

Supporting Information: Photocatalytic Selectivity Switch to C-C Scission: α -Methyl Ejection of tert-Butanol on TiO₂(110)

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Data Analysis:

During the thermal and photo-desorption experiments, the potential products were monitored with several masses: Isobutene with masses 56, 41 and 39; acetone with 58 and 43; tert-butanol with 59 and 31; tert-butanol-OD with 59, 31 and 32. The methyl-radical was detected during the experiments on mass 15. Further molecules and corresponding masses including H₂ (2), HD (3), CH₄ (16), H₂O (18), HDO (19), CO (28), CO₂ (44) were recorded, but found to be insignificant with the exception of water (see Fig. S2). To quantify the results, the coverages of tert-butanol normalized to the H₂O-TPD of a

monolayer according to the convention in the literature.¹ The tert-butanol-OD was quantified using masses 31 and 32, because some isotope exchange could not be avoided in the gas line and on the single crystal. Isobutene and acetone were quantified using masses 56 and 58 as well as by considering the fragmentation of tert-butanol and the respective other molecules. For the quantification, all molecule yields were corrected for their fragmentation pattern, their transmission through the quadrupole mass spectrometer, and their ionization cross-sections (see Fig. S3 and S4).²⁻⁴

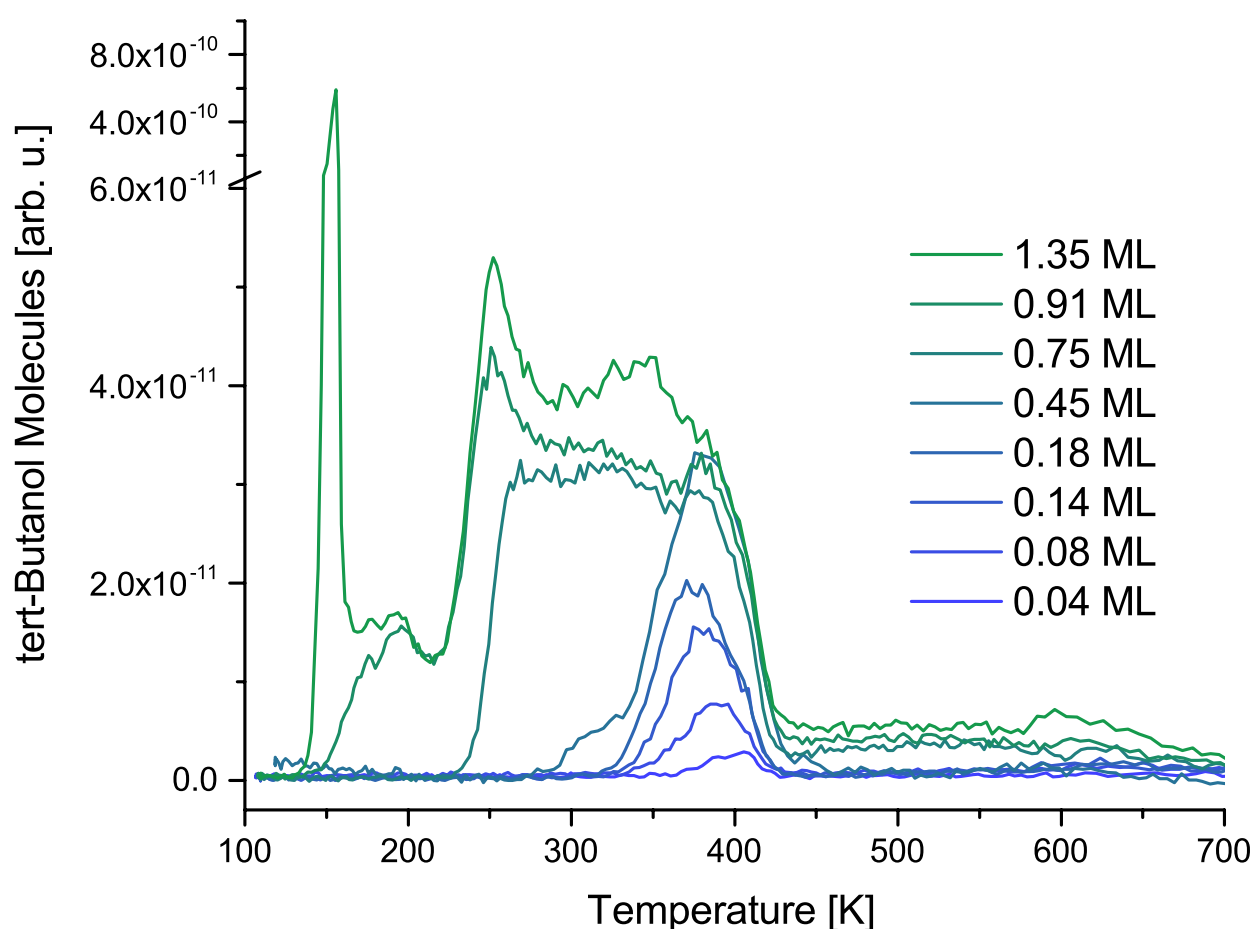


Figure S1: Coverage dependent TPD-series of tert-butanol-OD on a reduced TiO₂(110)-surface [r-TiO₂(110)]. At small coverages, a desorption feature at around 400 K arises, that is attributed to tert-butanol binding to the Ti-lattice sites. With higher coverages this feature saturates and a shoulder is growing to a peak at 250 K, which is assigned to the desorption from bridge-bonding oxygen (BBO) surface atoms. Another feature appearing below 200 K is attributed to multilayer desorption. The coverages are referenced to the

coverage determination of Dohnalek and co-workers and in very good agreement with their work.¹

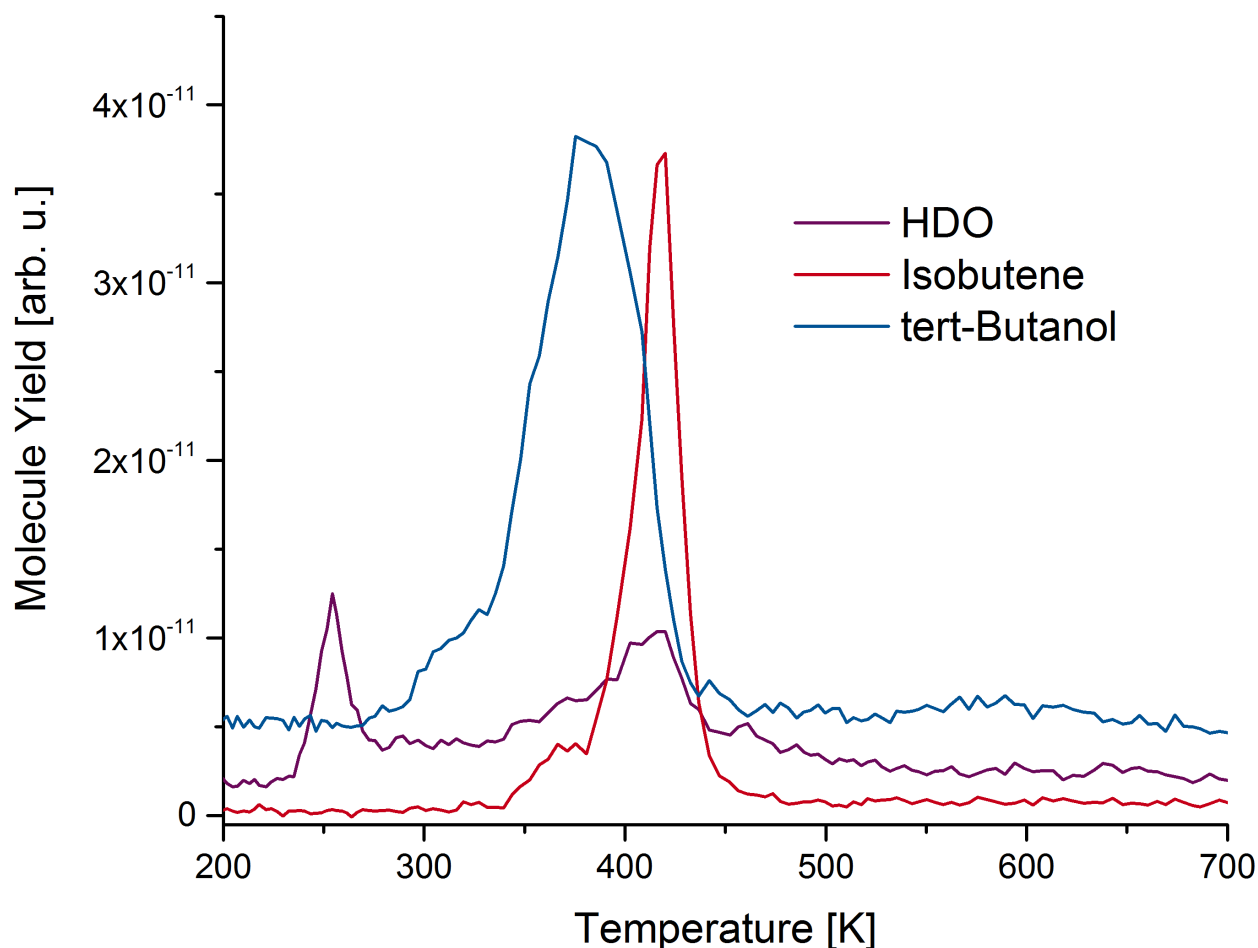


Figure S2: TPD of 0.45 ML tert-butanol-OD on r-TiO₂(110). Tert-butanol desorbs from the Ti-lattice sites, while a dehydration pathway to isobutene is observed at around 425 K, which is in agreement with previous studies.⁵⁻⁶ Additionally, the HDO ($m/z = 19$) was also monitored and two peaks occur: One is attributed to the direct dehydration pathway of tert-butanol-OD at 425 K, for which HDO is the by-product. In addition, another peak is observed at 250 K, which is attributed to the desorption of BBO-sites. It arises from water adsorption from the background and some dissociative adsorption, since some exchange to background adsorption from water is obtained.

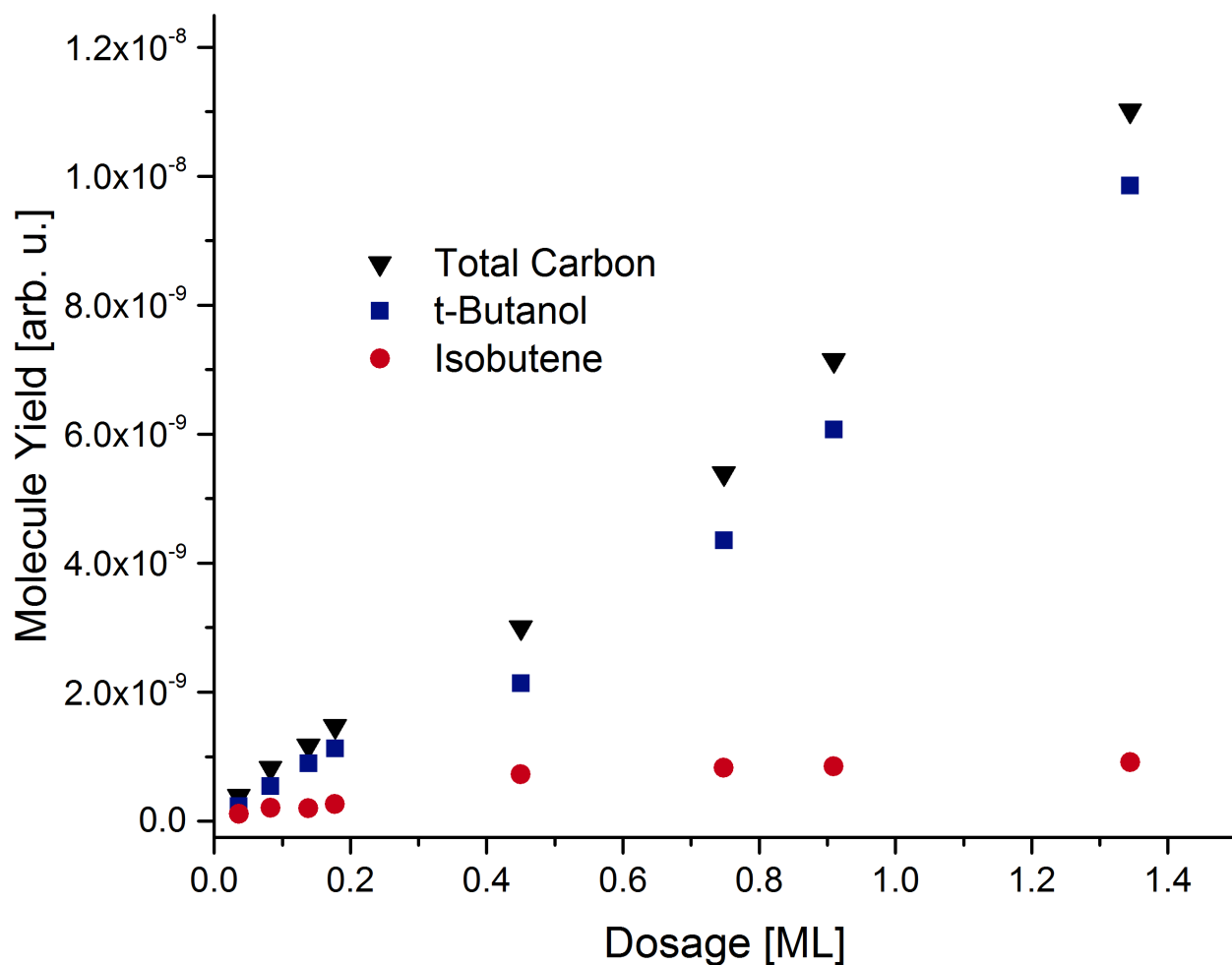


Figure S3: Integrated amounts of tert-butanol-OD and Isobutene for different coverages. While tert-butanol is shown in blue squares, the amount of isobutene is given in red circles. Auger electron spectroscopy and earlier studies¹ indicate that there are no carbon deposits for all alcohols on r-TiO₂(110). Hence, the carbon balance can be closed, which is addressed by black triangles showing the total carbon dosage by addition of the carbon containing desorbing molecules.

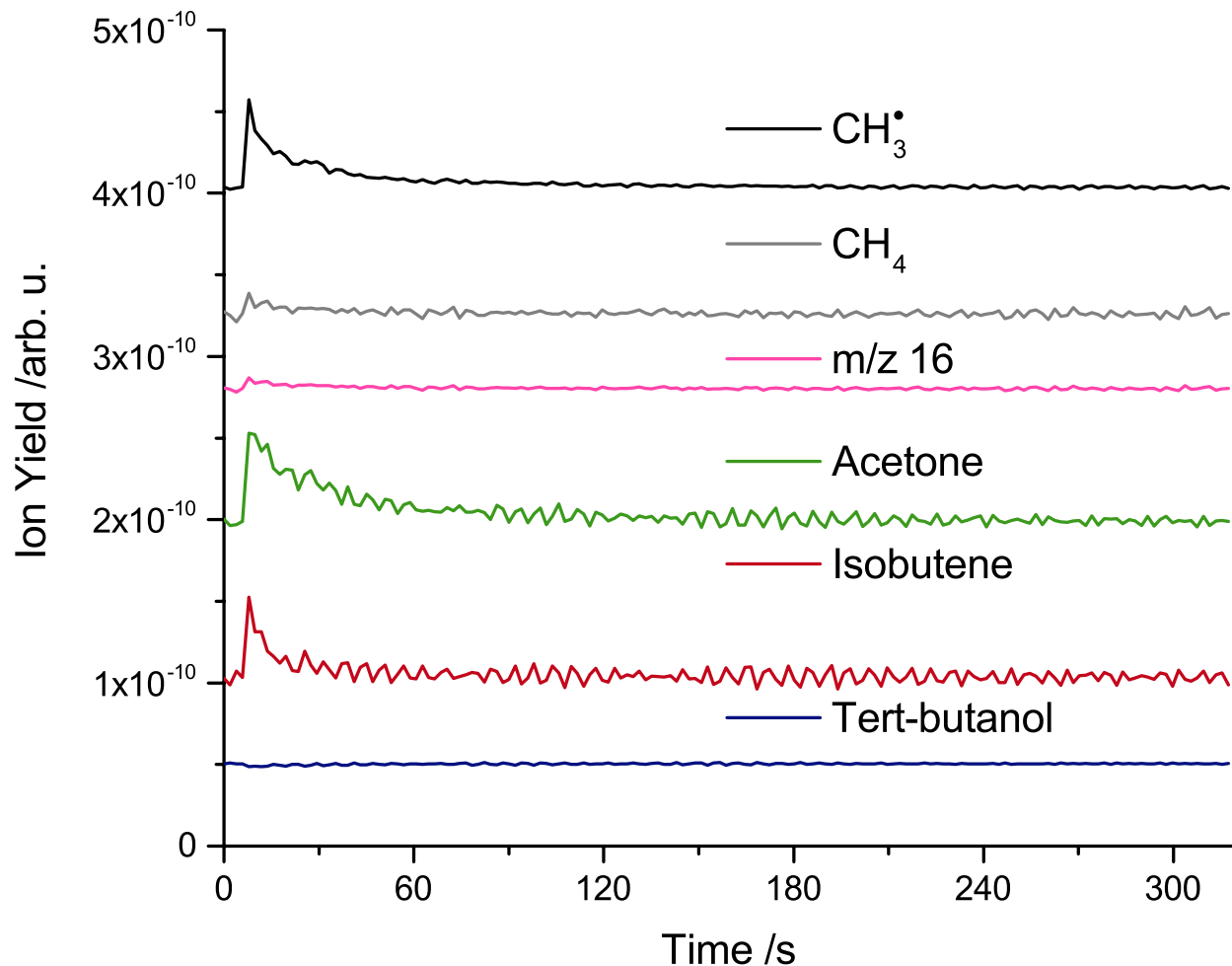


Figure S4: Isothermal photodesorption yield vs time for 0.18 ML of tert-butanol at 295 K on the r-TiO₂(110) surface. Note, that for the fully stated molecules, cracking pattern contributions are already accounted for. The traces are offset for clarity. The signal of m/z 15 is more than 8 times as much as for m/z 16. This is a clear indicator, that really a methyl radical is ejected during the photoreaction, while only trace amounts of methane are observed. The purple trace represents the raw data for mass 16. Note, that all correction factors as described above are included in that data, which increases also the noise in this data set.

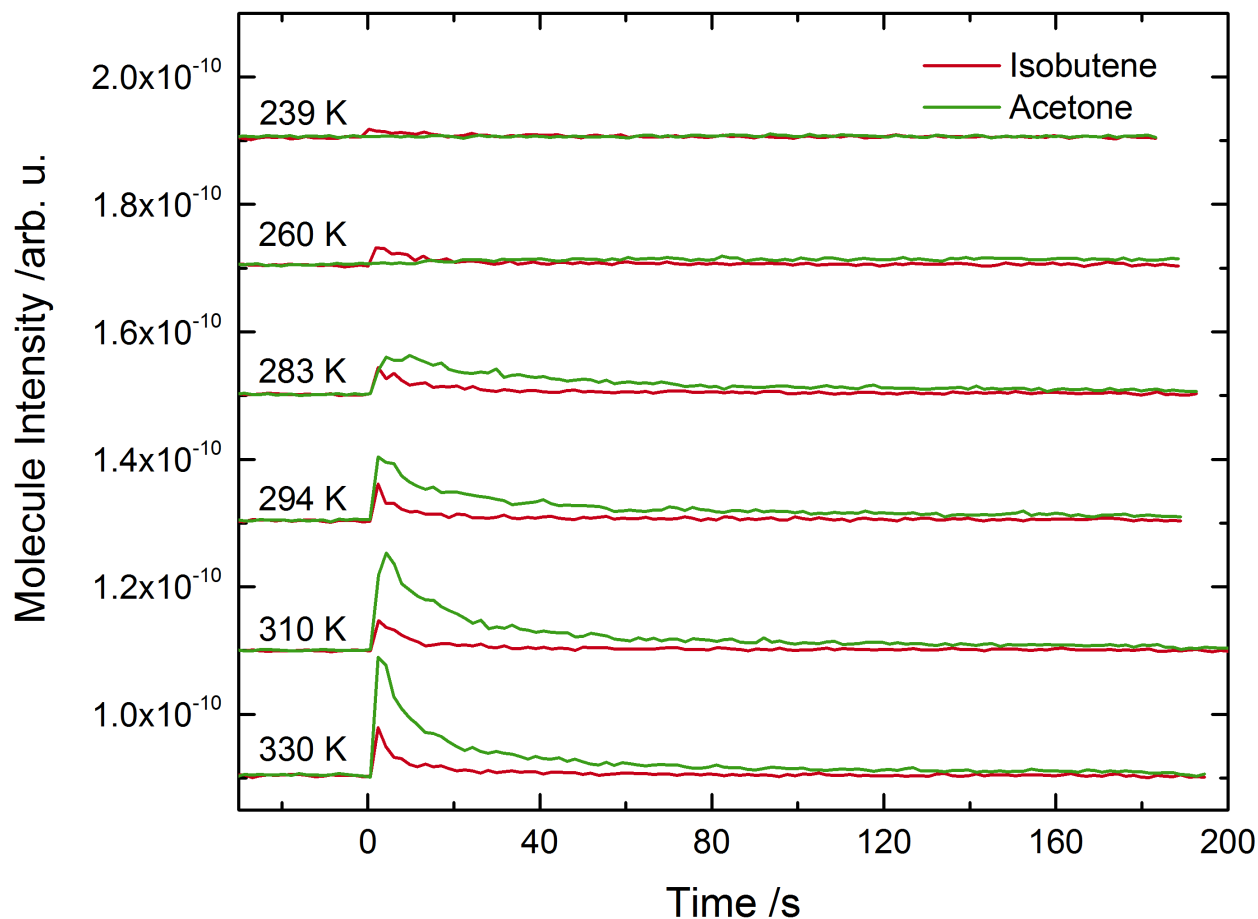


Figure S5: Isothermal photodesorption yield vs time for 0.18 ML of tert-butanol at different temperatures on a r-TiO₂(110) surface. The UV illumination is started at 0 s and ended after 180 s. For all temperatures, some desorption of both isobutene and acetone is observed, while no tert-butanol desorbs by irradiation. By increasing the temperature, both the overall apparent desorption rate is increased as well as the selectivity towards acetone. The traces are offset for clarity.

Notes and references:

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- 3 Irikura, Y.-K. K. K. In *BEB*, Proc. 2nd Int. Conf. on Atom. Molec. Data and Their Applications, Bell, K. A. B. K. L., Ed. AIP, New York, NY: 2000.

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