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Surface-structure dependence of water-related adsorbates on platinum

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Appendix

Appendix A

Supporting information to Chapter 7

Figure S1 shows oxygen desorbing from Pt(111), Pt(211), Pt(221) and Pt(553). Desorption between 500 and 850 K results from recombinative desorption. Several studies[1, 2], reported that oxygen saturates at 0.25 ML in the recombinative desorption region on Pt(111). The hatched area corresponds to our best estimate for $\theta_O = 0.25$ ML on Pt(111) and serves as our reference for subsequent TPD experiments.

In figure S2, we show the uptake curves of oxygen for Pt(111), Pt(211), Pt(221), Pt(533), and Pt(553). The uptake curve includes total amount O_2 desorption from the molecular and recombinative desorption regimes. For Pt(111), the saturation coverage is in good agreement with previous work done by Steininger et al.[1] (black squares). For combined molecular and recombinative desorption, the highest coverage obtained on Pt(111) is 0.53 ML. Figure S2 clearly shows that stepped surfaces exhibit significantly higher oxygen coverages.

To emphasize the different effects that the two step types have on the adsorption of oxygen on Pt surfaces, we show in figure S3 how the fraction of O_{ad} changes as a function of total O_2 coverage. For Pt(221) and (553), the fraction of O_{ad} drops to $\sim 25\%$ between $\theta_O^{tot} \approx 0.6$ and 0.90 ML, and increases to $\sim 55\%$ for $\theta_O^{tot} > 0.90$ ML. The O_{ad} desorption decrease between 0.6 ML and 0.90 ML results in a marked change in the ratio between $O_{2,ad}$ and O_{ad} desorption.

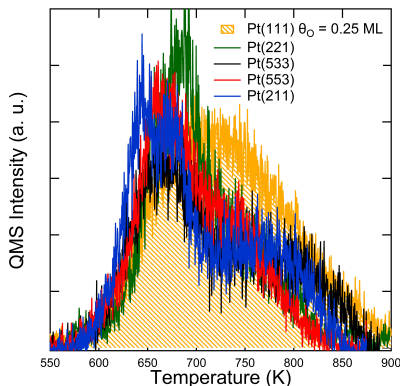


Figure S1: O₂ TPD spectra for Pt(111), Pt(211), Pt(221), Pt(533) and Pt(553).

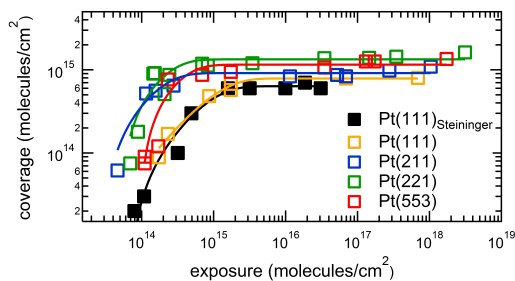


Figure S2: O₂ desorption from Pt(111), Pt(211), Pt(221) and Pt(553). Black squares show experimental data obtained by Steininger et al.[1]

Figure S4 shows TPD spectra of O₂ desorption taken at different angles from the Pt(553) surface for 2.2 L O₂ exposures at 100 K. Because of geometric constraints of the instrument, the angular variation is $\pm 12^\circ$. This is because the crystal is mounted off center from the rotational axis of the x, y, z, θ manipulator, and x,y, position is limited to $\pm 12/5$ mm. The crystal-to-orifice distance was aligned by eye, causing some variation in the absolute peak intensity. However, the relative intensities of the low (molecular) and high (recombinative desorption) desorption peaks would indicate biases in the desorption angles for the two processes. As shown in table A.1, only small variations in the percent of recombinative desorption versus total O₂ desorption is observed, indicating that the angular dependencies do not vary enough between the low and high temperature desorption features to affect the interpretation of our data in the manuscript.

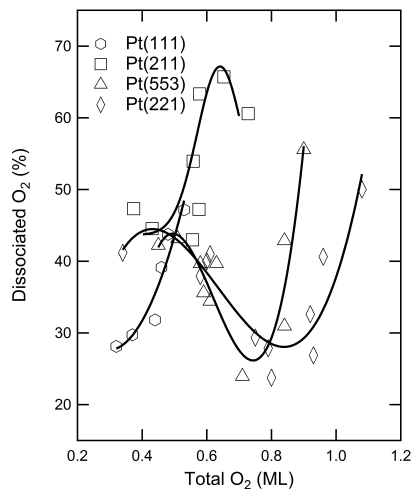


Figure S3: Fraction of adsorbed O₂ dissociated for Pt(111), Pt(211), Pt(221) and Pt(553) vs. θ_{O_2} . The lines through the data are to guide the eye.

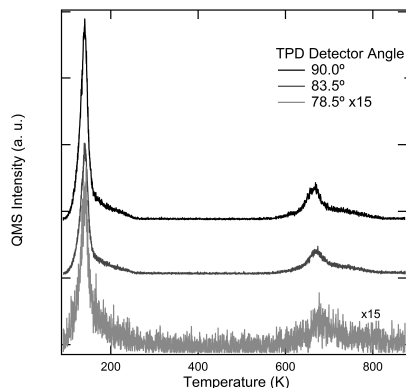


Figure S4: Angle-resolved TPD of O₂ desorbing from Pt(553). For each, the initial O/O₂ coverages were the same. Dose conditions: 2.2 L O₂, $T_s = 100$ K.

Because of their corrugation, stepped surfaces have higher actual geometric surface area than planar (111) surfaces[3]. In figure S5, we show a typical packing arrangement of the fcc unit cell, where α = lattice constant. The planes “x+y” show the actual geometric area of a stepped surface. For (100) and (110) stepped Pt(111) surfaces $\alpha = 125.4^\circ$ and 109.5° , respectively. The ratio of the geometric surface area of (211)/(111) and (533)/(111) is ~ 1.10 . For (221)/(111) and (553)/(111), it is slightly higher, ~ 1.15 .

Table A.1: Percentage of total O₂ from recombinative desorption for three different TPD angles.

Angle	% Recombinative
78.5	26
83.5	31
90.0	30

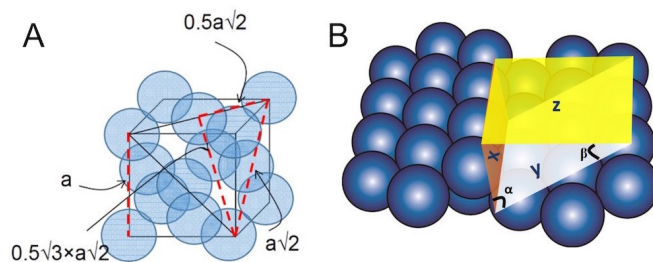


Figure S5: A) The packing arrangement of the face centered cubic (fcc) cell. B) (x+y) planes show the actual geometric area of a stepped Pt(211) surface. α is the angle between (111) and (100) planes and β is the angle between the (211) and (111) planes.

Figure S6A shows a representative STM image of an oxidized Pt(553) surface (figure 7.6 in main manuscript) and its corresponding line profile (figure S6B). This serves to illustrate the topography of the surface.

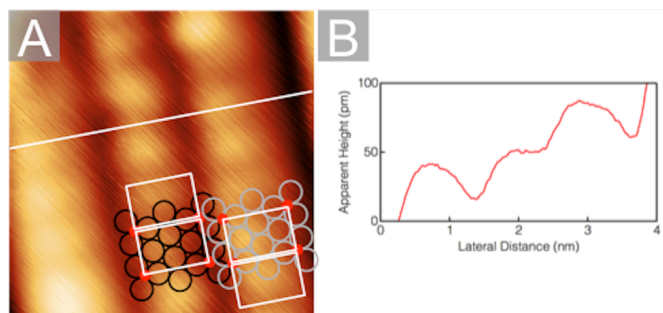


Figure S6: A) STM image from chapter 7 figure 7.6A with a profile line (white) drawn across oxidized terraces B) Extracted line profile from image.

List of Publications

- Badan, C.; Farber, R.; Heyrich, Y.; Koper, M.T.M.; Killelea, D.R. and Juurlink, L.B.F. : *Step-Type Selective Oxidation of Pt Surfaces*, Journal of Physical Chemistry C, 2016
- Badan, C.; Heyrich, Y.; Koper, M.T.M. and Juurlink, L.B.F. : *Surface Structure Dependence in Desorption and Crystallization of Thin Interfacial Water Films on Platinum*, The Journal of Physical Chemistry Letters, 2016, 7, 1682
- Kolb, M.J.; Farber, R.; Derouin, J.; Badan, C.; Calle-Vallejo, F.; Juurlink, L.B.F.; Killelea, D.R. and Koper, M.T.M.: *Double Stranded Water on Stepped Platinum Surfaces*, Phys. Rev. Lett., 2016, 116, 136101
- Badan, C.; Koper, M.T.M. and Juurlink, L.B.F. : *How Well Does Pt(211) Represent Pt[n(111) × (100)] Surfaces in Adsorption/Desorption?*, The Journal of Physical Chemistry C, 2015, 119, 13551
- den Dunnen, A.; van der Niet, M.J.T.C.; Badan, C.; Koper, M.T.M. and Juurlink, L.B.F. : *Long-Range Influence of Steps on Water Adsorption on Clean and D-Covered Pt Surfaces*, Physical Chemistry Chemical Physics, 2015, 17, 8530
- Badan, C.; Esenturk, O. and Yilmaz, A. : *Microwave-Assisted Synthesis of Eu³⁺ Doped Lanthanum Orthoborates, Their Characterizations and Luminous Properties*, Solid State Sciences, 2012, 14, 1710

Curriculum Vitae

Cansın Badan was born on January 30th, 1987 in Çukurova, Turkey. After finishing the *Anatolian High School*, he studied Chemistry at the Middle East Technical University, METU. In 2008, he did an internship in the group of Prof. J.W. (Hans) Niemantsverdriet at the Eindhoven University of Technology. In 2009, he moved to Netherlands for another internship at Leiden University under the supervision of Dr. Ludo Juurlink, studying “Water desorption from Pt(755) and its dependence on precoverage by hydrogen”. During his undergraduate studies, he was awarded the Vehbi Koç Scholarship. In 2011, he earned his bachelor’s degree with a research thesis on polymer composites.

Cansın continued at METU for his master’s degree in inorganic chemistry under the supervision of Dr. Okan Esentürk and Prof. Dr. Ayşen Yılmaz, studying the luminescence properties of lanthanum orthoborates. After obtaining his master’s degree in 2012, he joined the research group of Prof. Dr. Marc Koper as a PhD student as part of a TOP grant awarded to Prof. Dr. Marc Koper and Dr. Ludo Juurlink. In his PhD project, he studied the surface structure dependence of water related adsorbates on highly corrugated platinum surfaces. Cansın elucidated the kinetics of interfacial water on platinum in monolayer and thin-film regime. He also shed light on the influence of local surface structure to various chemical reactions on Pt surfaces. The results of his PhD research are presented in this thesis.

