

Hydroxylation of Platinum Surface Oxides Induced by Water Vapor

Rik V. Mom* and Axel Knop-Gericke



Cite This: *J. Phys. Chem. Lett.* 2022, 13, 879–883



Read Online

ACCESS |



Metrics & More

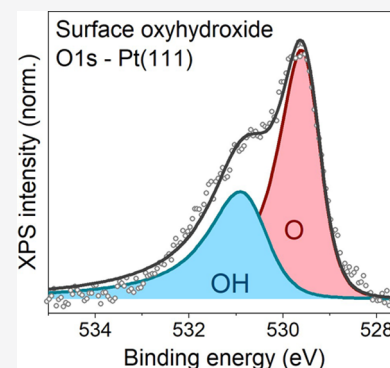


Article Recommendations



Supporting Information

ABSTRACT: With its high stability and well-tuned binding strength for adsorbates, platinum is an excellent catalyst for a wide range of reactions. In applications like car exhaust purification, the oxidation of hydrocarbons, and fuel cells, platinum is exposed to highly oxidizing conditions, which often leads to the formation of surface oxides. To reveal the structure of these surface oxides, the oxidation of Pt in O₂ has been widely studied. However, in most applications, H₂O is also an important or even dominant part of the reaction mixture. Here, we investigate the interaction of H₂O with Pt surface oxides using near-ambient-pressure X-ray photoelectron spectroscopy. We find that reversible hydroxylation readily occurs in H₂O/O₂ mixtures. Using time-resolved measurements, we show that O–OH exchange occurs on a time scale of seconds.



Platinum plays a central role in catalysis, both in present-day technologies such as car exhaust treatment¹ and in future technologies such as fuel cell catalysis.² Because Pt surface oxides are thought to be the catalytically active phase in many cases, knowledge of their structure is key to understanding the catalytic process. Therefore, the interaction of platinum with O₂ has been widely investigated.^{3–11} At very low oxygen pressures, only an adsorbate overlayer is formed, with ≤ 0.25 monolayer (ML) coverage for the case of Pt(111).^{11,12} Starting in the range between 0.1 and 1 mbar of O₂, the formation of oxides becomes possible.^{5,8–11} While thermodynamics predicts the onset of bulk oxidation in this pressure range (for modest temperatures),⁸ kinetic limitations ensure a wide range of stability for surface oxides up to 1 ML coverage.^{5,5,9,10} These surface oxides consist of one-dimensional chains of Pt atoms coordinated to four O atoms,^{3,5,11} following the motifs of PtO₂ bulk oxides. Despite this structural similarity to bulk PtO₂, the Pt atoms in the surface oxide carry very little charge, in contrast to the Pt⁴⁺ ions in bulk oxides.⁵ This makes the surface oxide much more reactive toward CO,^{13,14} thus confirming the belief that this surface state can participate in the catalytic cycle of oxidation reactions on platinum.

The effect of water on the structure of Pt surface oxides has not been investigated so far. This is surprising, because water generally makes up a large part of the reaction mixture in oxidation catalysis, with partial pressures often even exceeding that of O₂. Although water itself adsorbs only weakly on clean Pt surfaces,¹⁵ ultra-high-vacuum studies at low temperatures have shown that water readily reacts with adsorbed oxygen, forming somewhat more stable OH adsorbates.^{16,17} To investigate whether Pt surface oxides are similarly prone to hydroxylation, we oxidized Pt(111) and a roughened Pt foil in

0.5 mbar of O₂ at 473 K and subsequently exposed the samples to O₂/H₂O mixtures in the temperature range of 393–473 K (see section S1 of the Supporting Information for experimental details).

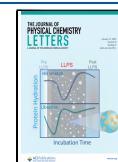
Using our NAP-XPS end-stations at the UES6-PGM1 and ISSS beamlines at the BESSY II synchrotron, we followed the chemical state of the surface through Pt 4f and O 1s spectra (details in section S2). Figure 1a shows Pt 4f spectra for the initial oxidation of the Pt(111) crystal. The asymmetric Gaussian–Lorentzian line shape used in the fitting was determined from the Pt 4f spectrum of clean Pt(111) obtained in vacuum (see section S3). Using this line shape, the fitting results for Pt surface oxides from the Nilsson group⁵ are reproduced accurately, confirming that the crystal was successfully oxidized. By comparing the O 1s/Pt 4f ratio to the 0.25 ML (2 × 2) adsorbate overlayer expected in 5×10^{-4} mbar of O₂ at 463 K, we estimate the oxygen coverage to be approximately 0.5–0.6 ML after exposure to 0.5 mbar of O₂ for 30 min.

When water is introduced into the system (0.25 mbar of H₂O and 0.25 mbar of O₂ at 393 K), the O 1s/Pt 4f ratio increases only 8%, indicating little to no increase in the surface coverage. This is also reflected in the Pt 4f peak shape, which is almost unchanged (see Figure 1b). However, dramatic changes are visible in the O 1s signal (Figure 1c). Under dry

Received: December 1, 2021

Accepted: January 13, 2022

Published: January 20, 2022



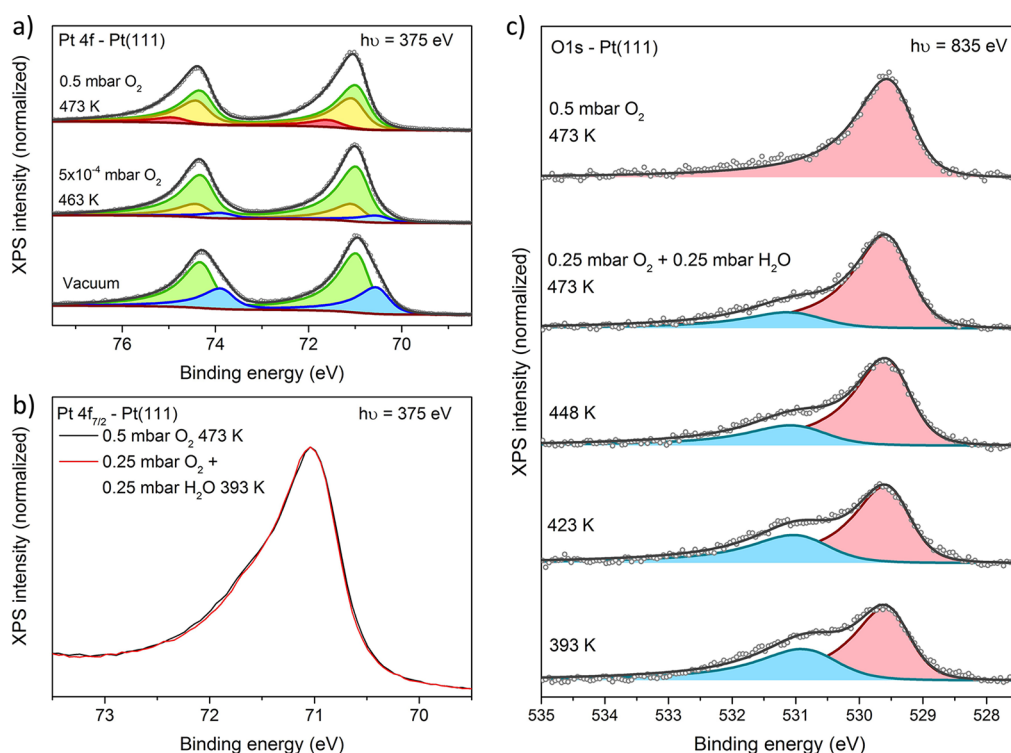


Figure 1. Oxidation and hydroxylation of Pt(111). (a) Initial oxidation in pure O₂. Spectral decomposition: clean surface (blue), bulk (green), chemisorbed/surface oxide (yellow), and surface oxide (red). Fitting model from ref 5. (b) Pt 4f_{7/2} spectra before and after the introduction of H₂O into the O₂ environment. (c) Shirley background-subtracted O 1s spectra showing the temperature-dependent surface structure in a H₂O/O₂ environment. Spectral decomposition: O (red) and OH (blue).

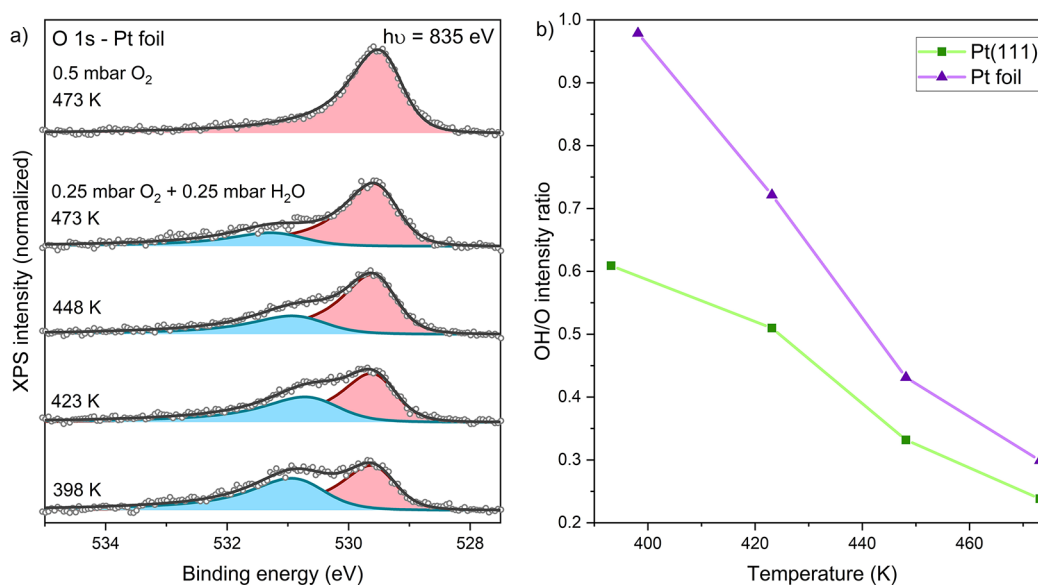
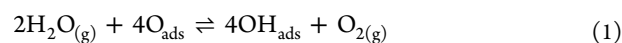


Figure 2. Hydroxylation of surface oxides on sputtered (defect-rich) Pt foil and comparison to Pt(111). (a) Shirley background-subtracted O 1s spectra showing the temperature-dependent surface composition in a H₂O/O₂ environment. Spectral decomposition: O (red) and OH (blue). (b) Peak area ratios of the OH and O peaks in Figures 1c and 2a.

conditions, only a single asymmetric peak at 529.5 eV is observed, in agreement with the literature.^{5,9} The presence of water in the gas feed causes the appearance of a new peak at 530.7–531 eV. This binding energy range is typical for OH adsorbates, whereas adsorbed H₂O would be expected at ≥532 eV.^{17–19} This assignment is further corroborated by O K-edge spectra (section S4), which display a resonance pattern consistent with an OH_{ads}/O_{ads} mixture on platinum.^{5,17,20}

Taking into account the fact that there is little to no change in the surface coverage, we conclude that an O–OH exchange reaction takes place:



This exchange reaction is also consistent with the observed temperature dependence of the OH peak in Figure 1c. Under the experimentally applied conditions, one can estimate the

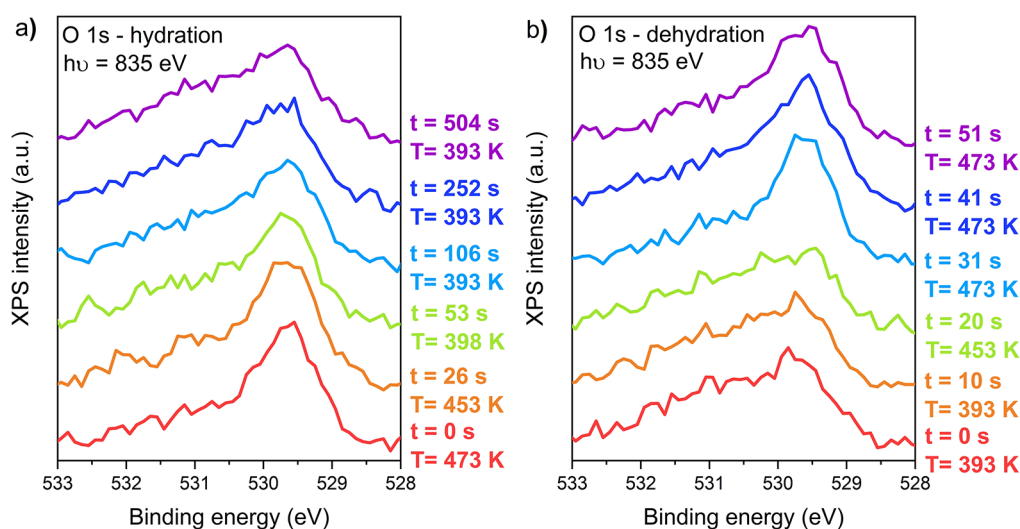


Figure 3. Time-resolved hydroxylation and dehydroxylation of Pt(111) in 0.25 mbar of H₂O and 0.25 mbar of O₂. (a) O 1s spectra while decreasing the temperature. (b) O 1s spectra while increasing the temperature. All spectra are shown Shirley background-subtracted.

entropy change of this reaction as $-0.0025 \text{ eV K}^{-1}$ (see section S5 for a derivation). Keeping in mind the fact that the free energy of the reaction is given as $\Delta G = \Delta H - T\Delta S$, this negative ΔS value implies that the reaction will be less favorable at an increased temperature (T). Indeed, Figure 1c shows that the extent of hydroxylation decreases when the temperature is increased. Note that we confirmed that the reaction can be reversed by repeatedly increasing and decreasing the temperature (see Figure S2) and that the levels of common contaminants like Si, C, and S remained below the detection limit.

To understand which sites on the Pt(111) surface become hydroxylated, it is important to consider the structural changes on the surface during the oxidation treatment prior to water exposure. Van Spronsen et al.³ showed that the formation of one-dimensional oxide chains is accompanied by significant surface roughening, creating approximately 10–15% step-edge sites. This number could be even higher in our case, because we performed oxidation at a slightly lower temperature (473 K here vs 526 K for van Spronsen et al.). Hence, undercoordinated sites such as step edges could provide a significant or even dominant contribution to the observed OH peak.

To investigate whether undercoordinated sites are preferentially hydroxylated, we created a defect-rich sample by prolonged Ar⁺ sputter bombardment of a Pt foil. Figure 2 shows that such a sample displays stronger hydroxylation than Pt(111), yet has a very similar temperature dependence of OH coverage. This suggests that the same hydroxylation process is occurring on the sputtered Pt foil, but that there are a larger number of favorable hydroxylation sites. Keeping in mind the large number of undercoordinated sites in the sputtered foil compared to Pt(111), we conclude that undercoordinated sites are preferentially hydroxylated.

Combining Figure 2b with the literature,⁷ one can obtain a rough estimate of the adsorption enthalpy of the hydroxides, approximately -1.1 eV per OH_{ads} (derivation in section S6). This is significantly higher than the value of approximately -0.9 eV for surface oxides in this coverage range,⁷ showing that the hydroxides are bound tightly to the surface. A possible explanation for this remarkably high stability could be hydrogen bonding in the hydroxide phases. However, we should also point out that the apparent adsorption enthalpy of

OH could be increased by any carbon contamination in the gas phase. Although no carbon was observed on the Pt surface, traces of hydrocarbons in the gas feed would likely preferentially react with O_{ads} rather than OH_{ads}, thereby increasing the observed OH_{ads}/O_{ads} ratio somewhat.

Because undercoordinated sites are often considered to be the most active in catalysis, it is important to know how dynamic the hydroxylation/dehydroxylation equilibrium in eq 1 is. To test this experimentally, we performed temperature ramping experiments and followed the surface composition using O 1s spectra. Figure 3 shows that both hydroxylation and dehydroxylation occur on the time scale of a few seconds, indicating that O/OH exchange on the undercoordinated sites is very dynamic. Hence, the undercoordinated sites are regularly vacated, leaving room for catalytic turnover.

In some cases, OH groups may be part of the catalytic cycle itself. To test their reactivity, we studied the catalytic combustion of hydrogen on Pt(111). As shown in Figure 4, the surface coverage of O and OH species under catalytic

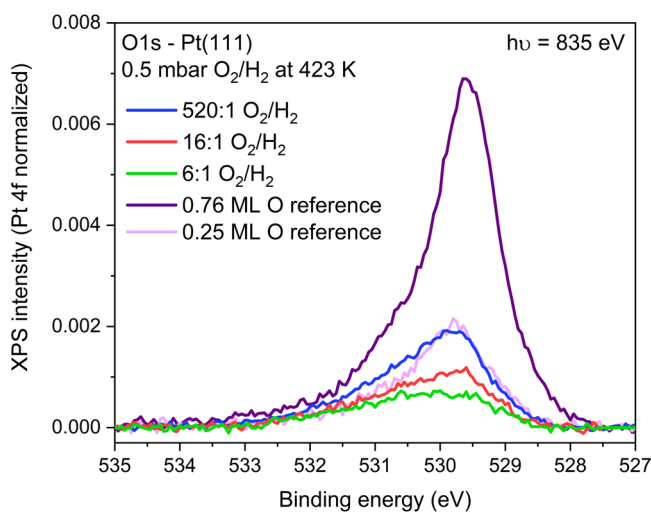


Figure 4. Catalytic combustion of H₂ on Pt(111). All spectra were normalized to the Pt 4f peak area recorded with the same electron kinetic energy and are shown Shirley background-subtracted.

conditions is low, even when only trace levels of H₂ are present in the reaction mixture. Because adsorbed OH is an intermediate of the reaction, this confirms that it is highly reactive toward hydrogen. We should point out, however, that the reactivity of the OH species may be coverage-dependent, similar to that of O species in CO oxidation.¹³

In conclusion, we have shown that Pt surface oxides are prone to hydroxylation, even at modest H₂O pressures (e.g., 0.25 mbar) and elevated temperatures (393–450 K). Hence, one may expect a significant fraction of OH groups on the surface of Pt catalysts under typical oxidation catalysis conditions. The OH species replace O atoms on the surface, with a preference for undercoordinated sites. In the probed temperature range (393–473 K), the hydroxylation/dehydroxylation is highly dynamic, with a response time of a few seconds toward changes in temperature. Hence, the presence of OH sites does not irreversibly block surface sites for catalytic turnover.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c03927>.

Details on sample preparation, analysis procedures, theoretical derivations, and additional experimental data (PDF)

Transparent Peer Review report available (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Rik V. Mom – *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany; Leiden Institute of Chemistry, Leiden University, 2333 CC Leiden, The Netherlands*; orcid.org/0000-0002-5111-5591;
Email: r.v.mom@lic.leidenuniv.nl

Author

Axel Knop-Gericke – *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany; Max-Planck-Institut für Chemische Energiekonversion, 45470 Mülheim an der Ruhr, Germany*

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c03927>

Notes

The authors declare no competing financial interest.

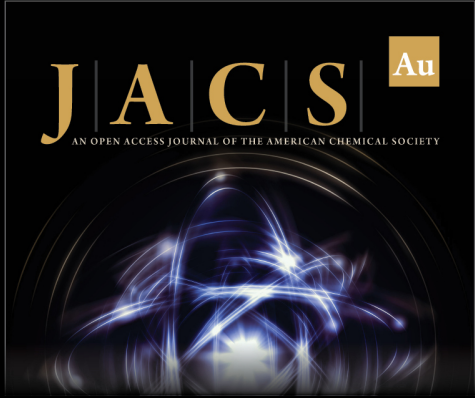
■ ACKNOWLEDGMENTS

This work was supported by the German Federal Ministry of Education and Research [BMBF project “Grundlagen elektrochemischer Phasengrenzen” (GEP), 13XP5023C]. The Helmholtz Zentrum Berlin (BESSY II synchrotron) is acknowledged for granting beam time. R.V.M. was financially supported through a Humboldt Research Fellowship by the Alexander von Humboldt Foundation. The authors thank Michael Hävecker and Eugen Stotz for their technical support and Timo Jacob and Björn Kirchoff for fruitful discussions.


■ REFERENCES

- (1) Lira, E.; Merte, L. R.; Behafarid, F.; Ono, L. K.; Zhang, L.; Roldan Cuenya, B. Role and Evolution of Nanoparticle Structure and Chemical State during the Oxidation of NO over Size- and Shape-Controlled Pt/ γ -Al₂O₃ Catalysts under Operando Conditions. *ACS Catal.* **2014**, *4*, 1875–1884.
- (2) Redmond, E. L.; Setzler, B. P.; Alamgir, F. M.; Fuller, T. F. Elucidating the Oxide Growth Mechanism on Platinum at the Cathode in PEM Fuel Cells. *Phys. Chem. Chem. Phys.* **2014**, *16*, 5301–5311.
- (3) van Spronsen, M. A.; Frenken, J. W. M.; Groot, I. M. N. Observing the Oxidation of Platinum. *Nat. Commun.* **2017**, *8*, 429.
- (4) Van Spronsen, M. A.; Frenken, J. W. M.; Groot, I. M. N. Surface Science under Reaction Conditions: CO Oxidation on Pt and Pd Model Catalysts. *Chem. Soc. Rev.* **2017**, *46*, 4347–4374.
- (5) Miller, D. J.; Öberg, H.; Kaya, S.; Sanchez Casalongue, H.; Friebel, D.; Anniyev, T.; Ogasawara, H.; Bluhm, H.; Pettersson, L. G. M.; Nilsson, A. Oxidation of Pt(111) under near-Ambient Conditions. *Phys. Rev. Lett.* **2011**, *107*, 195502.
- (6) Ono, L. K.; Croy, J. R.; Heinrich, H.; Roldan Cuenya, B. Oxygen Chemisorption, Formation, and Thermal Stability of Pt Oxides on Pt Nanoparticles Supported on SiO₂/Si(001): Size Effects. *J. Phys. Chem. C* **2011**, *115*, 16856–16866.
- (7) Bandlow, J.; Kaghazchi, P.; Jacob, T.; Papp, C.; Tränkenschuh, B.; Streber, R.; Lorenz, M. P. A.; Fuhrmann, T.; Denecke, R.; Steinrück, H. P. Oxidation of Stepped Pt(111) Studied by x-Ray Photoelectron Spectroscopy and Density Functional Theory. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2011**, *83*, 1–5.
- (8) Fantauzzi, D.; Krick Calderón, S.; Mueller, J. E.; Grabau, M.; Papp, C.; Steinrück, H. P.; Senftle, T. P.; van Duin, A. C. T.; Jacob, T. Growth of Stable Surface Oxides on Pt(111) at Near-Ambient Pressures. *Angew. Chemie - Int. Ed.* **2017**, *56*, 2594–2598.
- (9) Butcher, D. R.; Grass, M. E.; Zeng, Z.; Aksoy, F.; Bluhm, H.; Li, W. X.; Mun, B. S.; Somorjai, G. A.; Liu, Z. In Situ Oxidation Study of Pt(110) and Its Interaction with CO. *J. Am. Chem. Soc.* **2011**, *133*, 20319–20325.
- (10) Zhu, Z.; Tao, F.; Zheng, F.; Chang, R.; Li, Y.; Heinke, L.; Liu, Z.; Salmeron, M.; Somorjai, G. A. Formation of Nanometer-Sized Surface Platinum Oxide Clusters on a Stepped Pt(557) Single Crystal Surface Induced by Oxygen: A High-Pressure STM and Ambient-Pressure XPS Study. *Nano Lett.* **2012**, *12*, 1491–1497.
- (11) Fantauzzi, D.; Jacob, T.; Zhu, T.; Papp, C.; Steinrück, H.-P.; Farkas, A.; Mueller, J. E. On the Platinum-Oxide Formation under Gas-Phase and Electrochemical Conditions. *J. Electron Spectrosc. Relat. Phenom.* **2017**, *221*, 44–57.
- (12) Steininger, H.; Lehwald, S.; Ibach, H. Adsorption of Oxygen on Pt(111). *Surf. Sci.* **1982**, *123*, 1–17.
- (13) Miller, D.; Sanchez Casalongue, H.; Bluhm, H.; Ogasawara, H.; Nilsson, A.; Kaya, S. Different Reactivity of the Various Platinum Oxides and Chemisorbed Oxygen in CO Oxidation on Pt (111). *J. Am. Chem. Soc.* **2014**, *136*, 6340–6347.
- (14) van Spronsen, M. A.; Frenken, J. W. M.; Groot, I. M. N. Surface Science under Reaction Conditions: CO Oxidation on Pt and Pd Model Catalysts. *Chem. Soc. Rev.* **2017**, *46*, 4347–4374.
- (15) Picolin, A.; Busse, C.; Redinger, A.; Morgenstern, M.; Michely, T. Desorption of H₂O from Flat and Stepped Pt(111). *J. Phys. Chem. C* **2009**, *113*, 691–697.
- (16) Lew, W.; Crowe, M. C.; Karp, E.; Campbell, C. T. Energy of Molecularly Adsorbed Water on Clean Pt(111) and Pt(111) with Coadsorbed Oxygen by Calorimetry. *J. Phys. Chem. C* **2011**, *115*, 9164–9170.
- (17) Schiros, T.; Näslund, L.-Å.; Andersson, K.; Gyllenpalm, J.; Karlberg, G. S.; Odelius, M.; Ogasawara, H.; Pettersson, L. G. M.; Nilsson, A. Structure and Bonding of the Water-Hydroxyl Mixed Phase on Pt(111). *J. Phys. Chem. C* **2007**, *111*, 15003–15012.
- (18) Casalongue, H. S.; Kaya, S.; Viswanathan, V.; Miller, D. J.; Friebel, D.; Hansen, H. A.; Nørskov, J. K.; Nilsson, A.; Ogasawara, H. Direct Observation of the Oxygenated Species during Oxygen Reduction on a Platinum Fuel Cell Cathode. *Nat. Commun.* **2013**, *4* (May), ZZZ DOI: [10.1038/ncomms3817](https://doi.org/10.1038/ncomms3817).
- (19) Ogasawara, H.; Brena, B.; Nordlund, D.; Nyberg, M.; Pelmenchikov, A.; Pettersson, L. G. M.; Nilsson, A. Structure and Bonding of Water on Pt(111). *Phys. Rev. Lett.* **2002**, *89*, 25–28.


(20) Nagasaka, M.; Nakai, I.; Kondoh, H.; Ohta, T.; Carravetta, V. Oxygen K-Edge near Edge X-Ray Absorption Fine Structures of O and OH Overlayers on Pt(1 1 1). *Chem. Phys. Lett.* **2003**, 375 (3–4), 419–424.




JACS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY



Editor-in-Chief
Prof. Christopher W. Jones
Georgia Institute of Technology, USA

Open for Submissions 

pubs.acs.org/jacsau  ACS Publications
Most Trusted. Most Cited. Most Read.