

**Supplementary Materials for**  
**Photocatalytic Ethane Conversion on Rutile TiO<sub>2</sub>(110):**  
**Identifying the Role of Ethyl Radical**

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## Supplementary experimental results

### S1. Typical TPD spectra collected on 0.28 ML C<sub>2</sub>H<sub>6</sub> covered reduced R-TiO<sub>2</sub>(110) after UV irradiation.

Fig. S1 shows the TPD spectra of  $m/z = 18$  (H<sub>2</sub>O<sup>+</sup>), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>), 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup> and CHO<sup>+</sup>) and 30 (C<sub>2</sub>H<sub>6</sub><sup>+</sup>) collected on the reduced R-TiO<sub>2</sub>(110) surfaces after adsorbing 0.28 ML C<sub>2</sub>H<sub>6</sub> followed by 355 nm irradiation for 0 (black line) and 10 min (red line). Before irradiation, one sharp desorption peak at ~ 110 K appears in the TPD traces of  $m/z = 27, 29$  and 30, which is attributed to the desorption of C<sub>2</sub>H<sub>6</sub> on the Ti<sub>5c</sub> sites (C<sub>2</sub>H<sub>6</sub>(Ti)) of R-TiO<sub>2</sub>(110).<sup>1</sup> In addition, a tiny signal can also be observed in the TPD spectra of  $m/z = 29$ , which is contributed by the isotope of <sup>13</sup>CO from the <sup>12</sup>CO background. After UV irradiation, no products are detected, and all the TPD traces are almost identical to those without UV irradiation, indicating that reduced R-TiO<sub>2</sub>(110) is photo inactive for the conversion of C<sub>2</sub>H<sub>6</sub>.

### S2. The respective sketches of (a) LN<sub>2</sub> cooling system and (b) combined LN<sub>2</sub> and He cold head cooling system, and (c) typical TPD spectra acquired on the 0.3 L C<sub>2</sub>H<sub>6</sub> covered oxidized R-TiO<sub>2</sub>(110) surfaces at 100 K with LN<sub>2</sub> cooling system.

When only liquid nitrogen (LN<sub>2</sub>) is used for cooling the surface, the tantalum sample holder is as shown in Fig. S2a, which is mounted on two copper elbows. And the copper blocks are about 20 mm away from the center of tantalum sample holder. The diameter of our home-built molecular beam doser is 15 mm. When we dose C<sub>2</sub>H<sub>6</sub> on the R-TiO<sub>2</sub>(110) surface, the distance between the R-TiO<sub>2</sub>(110) surface and the front of the doser is about 6 mm. Even C<sub>2</sub>H<sub>6</sub> molecule beam is divergent, it is difficult to diffuse to the copper blocks and adsorb on it largely. As a result, no broad desorption peak between 400 K and 700 K in the TPD spectra of C<sub>2</sub>H<sub>6</sub> can be observed, as shown in Fig. S2b.

In contrast, when both LN<sub>2</sub> and He cold head are used for cooling the surface, the sample holder is modified as shown in Fig. S3c, in which the distance between the left and right ends (30.1 mm) is smaller than the former (53 mm). This modification brings the cold copper blocks closer to the center of tantalum sample holder. Correspondingly, the probability of C<sub>2</sub>H<sub>6</sub> adsorption on the cold copper blocks increases significantly. When the surface temperature arises to 400 K, the cold copper elbows will also be heated slowly. Then, the adsorbed C<sub>2</sub>H<sub>6</sub> molecules will be desorbed slowly. In addition, in this scheme, the cold copper blocks are also connected to the He cold head through a copper braid. Part of the C<sub>2</sub>H<sub>6</sub> adsorbed on the copper braid may also be desorbed during the TPD process and be detected by the mass spectrometer.

Therefore, we could conclude that the broad desorption peak between 400 K and 700 K is from the desorption of C<sub>2</sub>H<sub>6</sub> from the copper blocks that is used for mounting tantalum sample holder.

### S3. Typical TPD spectra collected at different masses on 0.21 ML acetaldehyde (CH<sub>3</sub>CHO) covered reduced R-TiO<sub>2</sub>(110).

TPD spectra was collected at  $m/z = 15$  (CH<sub>3</sub><sup>+</sup>), 29 (CHO<sup>+</sup>), 43 (CH<sub>3</sub>CO<sup>+</sup>) and 44 (CH<sub>3</sub>CHO<sup>+</sup> and CO<sub>2</sub><sup>+</sup>) on the CH<sub>3</sub>CHO covered R-TiO<sub>2</sub>(110) surface (Fig. S3). A tiny signal at ~ 160 K in the TPD spectra of  $m/z = 44$  is contributed by the CO<sub>2</sub> desorption, which is from the background. And the relative intensities of the CH<sub>3</sub>CHO desorption peak at 250 K in the TPD profiles of  $m/z = 15, 29$  and 43 were calculated to be

0.78:1:0.13, which is nearly consistent with the relative intensities of the product desorption at 365 K (0.80:1:0.14) in Fig. 1, demonstrating that the peak is contributed by CH<sub>3</sub>CHO production.

#### **S4. Typical TPD spectra collected on the 0.36 ML ethylene (C<sub>2</sub>H<sub>4</sub>) covered R-TiO<sub>2</sub>(110) surface.**

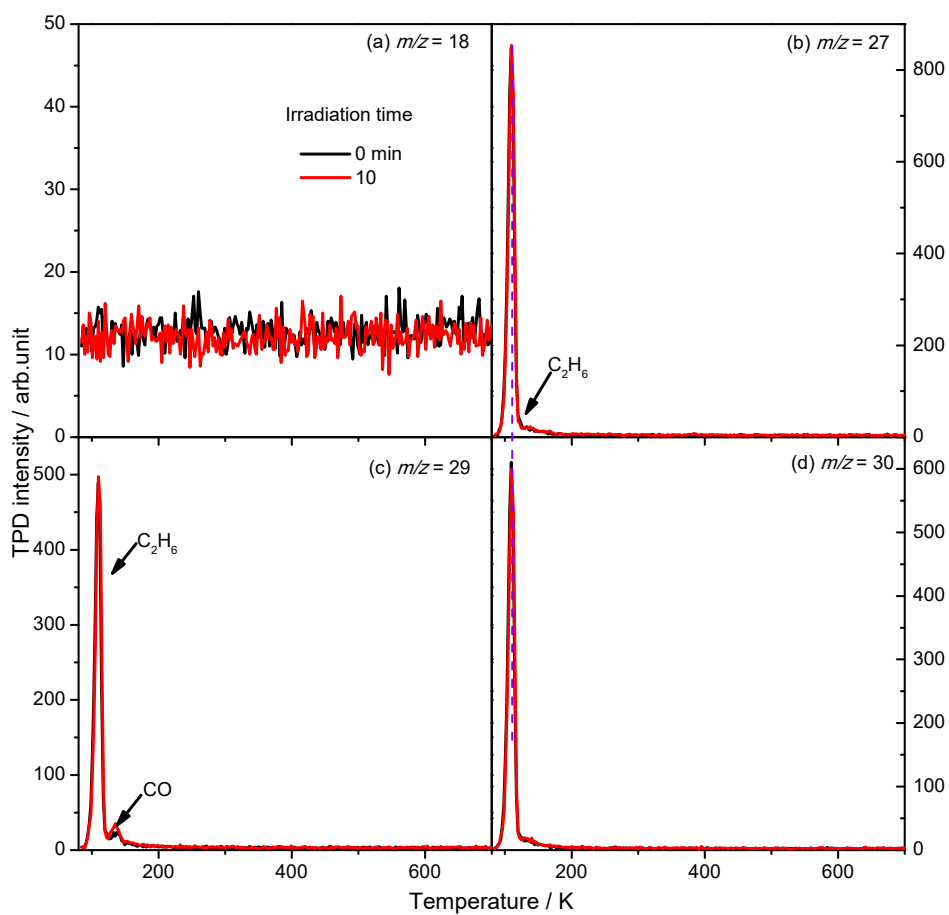
TPD spectra of a C<sub>2</sub>H<sub>4</sub> standard sample was collected at  $m/z = 26$  (C<sub>2</sub>H<sub>2</sub><sup>+</sup>), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>), 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>) and 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>) on the 0.36 ML C<sub>2</sub>H<sub>4</sub> covered R-TiO<sub>2</sub>(110) surface as shown in Fig. S4. The relative intensities of the desorption peak in the TPD traces of  $m/z = 26$  and 27 were calculated to be 0.86:1, which is very close to that of the peaks at 168 K (0.87:1), 423 K (0.89:1), and 580 K (0.88:1) in Fig. 1, respectively. And the tiny signal of 29 in C<sub>2</sub>H<sub>4</sub> standard sample is also detected in the NIST databases. The results indicate that all the three peaks are due to C<sub>2</sub>H<sub>4</sub> production from photocatalytic ODHE, but the reaction channels are different from each other as discussed in the manuscript.

#### **S5. Typical TPD spectra collected at different masses from the C<sub>2</sub>H<sub>5</sub>OH covered TiO<sub>2</sub>(110) surfaces.**

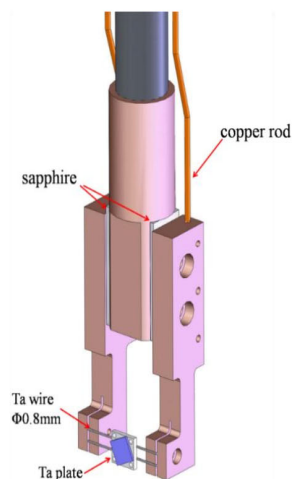
TPD spectra was collected at  $m/z = 15$  (CH<sub>3</sub><sup>+</sup>), 26 (C<sub>2</sub>H<sub>2</sub><sup>+</sup>), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>) 29 (C<sub>2</sub>H<sub>5</sub><sup>+</sup>) and 31 (CH<sub>2</sub>OH<sup>+</sup>) on the 0.05 ML C<sub>2</sub>H<sub>5</sub>OH covered R-TiO<sub>2</sub>(110) surface as shown in Fig. S5. Due to the small coverage of C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>5</sub>OH prefers to dissociatively adsorb at the O<sub>v</sub> sites, forming C<sub>2</sub>H<sub>5</sub>O<sub>b</sub> groups and H atoms at the O<sub>b</sub> sites (OH<sub>b</sub>). During the TPD process, C<sub>2</sub>H<sub>5</sub>O<sub>b</sub> groups will dissociate to C<sub>2</sub>H<sub>4</sub> at high surface temperature with a small amount of C<sub>2</sub>H<sub>5</sub>OH formation,<sup>2</sup> agreement with the result in the Fig. 1.

#### **S6. PSD signals collected on the C<sub>2</sub>H<sub>4</sub> covered oxidized R-TiO<sub>2</sub>(110) surface.**

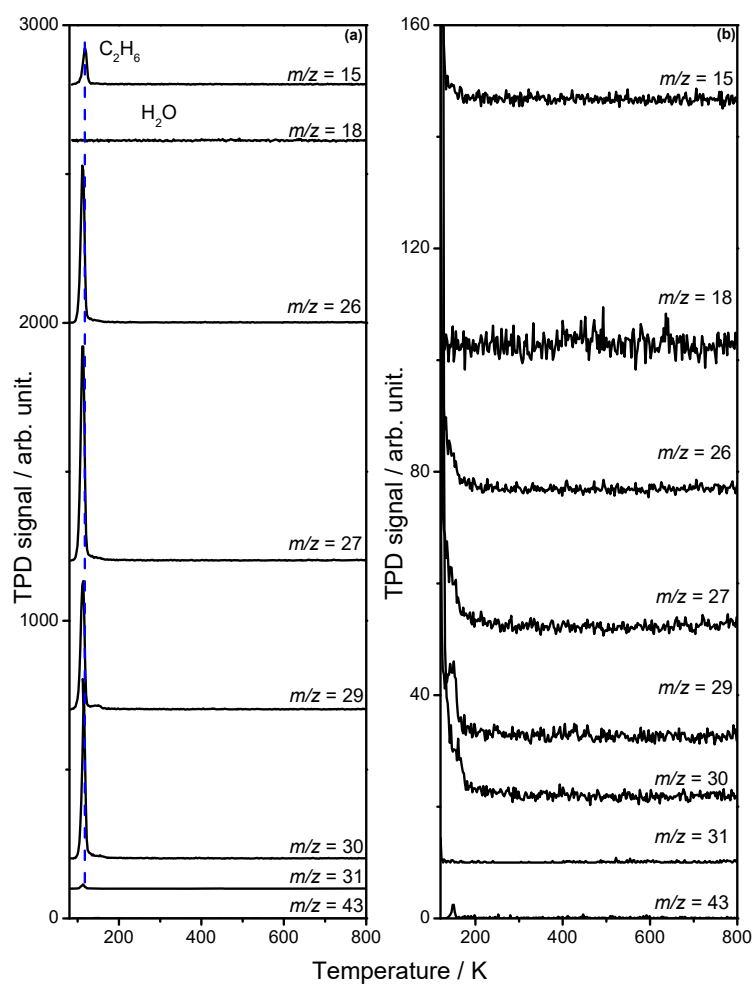
The PSD signals were collected at  $m/z = 26$  (C<sub>2</sub>H<sub>2</sub><sup>+</sup>), 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>) and 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>) from the 0.36 ML C<sub>2</sub>H<sub>4</sub> covered oxidized R-TiO<sub>2</sub>(110) surface during the UV irradiation, as shown in Fig. S6. A sharp increase of the desorption signal of C<sub>2</sub>H<sub>4</sub> is observed in all the mass traces immediately when the laser is turned on, and then the signal decreases rapidly. The results indicate that the desorption of C<sub>2</sub>H<sub>4</sub> is induced by light rather than heat, otherwise the signal should have increased slowly rather than a sharp peak after the light is turned on.



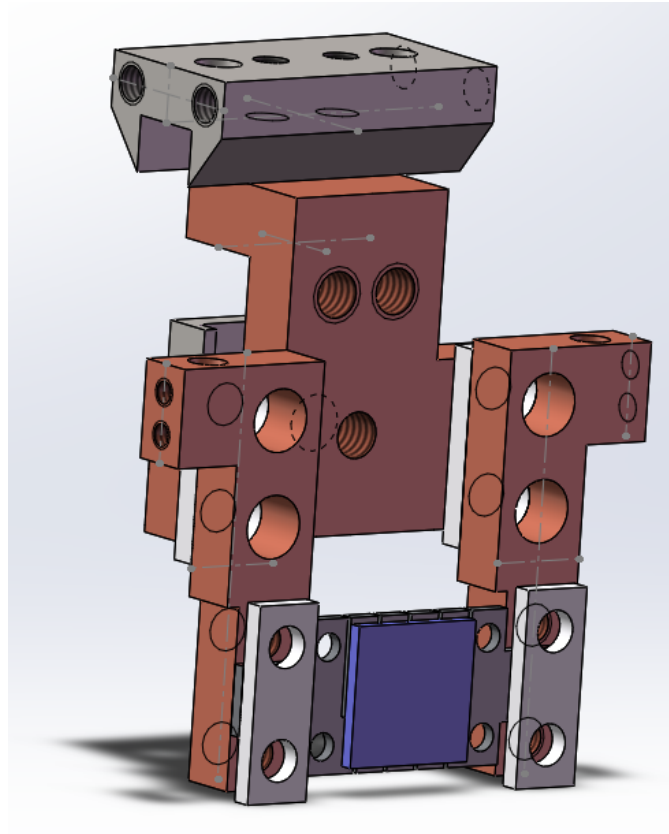
**Fig. S1.** Typical TPD spectra acquired at  $m/z = 18$  ( $\text{H}_2\text{O}^+$ ), 27 ( $\text{C}_2\text{H}_3^+$ ), 29 ( $\text{C}_2\text{H}_5^+$  and  $\text{CHO}^+$ ) and 30 ( $\text{C}_2\text{H}_6^+$ ) after adsorbing 0.28 ML  $\text{C}_2\text{H}_6$  on the reduced R- $\text{TiO}_2(110)$  surfaces at 75 K with (10 min, red lines) and without (0 min, black lines) 355 nm irradiation, respectively.



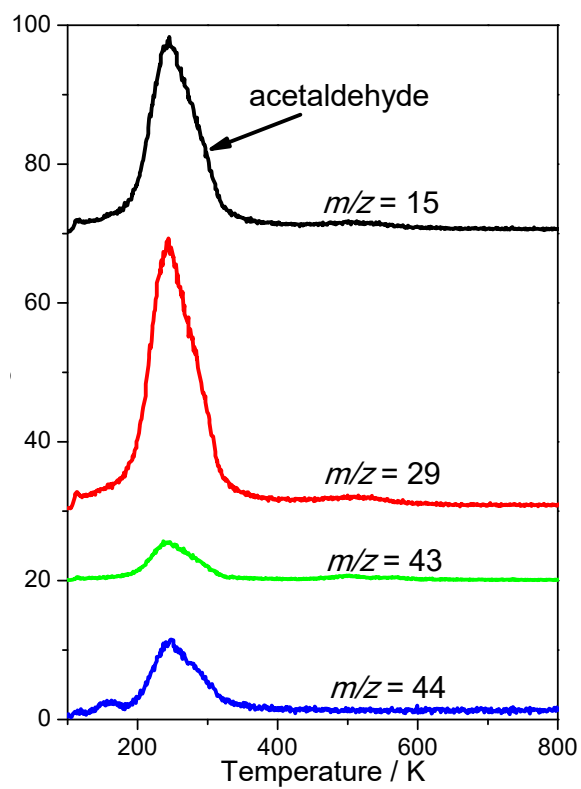
**Figure S2a.** The sketch of the LN<sub>2</sub> cooling system.



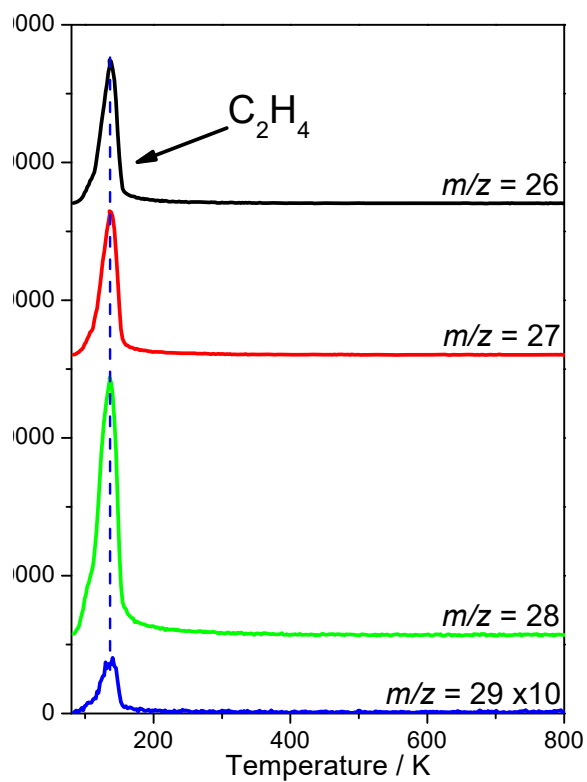
**Fig. S2b.** Left: Typical TPD spectra acquired at  $m/z = 15$  ( $\text{CH}_3^+$ ), 18 ( $\text{H}_2\text{O}^+$ ), 26 ( $\text{C}_2\text{H}_2^+$ ), 27 ( $\text{C}_2\text{H}_3^+$ ), 29 ( $\text{C}_2\text{H}_5^+$  and  $\text{CHO}^+$ ), 30 ( $\text{C}_2\text{H}_6^+$ ), 31 ( $\text{CH}_2\text{OH}^+$ ), and 43 ( $\text{CH}_3\text{CO}^+$ ) on the 0.3 L  $\text{C}_2\text{H}_6$  covered oxidized R-TiO<sub>2</sub>(110) surfaces at 100 K, respectively. Right: The TPD spectra in the left at the temperature range of  $> 140$  K are highlighted.



**Fig. S2c.** The sketch of combined LN<sub>2</sub> and He cold head cooling system.

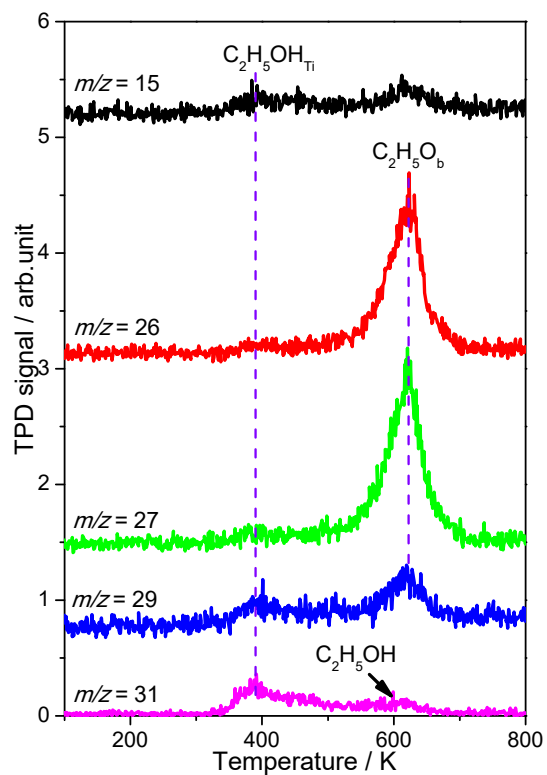


**Fig. S3.** Typical TPD spectra acquired at  $m/z = 15$  ( $\text{CH}_3^+$ ), 29 ( $\text{CHO}^+$ ), 43 ( $\text{CH}_3\text{CO}^+$ ) and 44 ( $\text{CH}_3\text{CHO}^+$  and  $\text{CO}_2^+$ ) on the 0.21 ML  $\text{CH}_3\text{CHO}$  covered R- $\text{TiO}_2(110)$  surface.

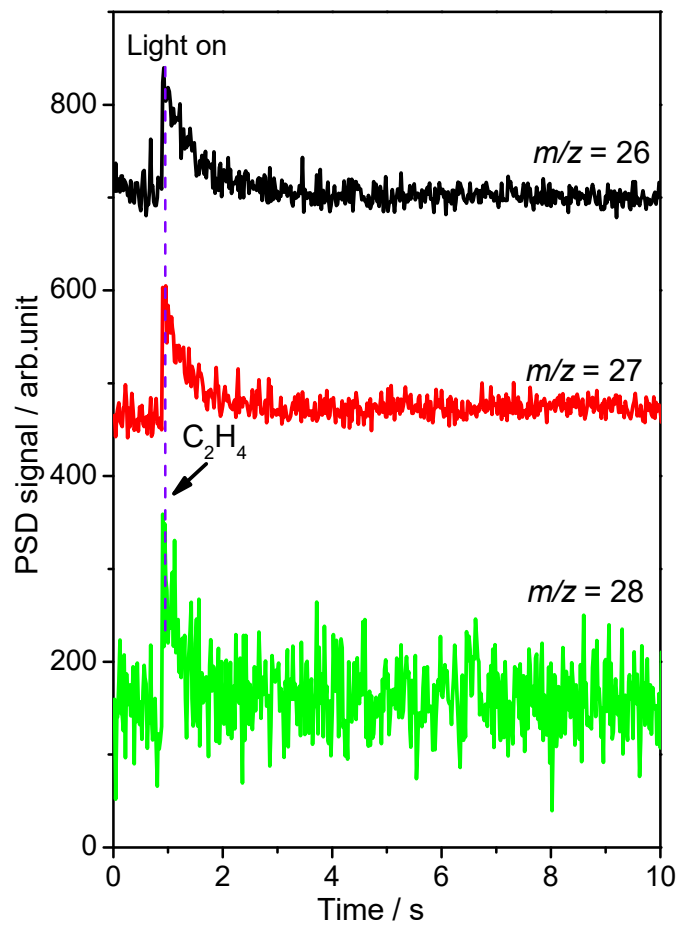


**Fig. S4.** Typical TPD spectra acquired at  $m/z = 26$  ( $C_2H_2^+$ ),  $27$  ( $C_2H_3^+$ ),  $28$  ( $C_2H_4^+$ ) and  $29$  on the  $0.36$  ML  $C_2H_4$  covered R-TiO<sub>2</sub>(110) surface.





**Fig. S5.** Typical TPD spectra acquired at  $m/z = 15$  ( $CH_3^+$ ), 26 ( $C_2H_2^+$ ), 27 ( $C_2H_3^+$ ), 29 ( $C_2H_5^+$ ) and 31 ( $CH_2OH^+$ ) on the 0.05 ML  $C_2H_5OH$  covered reduced R- $TiO_2(110)$ .



**Fig. S6.** The PSD spectra acquired at  $m/z = 26$  ( $C_2H_2^+$ ), 27 ( $C_2H_3^+$ ) and 28 ( $C_2H_4^+$ ) on the 0.36 ML  $C_2H_4$  covered oxidized R-TiO<sub>2</sub>(110) surfaces. The violet dashed line represents the moment when the light is turned on ( $t = 1$  s).

## References

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S1 L. Chen, R. S. Smith, B. D. Kay and Z. Dohnálek, *Surf. Sci.*, 2016, **650**, 83-92.

S2 Y. K. Kim, B. D. Kay, J. White and Z. Dohnálek, *Catal. Lett.*, 2007, **119**, 1-4.