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# Hydroxylation of Platinum Surface Oxides Induced by Water Vapor

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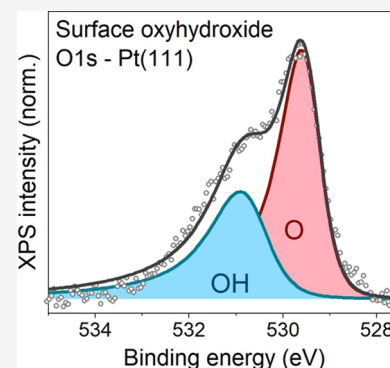


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Supporting Information

**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 O<sub>2</sub> has been widely studied. However, in most applications, H<sub>2</sub>O is also an important or even dominant part of the reaction mixture. Here, we investigate the interaction of H<sub>2</sub>O with Pt surface oxides using near-ambient-pressure X-ray photoelectron spectroscopy. We find that reversible hydroxylation readily occurs in H<sub>2</sub>O/O<sub>2</sub> 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 treatment<sup>1</sup> and in future technologies such as fuel cell catalysis.<sup>2</sup> 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 O<sub>2</sub> has been widely investigated.<sup>3–11</sup> At very low oxygen pressures, only an adsorbate overlayer is formed, with  $\leq 0.25$  monolayer (ML) coverage for the case of Pt(111).<sup>11,12</sup> Starting in the range between 0.1 and 1 mbar of O<sub>2</sub>, the formation of oxides becomes possible.<sup>5,8–11</sup> While thermodynamics predicts the onset of bulk oxidation in this pressure range (for modest temperatures),<sup>8</sup> kinetic limitations ensure a wide range of stability for surface oxides up to 1 ML coverage.<sup>5,5,9,10</sup> These surface oxides consist of one-dimensional chains of Pt atoms coordinated to four O atoms,<sup>3,5,11</sup> following the motifs of PtO<sub>2</sub> bulk oxides. Despite this structural similarity to bulk PtO<sub>2</sub>, the Pt atoms in the surface oxide carry very little charge, in contrast to the Pt<sup>4+</sup> ions in bulk oxides.<sup>5</sup> This makes the surface oxide much more reactive toward CO,<sup>13,14</sup> 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 O<sub>2</sub>. Although water itself adsorbs only weakly on clean Pt surfaces,<sup>15</sup> ultra-high-vacuum studies at low temperatures have shown that water readily reacts with adsorbed oxygen, forming somewhat more stable OH adsorbates.<sup>16,17</sup> 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 O<sub>2</sub> at 473 K and subsequently exposed the samples to O<sub>2</sub>/H<sub>2</sub>O mixtures in the temperature range of 393–473 K (see section S1 of the Supporting Information for experimental details).

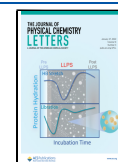
Using our NAP-XPS end-stations at the UES6-PGM1 and ISSS beamlines at the BESSY II synchrotron, we followed the chemical state of the surface through Pt 4f and O 1s spectra (details in section S2). Figure 1a shows Pt 4f spectra for the initial oxidation of the Pt(111) crystal. The asymmetric Gaussian–Lorentzian 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 group<sup>5</sup> 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  $5 \times 10^{-4}$  mbar of O<sub>2</sub> at 463 K, we estimate the oxygen coverage to be approximately 0.5–0.6 ML after exposure to 0.5 mbar of O<sub>2</sub> for 30 min.

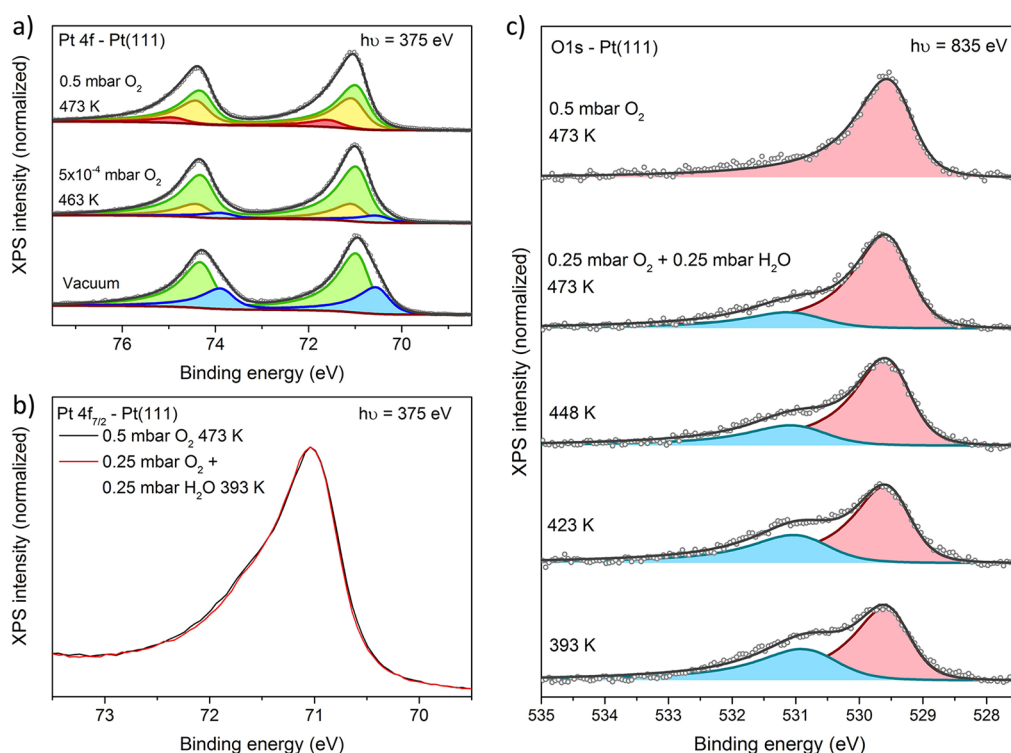
When water is introduced into the system (0.25 mbar of H<sub>2</sub>O and 0.25 mbar of O<sub>2</sub> at 393 K), the O 1s/Pt 4f ratio increases only 8%, indicating little to no increase in the surface coverage. This is also reflected in the Pt 4f peak shape, which is almost unchanged (see Figure 1b). However, dramatic changes are visible in the O 1s signal (Figure 1c). Under dry

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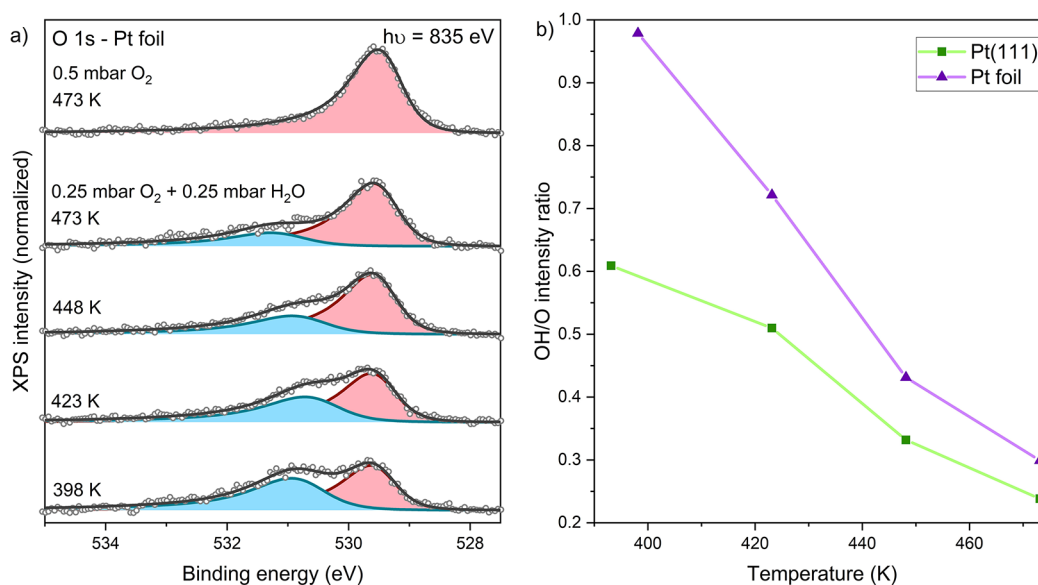
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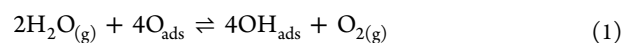
**Figure 1.** Oxidation and hydroxylation of Pt(111). (a) Initial oxidation in pure O<sub>2</sub>. Spectral decomposition: clean surface (blue), bulk (green), chemisorbed/surface oxide (yellow), and surface oxide (red). Fitting model from ref 5. (b) Pt 4f<sub>7/2</sub> spectra before and after the introduction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



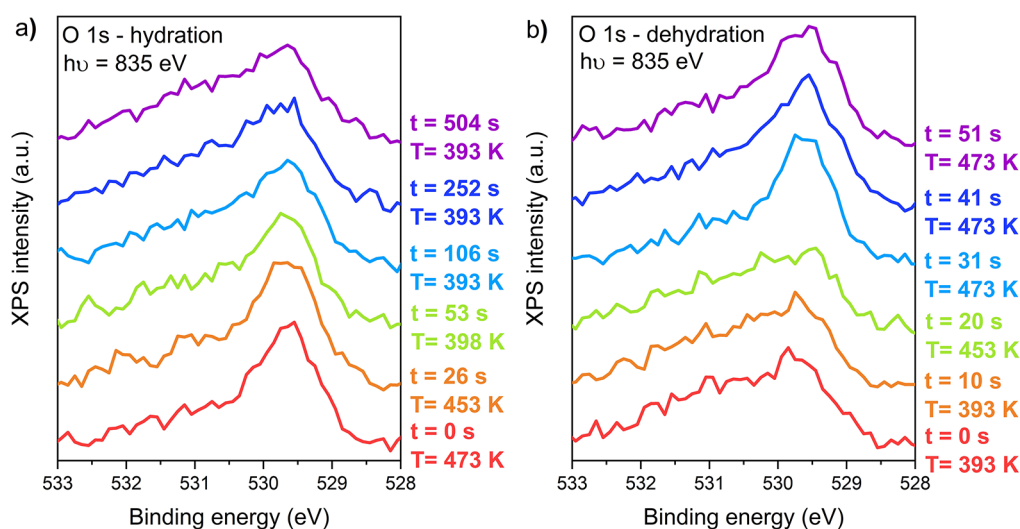
**Figure 2.** Hydroxylation of surface oxides on sputtered (defect-rich) Pt foil and comparison to Pt(111). (a) Shirley background-subtracted O 1s spectra showing the temperature-dependent surface composition in a H<sub>2</sub>O/O<sub>2</sub> environment. Spectral decomposition: O (red) and OH (blue). (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.<sup>5,9</sup> 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 H<sub>2</sub>O would be expected at ≥532 eV.<sup>17–19</sup> This assignment is further corroborated by O K-edge spectra (section S4), which display a resonance pattern consistent with an OH<sub>ads</sub>/O<sub>ads</sub> mixture on platinum.<sup>5,17,20</sup>

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 H<sub>2</sub>O and 0.25 mbar of O<sub>2</sub>. (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  $\Delta S$  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.<sup>3</sup> 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.

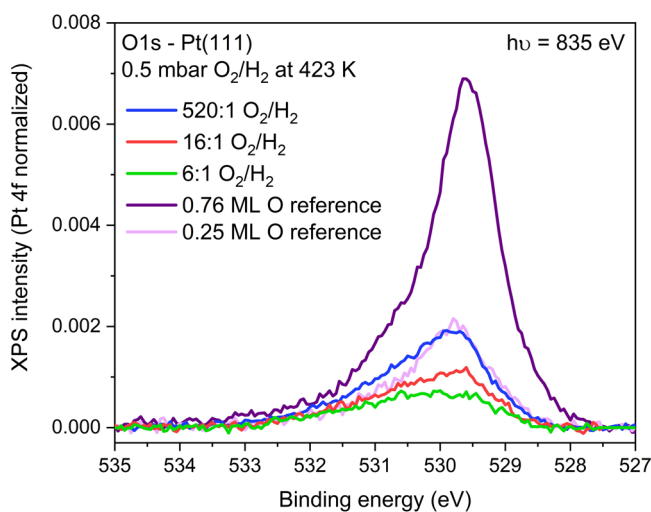
To investigate whether undercoordinated sites are preferentially hydroxylated, we created a defect-rich sample by prolonged Ar<sup>+</sup> sputter bombardment of a Pt foil. Figure 2 shows that such a sample displays stronger hydroxylation than Pt(111), yet has a very similar temperature dependence of 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,<sup>7</sup> one can obtain a rough estimate of the adsorption enthalpy of the hydroxides, approximately  $-1.1 \text{ eV}$  per OH<sub>ads</sub> (derivation in section S6). This is significantly higher than the value of approximately  $-0.9 \text{ eV}$  for surface oxides in this coverage range,<sup>7</sup> 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<sub>ads</sub> rather than OH<sub>ads</sub>, thereby increasing the observed OH<sub>ads</sub>/O<sub>ads</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> 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.<sup>13</sup>

In conclusion, we have shown that Pt surface oxides are prone to hydroxylation, even at modest H<sub>2</sub>O 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)

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### Notes

The authors declare no competing financial interest.

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