Conversion of 1,2-Propylene Glycol on Rutile $TiO_2(110)$

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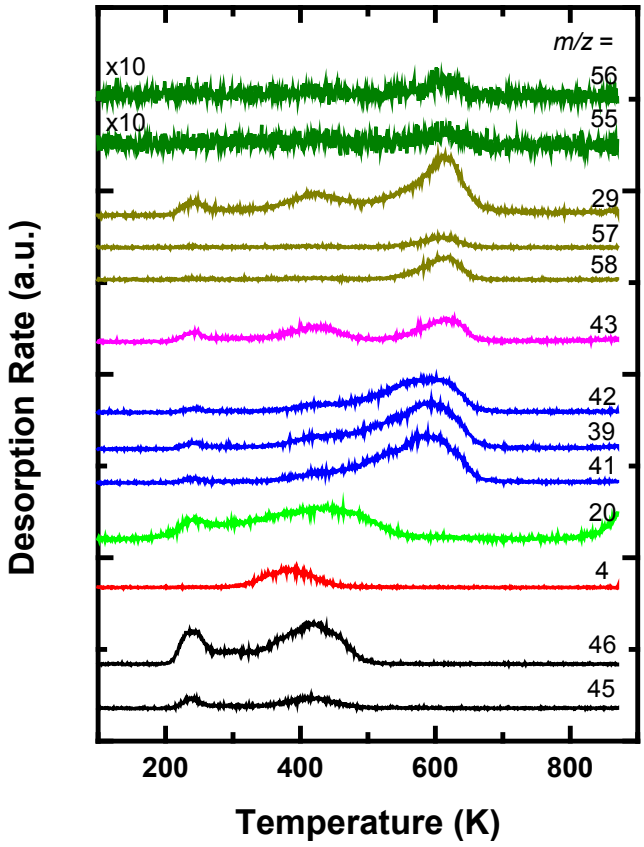

Figure S1. Set of TPD spectra with different mass fragments from the initial survey experiments obtained for 0.7 ML of 1,2-PG, $DOCH(CH_3)CH_2OD$, on *r*-TiO_2(110)at 80 K.

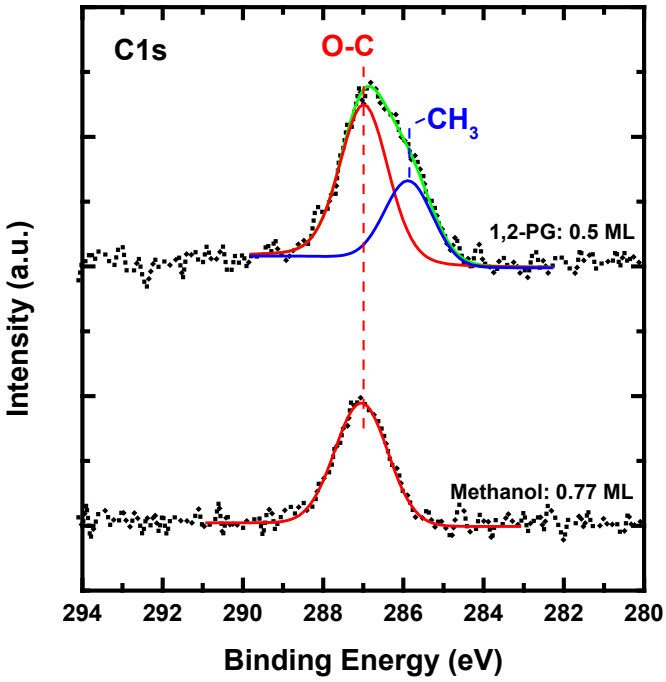

Figure S2. C1s XPS spectra for methanol and 1,2-PG adsorbed on *r*-TiO_2(110) at 80 K. The coverages for both molecules were fixed at saturation coverage by accurately controlling the beam flux and coverage. The spectra were peak-fitted with the "XPS Peak" software (freeware). As expected, methanol has only one type of carbon (C-OH moiety), while 1,2-PG has two types of carbon (C-OH and CH_3 moieties) that can be deconvoluted from the spectral envelopes. The component peaks at ~287.0 eV correspond to C-OH moieties, and the peak at ~285.6 eV corresponds to the $–CH_3$ moiety. The methanol saturation coverage on Ti_{5c} sites has been determined previously by QCM to be 0.77 ML.[1] By normalizing the 1,2-PG C1s peak area to the methanol C1s peak area, the saturation coverage of 1,2-PG on Ti_{5c} sites is calculated to be 0.5 ML.

Reference

1. Li, Z.; Smith, R. S.; Kay, B. D.; Dohnálek, Z. Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO_2(110). *J. Phys. Chem. C* **2011,** *115* (45), 22534-22539.

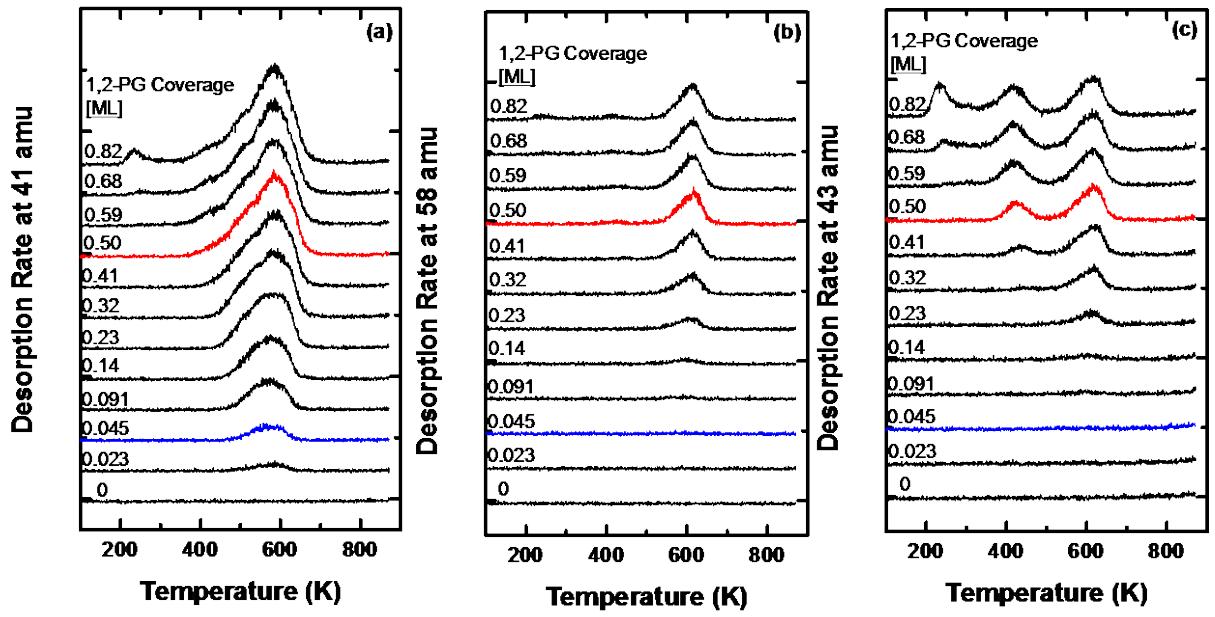

Figure S3. The unprocessed coverage dependent TPD spectra for (a) $CH_3CH{=}CH_2$ obtained at *m/z* = 41 amu, (b) CH_3CH_2CHO at 58 amu, and (c) $(CH_3)_2C{=}O$ at 43 amu. TPD traces for the 1,2-PG coverages that correspond to the V_O concentration and Ti_{5c} saturation are highlighted with blue and red, respectively.

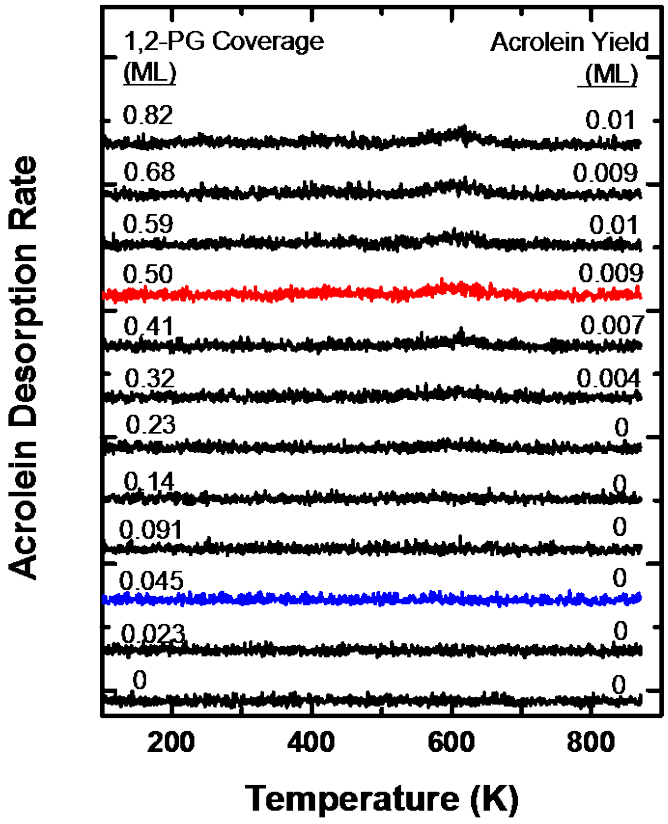

Figure S4. Coverage dependent TPD spectra of acrolein following 1,2-PG doses at 80 K. The acrolein spectra were obtained using the $C_3H_4O^+$ mass fragment at *m/z* = 56 amu. TPD traces for 1,2-PG coverages that correspond to the V_O concentration and the saturation of Ti_{5c} sites are highlighted with blue and red, respectively. The integrated yields of desorbing acrolein are listed on the right side of the figure.

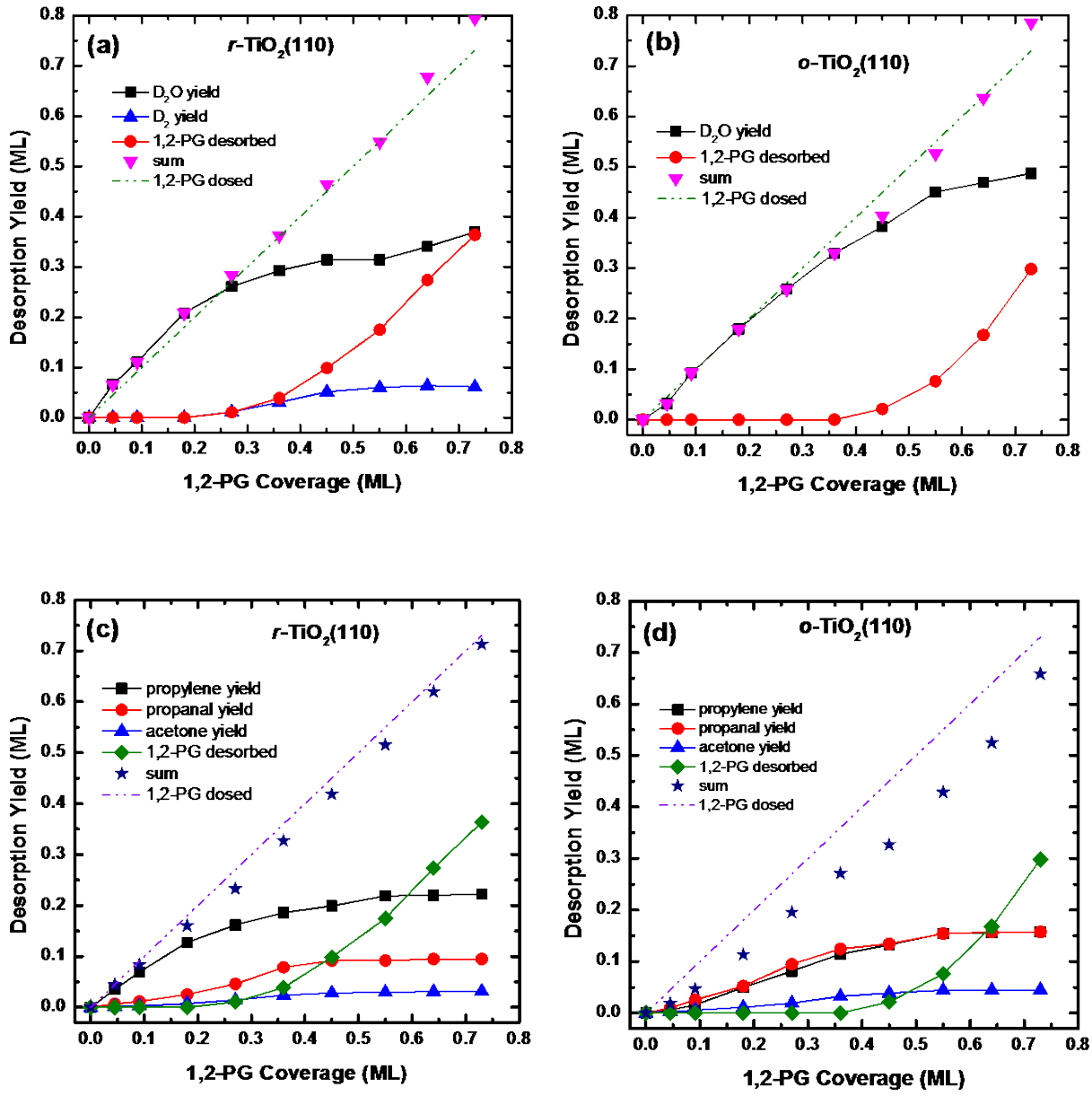

Figure S5. (a-b) Integrated amounts of desorbing D_2O (black squares), D_2 (blue triangles), 1,2-PG (red circles) and their sum (magenta triangles) as a function of 1,2-PG coverage on (a) *r*-TiO_2(110) and (b) *o*-TiO_2(110). Short dash dot line represents the total amount of deuterium expected based on the 1,2-PG dose. (c-d) Integrated amounts of desorbing $CH_3CH{=}CH_2$ (black squares), CH_3CH_2CHO (red circles), $(CH_3)_2C{=}O$ (blue triangles), 1,2-PG (green diamonds) and their sum (navy stars) as a function of 1,2-PG coverage on (c) *r*-TiO_2(110) and (d) *o*-TiO_2(110). Short dash dot lines represent the total amount of carbon expected based on the 1,2-PG dose.