Conversion of Alcohols on Stoichiometric and Reduced Rutile TiO_2 (110): Point Defects Meet Bifunctionality in Oxide (Photo-)Chemistry

Supporting Information

Lars Mohrhusen[§*] *and Katharina Al-Shamery*

Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Carl-von-Ossietzky Strasse 9-11, D-26129 Oldenburg, Germany

[§]current affiliation: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge MA 02138, United States

**corresponding author:* lars.mohrhusen@uni-oldenburg.de

Calculation of desorption energies according to Redheads equation as used for fig. 3

$$E_d = RT\left(ln\left(\frac{\upsilon_d T}{\beta}\right) - 3.64\right) \qquad \text{with} \qquad \upsilon_d = T\frac{k_b}{h} \qquad \textbf{(eq. S1)}$$

Herein, E_d is the desorption energy, R denotes the universal gas constant, T denotes the temperature of the desorption peak maximum, υ_d is the pre-exponential coefficient, β gives the slope of the temperature ramp, k_b is the Boltzmann constant while h denotes the Planck constant. Generally, υ_d is often assumed to be $10^{13}\ s^{-1}$, however, our own evaluation for the desorption of several small molecules from rutile surfaces indicated, that the term used here, which is derived from transition state theory, yields more precise values.[1, 2] For fig. 3, υ_d ranges from $2.1 \cdot 10^{12}\ s^{-1}$ (for 100 K) to $1.6 \cdot 10^{13}\ s^{-1}$ (for 750 K).

Table S1: Overview on desorption features of unconverted methanol and possible products based on TPRS studies, as used for fig. 3.

Compound	Species and Conditions	Desorption Temperature	Reference
methanol (no reaction)	physisorbed multilayer	145 K 144 K 134 K 145 K	[3] [4] [5] [6]
	bilayer (adsorbed at O_{br})	181 – 210 K 193 K 180 K, 170 K 165 K	[3] [7] [4] [6]
	monolayer (adsorbed at Ti_{5c})	293 – 310 K 283 K 268 K, 297 K 295 K, 350 K, 480 K	[3] [7] [4] [6]
methane (deoxygenation)		616 K, 590 – 681 K 667 – 720 K 665 K	[4] [3] [7]
LT formaldehyde (partial oxidation)	oxygen coadsorption	231 K, 263 K 280 K	[4] [3]
HT formaldehyde (partial oxidation)	oxygen coadsorption	640 K, 624 K 654 – 670 K 670 K	[4] [3] [8]
methane (deoxygenation)	after UV irradiation	541 K, 607K; 576 K, 643 K 610 K, 661 K	[9]
LT formaldehyde (partial photo-oxidation)	oxygen coadsorption, UV irradiation	240 K 236 K, 252 K (243 K and 263 K without O_2) 250 K	[10] [9] [8]

Table S2: Overview on reactive and non-reactive desorption features after adsorption of small oxygenates on rutile TiO_2 (110), as used in fig. 4.

Compound	Unconverted Desorption	Deoxygenation or Dehydration	Partial Oxidation	Reference
isopropanol	313 K, 306 K	550 K, 542 K		[11]
	345 – 360 K	555-565 K		[12]
	315 – 410 K	560 – 580 K		[13]
	303 K	567 K, 625 K		[14]
(+UV)	298 K, 293 K	543 K	192 K	[11]
	309 K	567 K, 625 K	175 – 201 K	[14]
ethanol	300 K, 345 K	630 – 517 K	610 K	[15]
(+UV)			195 K	[16]
ethylene glycol	396 K	487 K, 635 K	626 K	[15]
	450 K	567 -620 K	630 K	[17]
n-propanol	347 K	598-630 K	590 K	[15]
formaldehyde	270 – 300 K			[18]
	290 K, 268 K	620 K	268 K	[19]
(+UV)	280 K	615 K	486 K, 580 K	[20]
	306-286 K	680 K	620 K	[21]

Table S3: Dissociation energies for the respective homolytic bond cleavage in the free methanol molecule as derived from theoretical calculations (courtesy of Luca Gerhards, Def2-TZVP / CCSD(T))

Bond	Dissociation Energy
C-O	371.47 kJ mol^{-1}
C-H	400.46 kJ mol^{-1}
O-H	411.94 kJ mol^{-1}

References

1. Mohrhusen L, Gerhards L, Hirsch D, et al. (2021) Multidentate Interaction of Methylamine with Rutile TiO_2 (110). J Phys Chem C 125:11975–11986. https://doi.org/10.1021/acs.jpcc.1c02166

2. Atkins P, de Paula J (2006) Physical Chemistry, 8. Edition. Oxford Univ. Press, Oxford

3. Osmić M, Mohrhusen L, Al-Shamery K (2019) Bulk Defect Dependence of Low-Temperature Partial Oxidation of Methanol and High-Temperature Hydrocarbon Formation on Rutile TiO_2 (110). J Phys Chem C 123:7615–7626. https://doi.org/10.1021/acs.jpcc.8b02953

4. Mohrhusen L, Al-Shamery K (2021) Conversion of methanol on rutile TiO_2 (110) and tungsten oxide clusters: 1. population of defect-dependent thermal reaction pathways. Phys Chem Chem Phys 23:12137–12147. https://doi.org/10.1039/D1CP01175H

5. Shen M, Henderson MA (2011) Site Competition during Coadsorption of Acetone with Methanol and Water on TiO_2 (110). Langmuir 27:9430–9438. https://doi.org/10.1021/la2016726

6. Henderson MA, Otero-Tapia S, Castro ME (1999) The chemistry of methanol on the TiO_2 (110) surface: the influence of vacancies and coadsorbed species. Faraday Discuss 114:313–329. https://doi.org/10.1039/a902070e

7. Kräuter J, Mohrhusen L, Thiedemann T, et al. (2019) Activation of Small Organic Molecules on Ti^{2+}-Rich TiO_2 Surfaces: Deoxygenation vs. C–C Coupling. Zeitschrift für Naturforsch A 74:697–707. https://doi.org/10.1515/zna-2019-0135

8. Phillips KR, Jensen SC, Baron M, et al. (2013) Sequential Photo-oxidation of Methanol to Methyl Formate on TiO_2 (110). J Am Chem Soc 135:574–577. https://doi.org/10.1021/ja3106797

9. Mohrhusen L, Kräuter J, Al-Shamery K (2021) Conversion of methanol on rutile TiO_2 (110) and tungsten oxide clusters: 2. The role of defects and electron transfer in bifunctional oxidic photocatalysts. Phys Chem Chem Phys 23:12148–12157. https://doi.org/10.1039/D1CP01176F

10. Walenta CA, Courtois C, Kollmannsberger SL, et al. (2020) Surface Species in Photocatalytic Methanol Reforming on Pt/TiO_2 (110): Learning from Surface Science Experiments for Catalytically Relevant Conditions. ACS Catal 10:4080–4091. https://doi.org/10.1021/acscatal.0c00260

11. Kräuter J, Mohrhusen L, Waidhas F, et al. (2021) Photoconversion of 2-Propanol on Rutile Titania: A Combined Liquid-Phase and Surface Science Study. J Phys Chem C 125:3355–3367. https://doi.org/10.1021/acs.jpcc.0c10734

12. Farfan-Arribas E, Madix RJ (2002) Role of defects in the adsorption of aliphatic alcohols on the TiO_2(110) surface. J Phys Chem B 106:10680–10692. https://doi.org/10.1021/jp020729p

13. Bondarchuk O, Kim YK, White JM, et al. (2007) Surface Chemistry of 2-Propanol on TiO_2 (110): Low- and High-Temperature Dehydration, Isotope Effects, and Influence of Local Surface Structure. J Phys Chem C 111:11059–11067. https://doi.org/10.1021/jp072298m

14. Kräuter J, Franz E, Waidhas F, et al. (2022) The Role of Defects in the Photoconversion of 2-Propanol on Rutile Titania: Operando Spectroscopy Combined with Elementary Studies. J Catal. https://doi.org/10.1016/j.jcat.2021.12.025

15. Farfan-Arribas E, Madix RJ (2002) Role of Defects in the Adsorption of Aliphatic Alcohols on the TiO_2 (110) Surface. J Phys Chem B 106:10680–10692. https://doi.org/10.1021/jp020729p

16. Walenta CA, Kollmannsberger SL, Kiermaier J, et al. (2015) Ethanol photocatalysis on rutile TiO_2 (110): the role of defects and water. Phys Chem Chem Phys 17:22809–22814. https://doi.org/10.1039/C5CP03550C

17. Li Z, Kay BD, Dohnálek Z (2013) Dehydration and dehydrogenation of ethylene glycol on rutile TiO_2 (110). Phys Chem Chem Phys 15:12180. https://doi.org/10.1039/c3cp50687h

18. Yu X, Zhang Z, Yang C, et al. (2016) Interaction of Formaldehyde with the Rutile TiO_2 (110) Surface: A Combined Experimental and Theoretical Study. J Phys Chem C 120:12626–12636. https://doi.org/10.1021/acs.jpcc.6b03689

19. Qiu H, Idriss H, Wang Y, Wöll C (2008) Carbon−Carbon Bond Formation on Model Titanium Oxide Surfaces: Identification of Surface Reaction Intermediates by High-Resolution Electron Energy Loss Spectroscopy. J Phys Chem C 112:9828–9834. https://doi.org/10.1021/jp801327b

20. Xu C, Yang W, Guo Q, et al. (2013) Photoinduced Decomposition of Formaldehyde on a TiO_2 (110) Surface, Assisted by Bridge-Bonded Oxygen Atoms. J Phys Chem Lett 4:2668–2673. https://doi.org/10.1021/jz401349q

21. Yuan Q, Wu Z, Jin Y, et al. (2014) Surface Chemistry of Formaldehyde on Rutile TiO_2 (110) Surface: Photocatalysis vs. Thermal-Catalysis. J Phys Chem C 118:20420–20428. https://doi.org/10.1021/jp5061733