.

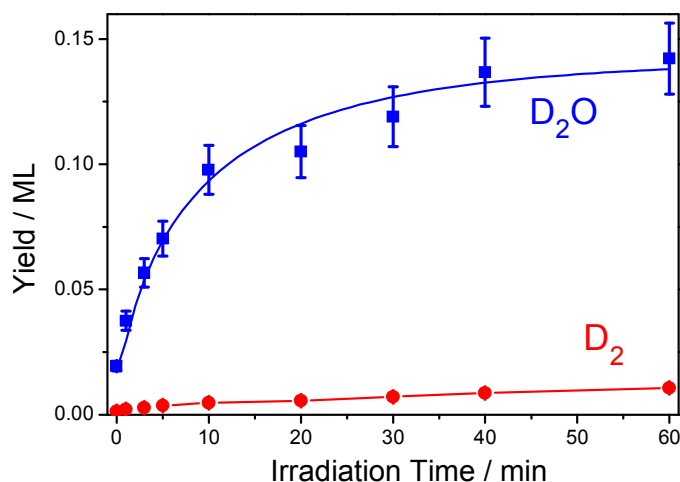


Figure S6. Yields of the molecular hydrogen (D₂), water (D₂O) TPD product as a function of laser irradiation time on 0.5 ML of CD₃OD covered R-TiO₂(110) surface.

S1 Herman, G. S.; Dohnálek, Z.; Ruzycki, N.; Diebold, U. *J. Phys. Chem. B* **2003**, *107*, 2788-2795.

S2 Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. *Faraday Discuss.* **1999**, *114*, 313-319.

S3 Shen, M.; Henderson, M. A. *J. Phys. Chem. Lett.* **2011**, *2*, 2707-2710.