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THE INTERACTION OF WATER WITH THE Pt(111) SURFACE

Galen B. FISHER and John L. GLAND
Physical Chemistry Department, General Motors Research Laboratories, Warren, Michigan 48090, USA

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The interaction of water with a platinum (111) surface has been examined by thermal desorption (TDS), ultraviolet photoemission (UPS), and X-ray photoemission (XPS) spectroscopies. UPS and XPS results indicate that water adsorbs molecularly at 100 K. TDS studies show that water desorbs with approximately zero order kinetics and that a monolayer of water has a maximum desorption rate at 180 K. Heavier coverages exhibit additional desorption from multilayer water (ice) which peaks at temperatures near 165 K. The coadsorption of atomic oxygen with water leads to an increase in the desorption temperature of water of about 30 K. XPS studies of this surface indicate that adsorbed OH species are involved in the reaction mechanism which increases the water desorption temperature.

1. Introduction

The catalytic formation of water from hydrogen and oxygen over platinum has been studied repeatedly since the time of Faraday [1]. However, few studies have been reported on the interaction of water with platinum surfaces. This type of information is interesting for catalytic systems in which water is either a reactant or product. In either case, the adsorption and desorption of water may compete with or otherwise influence other reactions.

This paper presents the first detailed thermal desorption study of water adsorbed on a platinum surface. We have chosen the close-packed (111) face for study. This is the surface of lowest surface energy, which is preferentially formed after heating polycrystalline films. The adsorbed water has been characterized by ultraviolet photoemission spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). Desorption kinetics have been monitored by thermal desorption spectroscopy (TDS). Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were used to examine surface order and cleanliness.

In conjunction with a study of the reduction of oxygen on Pt foils [2], Norton characterized thick layers of adsorbed water (ice) on these foils at 100 K. He observed desorption near 160 K. A $\sqrt{3} \times \sqrt{3}$ R 30° LEED pattern was observed by Firment and Somorjai [3] and Tucker [4] for water adsorbed on a Pt(111) surface. Our work comprises the first detailed report of water adsorbed on platinum in submonolayer to multilayer quantities. We conclude that water adsorbs molecularly at 100 K at all coverages.

2. Experimental

The experiments were carried out in an ion pumped stainless steel chamber with a liquid nitrogen trap which shrouds a titanium sublimation pump. Base pressures in the 10^{-10} Torr (1.3×10^{-8} Pa) range were attained. The system has provisions for LEED, AES, UPS ($h\nu = 21.2$ eV, 40.8 eV), and XPS ($h\nu = 1253.6$ eV). Electron energies are measured using a double pass cylindrical mirror analyzer which has been calibrated to ±0.2 eV for electrons with kinetic energies from 300 to 1300 eV. Several Pt core level binding energies were measured relative to a Fermi level reference determined to ±0.1 eV. The sample was biased by multiples of 100 V with a power supply calibrated to ±0.1 V relative to a secondary standard of the National Bureau of Standards. Apparent and actual shifts in the binding (kinetic) energy of the levels were compared to obtain the calibration.

The platinum crystal was oriented within $\pm 1/2^\circ$ of the (111) face using usual metallographic techniques. The sample was heated resistively by passing a current through Pt wires spotwelded to the back surface of the crystal. A chromel–alumel thermocouple was spotwelded to the back surface so that the temperature could be monitored over the 100 to 1300 K range of the experiments. Cleaning was done by cycled heating in oxygen followed by heating in vacuum. Care was taken to avoid platinum oxide formation.

Partial pressures of gases were measured by a quadrupole mass spectrometer with provisions for multiplexed detection of up to eight mass peaks during a thermal desorption. The desorption spectra were analyzed using the isotherm and isostere method implemented by Falconer and Madix [5]. The water (H_2O or D_2O) was admitted as an ambient into the chamber. An exposure of 1 L corresponds to 5.0×10^{14} molecules/cm^2. Although the pumping speed for water remained relatively constant as measured by a flash filament method, the titanium pump was flashed between each adsorption–desorption cycle.

3. Results and discussion

3.1. Adsorption of water on Pt(111) at 100 K

The adsorption of water was characterized using UPS and XPS. The UPS spectra shown in fig. 1 indicate that adsorbed water is molecular at 100 K on the Pt(111) surface. The spectrum of the clean Pt(111) surface and the Pt(111) surface with an adsorbed monolayer of water are shown in curves a and b of fig. 1, respectively. The difference spectrum (b – a) for an adsorbed monolayer of water is also shown

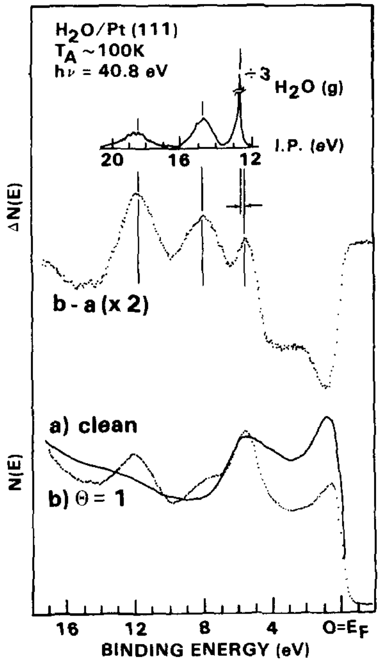


Fig. 1. UPS spectra ($h\nu = 40.8$ eV) of clean Pt(111) (a, solid) and of a monolayer of water adsorbed on Pt(111) (b, dots). The Pt(111) surface was exposed to approximately 2.0 L of water at 100 K in order to form the adsorbed layer of water. The unsmoothed difference spectrum (b – a) for adsorbed water is shown immediately above the constituent spectra. The gas phase spectrum taken at 40.8 eV of H_2O [6] is shown above the difference spectrum, with its deepest valence level (ionization potential [IP] ~18.5 eV) aligned with the corresponding level of adsorbed water (binding energy ~11.9 eV). The correspondence between the gas phase and adsorbed water's valence levels indicates water is adsorbed molecularly.

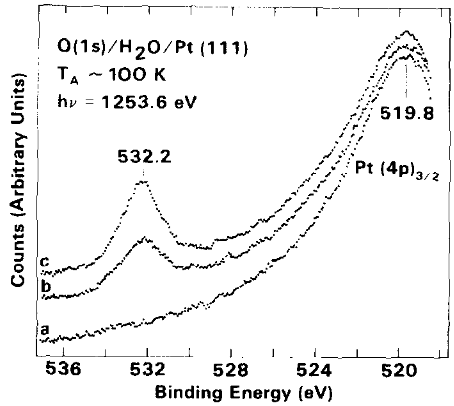


Fig. 2. XPS spectra of the O(1s) and $Pt(4p)_{3/2}$ levels for (a) clean Pt(111) and after water exposures of (b) 0.5 L and (c) 1.0 L at 100 K. Each 20 eV wide spectrum contains 2048 scans of 256 channels with a scan rate of 20 eV/s.

in fig. 1 together with a gas phase UPS spectrum of water. Three primary adsorbate induced levels are observed in the difference spectrum at 11.9, 8.2, and 5.9 eV below the Fermi level. Alignment of the most tightly bound valence level of the water gas phase spectrum [6] with the corresponding level in adsorbed water results in alignment of the other two levels within 0.2 eV. This correspondence indicates that molecular water is the adsorbed species. The slight shift of the least tightly bound energy level suggests that hydrogen bonding is present even in the initial adsorbed layer of water [7,8]. The energies of the three water induced levels do not depend on coverage in the submonolayer regime [7]. That is, these peaks are present at the same binding energies indicating that molecular water predominates even at the lowest coverages studied ($\theta < 0.2$). Further details concerning the work function changes, coverage dependence of the energy levels and relaxation effects are discussed elsewhere [7]. In fig. 2, XPS spectra of the O(1s) region show that water exhibits a single level at 532.2 ± 0.3 eV. The water O(1s) position is shifted by about 2 eV from the O(1s) position for adsorbed dissociated oxygen at 529.8 ± 0.3 eV. This shift to higher binding energy is again characteristic of molecular adsorption since molecular adsorbates are expected to induce less charge transfer from the substrate to the adsorbate. Thus, XPS indicates a single molecular adsorbed state with the available resolution. Molecular adsorption of water at low temperatures on metals has also been reported for Ni [9], Ru [10], and Au [9a].

The coverage of water increases monotonically as a function of exposure. The coverage was obtained by integration of the thermal desorption spectra. The sticking coefficient obtained from these data is between 0.5 and 1.0. This indicates that water adsorption is not an activated process.

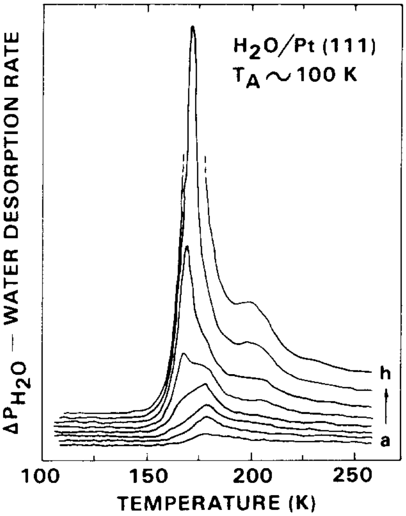
Up to exposures of 1 L at 100 K no new LEED features were observed, but above that the new features of a $\sqrt{3} \times \sqrt{3}$ R 30° pattern were observed. This has been previously noted by Firment and Somorjai [3] and by Tucker [4]. This pattern weakened as multilayer water (ice) was formed at higher exposures.

3.2. *Thermal desorption of water adsorbed on Pt(111)*

The thermal desorption of water over a wide range of coverages is examined in the following three figures. Fig. 3 shows the desorption spectra resulting from low initial coverages. In curves (a) through (d) for the lowest initial coverages, a peak at 180 K is dominant but quickly saturates. The shoulder below 170 K in curve (c) forms a peak in curve (d) and continues to grow with increasing exposure. This trend can be followed more clearly in fig. 4. This sharp peak shifts to 180 K with increasing initial coverage (curve j).

For exposures above 2 L a new desorption peak appears at 160 K. For high initial coverages shown in fig. 5 the peak temperature increases as the surface population increases. This peak which appears for high initial coverage may be related to multilayer coverages of adsorbed water (ice).

Curve (j) also has a shoulder at 205 K due to water desorbing at elevated temperatures. This shoulder first develops in curve (e), fig. 3. The peaks overlap and baselines are difficult to determine, however we estimate that 5–10% of the adsorbed water desorbs in this high temperature shoulder. After exposure of the surface with a doser to minimize experimental artifacts, this shoulder was less pronounced suggesting that sample supports contribute substantially to the high temperature shoulder. As a test for the existence of dissociation and recombination in water formation, sequential adsorptions of equal amounts of H_2O and D_2O were made for submonolayer to multilayer coverages. Desorption of water yielded a statistical mixture (1 : 2 : 1) of masses 18, 19 (HDO), and 20, respectively,



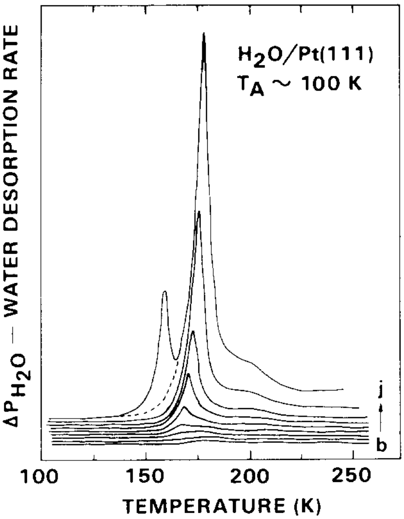


Fig. 3. Thermal desorption spectra of water adsorbed on Pt(111) at about 100 K at low coverages. Note that shoulder at about 200 K. The exposures in langmuirs are (a) 0.035, (b) 0.075, (c) 0.12, (d) 0.18, (e) 0.25, (f) 0.40, (g) 0.65, and (h) 1.0.

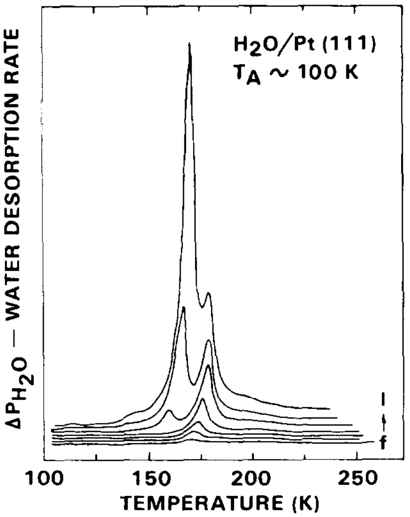
Fig. 4. Thermal desorption spectra of water adsorbed on Pt(111) at about 100 K up to monolayer coverages. The peak at 160 K in curve j is desorption from a water multilayer. The exposures in langmuirs are (b) 0.075, (c) 0.12, (d) 0.18, (e) 0.25, (f) 0.40, (g) 0.65, (h) 1.0, (i) 2.0, and (j) 4.0. The vertical scale units are seven times larger than those in fig. 3.

throughout desorption spectra in the first monolayer. An enhancement of the second mass adsorbed was found in the ice layer peak. Clearly, complete exchange occurs rapidly in the adsorbed layer and less rapidly in ice. EELS spectra of coadsorbed layers of D_2O and H_2O clearly indicate exchange occurs even at 100 K [8].

3.3. Desorption of water from modified platinum surfaces

Since hydrogen and oxygen are often present with water, the desorption of water from platinum after preexposure to hydrogen or oxygen is of interest. Hydrogen normally desorbs from Pt(111) by 420 K [11], but adsorbed dissociated oxygen remains to much higher temperatures, about 850 K, before desorbing [12].

Studies of the desorption of water from Pt previously exposed to varying amounts of hydrogen indicate that the desorption peak temperature is approximately independent of hydrogen coverage. However, oxygen preadsorption dramatically alters the desorption of water as indicated in fig. 6. A desorption spectrum for water desorption from the clean surface is shown in fig. 6 curve (a), while curves (b) through (d) are for 0.15, 0.35 and 0.5 L oxygen pre-exposures, respectively. Pre-exposures larger than 0.5 L have no further effect on the water desorption. Molecular oxygen was preadsorbed at 100 K for these experiments. Similar experi-



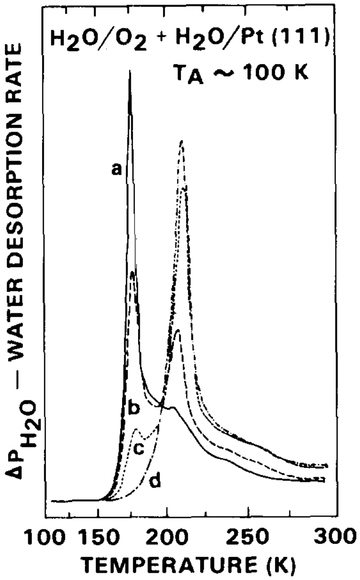


Fig. 5. Thermal desorption spectra of water adsorbed on Pt(111) at about 100 K up to multilayer coverages. The desorption peaking at 180 K is associated with the initial adsorbed layer, while the lower temperature desorption is from multilayer water (ice). The exposures are (f) 0.40, (g) 0.65, (h) 1.0, (i) 2.0, (j) 4.0, (k) 8.0, and (l) 16.0. The vertical scale units are 42 times larger than those in fig. 3.

Fig. 6. Thermal desorption of water adsorbed at 100 K on (a) clean Pt(111) (solid) and on Pt(111) after pre-exposure to oxygen. The oxygen pre-exposures at 100 K were (b) 0.15 L (dashed), (c) 0.35 L [dots], and (d) 0.5 L (dash-dot). The water post-exposure was 0.3 L. Note the 30 K increase in the peak water desorption temperature in the presence of oxygen.

ments were also performed with preadsorbed atomic oxygen. The results were nearly identical for equivalent atomic oxygen coverages, since adsorbed molecular oxygen dissociates below 150 K [12]. In fig. 6 oxygen clearly has a marked effect on the water desorption and gradually shifts all of the desorption to a temperature near 210 K. Curves taken on a finer grid of pre-exposure suggest that the new peak simply grows from the high temperature feature in the clean spectrum near 205 K.

Preliminary thermal desorption experiments which examine water formation from coadsorbed hydrogen and oxygen indicate a reaction limited water formation peak also occurs at approximately 200 K as indicated in figs. 7a and 7b. This result suggests that common chemical species may be involved in both the production of water from oxygen and hydrogen and the desorption of water from a surface with adsorbed atomic oxygen. Water formation may also occur below the water desorption temperature (180 K) when atomic oxygen and atomic hydrogen are coadsorbed as indicated by the low temperature desorption limited water peak in fig. 7a.

3.4. Photoemission studies of water on oxygen-covered surfaces

The intriguing thermal desorption spectra shown in fig. 6 indicate that the water desorption peak is shifted by at least 30 K in the presence of preadsorbed oxygen. This may imply either a strong attractive interaction between water and the oxygen or an actual chemical change in the surface layer. A series of XPS experiments were performed in order to address this question. XPS spectra were first taken of a full p(2 X 2) oxygen coverage on the Pt(111) surface (fig. 8c). Spectra were then taken of a monolayer of water adsorbed onto the oxygen layer at 100 K (fig. 8a). The resulting adsorbed layer was then heated to 190 K and its XPS spectrum taken (fig. 8b). One hundred-ninety K was chosen because it is above the temperature at

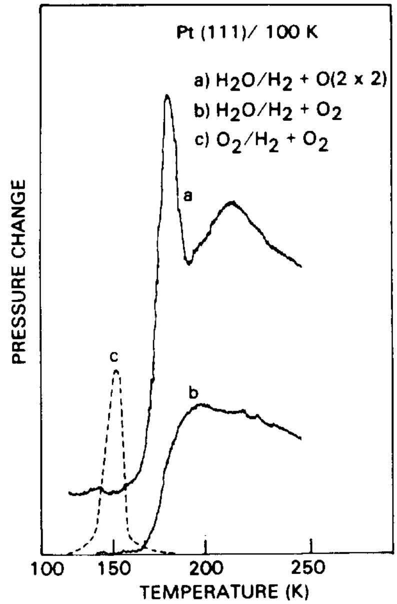


Fig. 7. (a) Water desorption spectrum following exposure of the Pt(111) surface to 3 L H_2 at 100 K on a preadsorbed p(2 X 2) layer of atomic oxygen. The p(2 X 2) structure was formed by saturating the surface with molecular oxygen at 100 K and heating to 300 K, then cooling prior to hydrogen adsorption. The heating rate for desorption was 10 K/s. (b) Water desorption spectrum following exposure of the Pt(111) surface first to 2 L O_2 at 100 K then to 1 L H_2 at 100 K. The heating rate for desorption was 10 K/s. (c) Molecular oxygen desorption observed during the water formation experiment described in (b) above.

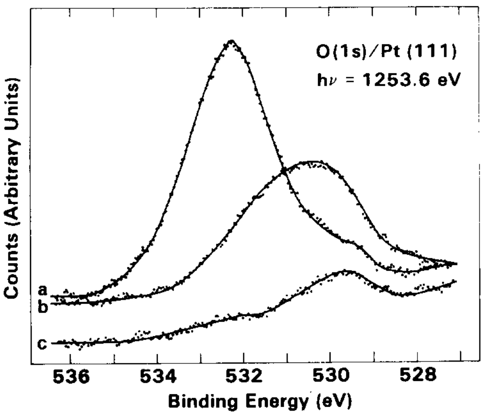


Fig. 8. XPS spectra of the O(1s) level for (a) a 1 L exposure of water at 100 K onto a p(2 X 2) layer of oxygen, (b) the same layer after heating to 190 K, and (c) a p(2 X 2) layer of adsorbed oxygen. Each 10 eV wide spectrum contains 4096 scans of 256 channels with a scan rate of 20 eV/s.

which water normally desorbs from clean Pt(111) and just below the desorption temperature in the presence of oxygen. Each curve is actually the sum of four separate runs made to reproduce these conditions. The XPS spectrum shown in fig. 8a exhibits a large peak near 532.3 eV due to molecular water. The weak shoulder near 529.5 eV is caused by the presence of atomic oxygen. Spectrum (b) shows a broad structure centered at 530.5 eV. In several of the constituent spectra there was evidence for a double peak within the broad structure. The O(1s) level from the p(2 × 2) overlayer of atomic oxygen shown in fig. 8c overlaps in energy with part of the broad peak in fig. 8b. The chemical nature of the oxygen-containing species on the surface appears to have actually changed by heating 90 K since negligible intensity is found at the binding energy of molecular water even though no water desorbs. At temperatures below 190 K, the water has dissociated to form a new species on the surface in the presence of adsorbed oxygen.

4. Discussion

One goal of our research has been to characterize the adsorbed state of water on Pt(111). At 100 K the UPS and XPS spectra indicate the predominance of adsorbed molecular water. The UPS valence spectrum of adsorbed water at 100 K on the Pt(111) surface matches the UPS valence spectrum of gas phase molecular water very closely. The XPS binding energy for monolayer amounts is within 1 eV of that found for water on Ni and Au [9a]. Furthermore, the work function is lower than the clean surface value which is also consistent with molecular adsorption [13]. We also note that no XPS intensity is seen in the region where atomic oxygen appears which argues against dissociative adsorption.

Water desorption is also of interest. The data which had been recorded digitally were analyzed [5] to determine the order and the heat of the desorption process. Detailed analysis of these data indicated the desorption was complex. Possible changes in the reaction mechanism and the heat of desorption with coverage may account for this complexity. The upward shift in desorption temperature with coverage suggests a desorption order less than one. Assuming zero order desorption for the monolayer peak a heat of approximately 65 kJ/mol (15 kcal/mol) is obtained. Using the same approach for the multilayer peak yields a heat of approximately 40 kJ/mol (10 kcal/mol). This is close to the heat of sublimation of water [50 kJ/mol (12 kcal/mol)] [10]. The desorption at 180 K at the lowest coverages ($\theta \lesssim 0.05$) (fig. 3, a–d) appears to be first order until the shoulder below 170 K grows in (fig. 3, d–f) which evolves into a peak moving to higher temperatures. While isolated water molecules may desorb at low coverages, the appearance of the shoulder may indicate that a sufficient coverage of water exists to form islands which change the desorption mechanism to less than first order. Island formation is also consistent with the evidence for hydrogen bonding at low coverages.

The increase in the peak temperature for water desorption from an oxygen covered surface is caused by water dissociation at temperatures below 190 K. The dissociated water recombines near 210 K and desorbs as water. The XPS data confirm that a chemical change has occurred in the water when heated in the presence of adsorbed oxygen. The shift in desorption temperature is not caused by a new mode of bonding between water and the surface (i.e., hydrogen bonding). Two species may be present, as evidenced by the peak's width and the doublet character of its constituent spectra as shown in fig. 8b. If one component is attributed to some acount of atomic oxygen, then a second peak at about 531 eV would yield the observed curve in fig. 8b. A peak at 531 eV is a plausible location for an adsorbed OH species because charge transfer to adsorbed OH from the Pt surface would be expected to be intermediate between adsorbed oxygen and adsorbed water. An O(1s) level on Ni at 531.4 eV has been ascribed to OH [14]. In fact, recent UPS and EELS studies have confirmed the presence of OH on Pt(111) under these conditions [15]. Thus, the apparent shift in the desorption temperature of water actually indicates the temperature at which hydroxyl species recombine and desorb. This may explain the small peak at 205 K in the water desorption spectra which is attributed partially to leads. The Pt leads, being polycrystalline, may not be entirely oxygen free. Thus, water desorbing from them may have dissociated before desorbing above 200 K.

The initial peak in the reaction-limited desorption of water has been found to occur (fig. 7b) just above 200 K. The recombination of hydroxyl species occurs in this same temperature range (fig. 6d). At this time this coincidence in temperature is only suggestive. However, it is reasonable to suggest from this data that the reaction of the dissociated surface species, H(ads) and O(ads), and the recombination of dissociated water may proceed via the same reaction intermediate. The data implies that water formation on platinum in this temperature range may proceed via an adsorbed OH species. This possibility is being tested in further studies of water formation.

5. Conclusions

Water adsorbs as a molecule on the Pt(111) surface at 100 K and desorbs from a molecular adsorbed layer. Most of the water in the first monolayer also desorbs with approximately zero order kinetics at temperatures near 180 K. Water also adsorbs as a molecule on an oxygen covered surface of Pt(111) at 100 K. However, upon heating it dissociates to form hydroxyl species and recombines to desorb as water near 200 K. Water desorption at 200 K, which arises from the reaction of H and O, may occur with OH as a possible intermediate, since XPS provides evidence that OH can exist on Pt(111) at temperatures just below 200 K.

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