Supporting Information

for

Photocatalytic Oxidative Dehydrogenation of Propane for Selective Propene Production with TiO₂

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The TPD spectra of the C₃H₆ standard sample. The TPD spectra of a C₃H₆ standard sample was collected at m/z = 39 (C₃H₃⁺), 40 (C₃H₄⁺), 41 (C₃H₅⁺) and 42 (C₃H₆⁺), as shown in Figure S1. The relative intensities of the desorption peak in the TPD traces of m/z = 39, 40, 41 and 42 were calculated to be 0.70:0.27:1:0.68.

Figure S1. Typical spectra acquired at m/z = 39 (C₃H₃⁺), 40 (C₃H₄⁺), 41 (C₃H₅⁺) and 42 (C₃H₆⁺) after the R-TiO₂(110) surface was dosed with 0.42 ML C₃H₆ standard sample at 90 K.
The TPD spectra of different masses collected on the 0.36 ML C₃H₈ covered oxidized R-TiO₂(110) surface. As shown in Figure S2a, the TPD spectra of different masses were collected on the 0.36 ML C₃H₈ covered oxidized R-TiO₂(110) surface followed by irradiating for 0 (black lines) and 5 min (red lines) at 90 K, respectively. As described in the main manuscript, the desorption peak at 137 K is assigned to C₃H₈ molecule adsorbed at Ti₅c sites.¹ After irradiation, two new peaks at 190 K (m/z = 39 (C₃H₅⁺), 40 (C₃H₆⁺), 41 (C₃H₇⁺) and 42 (C₃H₈⁺)) and 310 K (m/z = 18 (H₂O⁺)) appear. The 310 K peak is due to the desorption of H₂O molecules on the Ti₅c sites (H₂Oᵦ) or the recombination desorption of terminal OH groups on the Ti₅c sites (OHᵦ).² The relative intensities of the190 K at m/z = 39, 40, 41 and 42 is nearly the same with that of the standard C₃H₆ sample (Figure S1), demonstrating that the 190 K product is attributed to C₃H₆ formation. Besides, the small shoulders in the TPD traces of m/z = 28 (C₂H₄⁺ or CO⁺) and 44 (CO₂⁺) are due to the adsorption of CO and CO₂ from the background.

In addition, the details of Figure S2a in the temperature range of 230 - 800 K are highlighted in Figure S2b. Broad peaks from 250 K to 350 K in the TPD profile of m/z = 29 (C₂H₅⁺), 39 (C₃H₃⁺), 40 (C₃H₄⁺), 41 (C₃H₅⁺), 42 (C₃H₆⁺) 43 (C₃H₇⁺) and 44 (C₃H₈⁺ or CO₂⁺) are observed. Although the desorption peaks are hard to be assigned due to the tiny signals, the appearance of the peak at 300 K in the TPD trace of m/z = 44 suggests that the peak is likely due to the recombination desorption of C₃H₈. In addition, an unimpressive peak at 340 K is observed in the TPD trace of m/z = 42, and the signal of this peak does not appear in the TPD profile of m/z = 44 (C₃H₈⁺ or CO₂⁺). Therefore, the peak is likely to be attributed to C₃H₆ product as well. These two peaks may be derived from the recombination and second dehydrogenation of tiny amount of C₃H₇ moiety adsorbed on the surface, respectively. In addition, a tiny peak at 560 K is observed in the TPD traces of m/z = 39 (C₃H₅⁺), 40 (C₃H₆⁺), 41 (C₃H₇⁺) and 42 (C₃H₈⁺), which may be attributed to C₃H₆ produced via second dehydrogenation of C₃H₇ group adsorbed on the Oₖ atoms.³
Figure S2a. Typical spectra acquired at different masses after adsorbing 0.36 ML C₃H₈ on oxidized R-TiO₂(110) surfaces followed by irradiating the surface for 0 (black lines) and 5 min (red lines) at 90 K, respectively.
Figure S2b. The enlarged view of Figure S2a in the temperature range of 230 K to 800 K.
The control experiment on the $^{18}$O$_2$ oxidized R-TiO$_2$(110) surface. A control experiment was performed on the R-TiO$_2$(110) surface oxidized by 200 L $^{18}$O$_2$ at 300 K. According to Lira’s results,$^4$ the O$_v$ will be occupied by $^{18}$O atoms and $^{18}$O$_{Ti}$ atoms (18O atoms adsorbed at Ti$_{5c}$ sites) will be produced after adsorbing 200 L $^{18}$O$_2$ on the reduced R-TiO$_2$(110) surface at 300 K. Subsequently, photocatalytic ODHP was carried out on the oxidized surfaces. Similarly, C$_3$H$_6$(Ti) product is observed in the TPD trace of m/z = 42 (C$_3$H$_6$) after 355 nm irradiation (Figure S3). Correspondingly, the peak at 310 K in the TPD traces of m/z = 18 (H$_2^{16}$O$^+$ or $^{18}$O$^+$), 19 (H$^{18}$O$^+$) and 20 (H$_2^{18}$O$^+$) is attributed to H$_2^{18}$O$_{Ti}$ product (H$_2^{18}$O adsorbed at the Ti$_{5c}$ sites). No signal in the TPD trace of m/z = 17 (H$^{16}$O$^+$) demonstrates that $^{18}$O$_{Ti}$ atoms are involved in photocatalytic C-H bond cleavage directly.

![Figure S3](https://example.com/figure.png)

Figure S3. Typical TPD spectra acquired at m/z = 17 (H$^{16}$O$^+$), 18 (H$_2^{16}$O$^+$, $^{18}$O$^+$), 19 (H$^{18}$O$^+$), 20 (H$_2^{18}$O$^+$), 29 (C$_3$H$_6^+$) and 42 (C$_3$H$_6$) after adsorbing 0.36 ML C$_3$H$_8$ on R-TiO$_2$(110) surfaces oxidized by 200 L $^{18}$O$_2$ at 300 K followed by irradiating the surface for 0 (black lines) and 5 min (red lines) at 90 K, respectively.
The adsorption configurations of C₃H₈. Different adsorption configurations and energies of C₃H₈ on R-TiO₂(110) are shown in Figure S4. According to previous studies about small alkanes on the rutile RuO₂(110) surface, the 2p-η¹ structure is the most stable configuration, in which two primary C atoms along with a C-H bond are close to two adjacent Ti₅c sites on the surface, respectively. However, the differences among the three configurations are relatively small.

When the systems are calculated without van der Walls correction, the adsorption energy is close to zero for all the configurations. In addition, the adsorption of C₃H₈ is also calculated on the oxidized R-TiO₂(110) surface, and the adsorption energy is almost the same with that on the stoichiometric surface, indicating that the existence of O₅Ti atoms has little effect on the adsorption of C₃H₈.

**Figure S4.** The adsorption of C₃H₈ on the stoichiometric surfaces is shown in side and top view (up panel), and the adsorption of C₃H₈ on the oxidized surface is only shown in side view (down panel). The corresponding adsorption energies are figured out with the DFT-D3 method.
The adsorption structure of dissociated C$_3$H$_7$ intermediate. The adsorption structures of dissociated C$_3$H$_8$ with and without photoexcitation are shown in Figure S5. As described in the manuscript, both the C$_3$H$_7$ intermediates on the reduced and O$_{Ti}$ atom covered surfaces are C$_3$H$_7^-$ groups formed via the heterolytic C-H bond cleavage without photoexcitation. Correspondingly, the C-Ti bonds of C$_3$H$_7^-$ groups on the reduced surface and O$_{Ti}$ atom covered surface are 2.10 and 2.09 Å, respectively. In comparison, the C-Ti bond (2.76 Å) for the hole-trapped propyl group (C$_3$H$_7^*$ radical) with photoexcitation is much longer. As described in the manuscript, alkyl groups have good hole scavenging ability to stabilize the photo-induced hole and thus the C-H cleavage would be promoted thermodynamically via a hole-mediated HAT process. In addition, the C-Ti bond (2.76 Å) also suggests that C$_3$H$_7^*$ radicals can physically adsorb on R-TiO$_2$(110).

Figure S5. The structures of the $1^\circ$-dissociated C$_3$H$_8$ (H-CH$_2$CH$_2$CH$_3$) on the stoichiometric surface, oxidized surface and oxidized surface with hole trapping (from left to right) respectively. The C-Ti bond and distance (Å) are figured out with van der Walls correction.
References

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