Conversion of 1,2-Propylene Glycol on Rutile $\text{TiO}_2(110)$

*Long Chen, Zhenjun Li,[†] R. Scott Smith, Bruce D. Kay, Zdenek Dohnálek**

Fundamental and Computational Sciences Directorate and Institute for Integrated Catalysis,
Pacific Northwest National Laboratory, P.O. Box 999, Mail Stop K8-88, Richland, Washington
99352, United States

Figure S1. Set of TPD spectra with different mass fragments from the initial survey experiments obtained for 0.7 ML of 1,2-PG, $\text{DOCH}(\text{CH}_3)\text{CH}_2\text{OD}$, on $r\text{-TiO}_2(110)$ at 80 K.

Figure S2. C1s XPS spectra for methanol and 1,2-PG adsorbed on *r*-TiO₂(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 CH₃ 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 –CH₃ 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 TiO₂(110). *J. Phys. Chem. C* **2011**, *115* (45), 22534-22539.

Figure S3. The unprocessed coverage dependent TPD spectra for (a) $\text{CH}_3\text{CH}=\text{CH}_2$ obtained at $m/z = 41$ amu, (b) $\text{CH}_3\text{CH}_2\text{CHO}$ at 58 amu, and (c) $(\text{CH}_3)_2\text{C}=\text{O}$ 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 $\text{C}_3\text{H}_4\text{O}^+$ 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) $r\text{-TiO}_2(110)$ and (b) $o\text{-TiO}_2(110)$. Short dash dot line represents the total amount of deuterium expected based on the 1,2-PG dose. (c-d) Integrated amounts of desorbing $\text{CH}_3\text{CH}=\text{CH}_2$ (black squares), $\text{CH}_3\text{CH}_2\text{CHO}$ (red circles), $(\text{CH}_3)_2\text{C}=\text{O}$ (blue triangles), 1,2-PG (green diamonds) and their sum (navy stars) as a function of 1,2-PG coverage on (c) $r\text{-TiO}_2(110)$ and (d) $o\text{-TiO}_2(110)$. Short dash dot lines represent the total amount of carbon expected based on the 1,2-PG dose.