Hydrogenation of O and OH on Pt(111): A comparison between the reaction rates of the first and the second hydrogen addition steps

Lars-Åke Näslund

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Lars-Åke Näslund, Hydrogenation of O and OH on Pt(111): A comparison between the reaction rates of the first and the second hydrogen addition steps, 2014, Journal of Chemical Physics, (140), 10, 104701.

<http://dx.doi.org/10.1063/1.4867535>

Copyright: American Institute of Physics (AIP)

<http://www.aip.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-116405>

Hydrogenation of O and OH on Pt(111): A comparison between the reaction rates of the first and the second hydrogen addition steps

L.-Å. Näslund

Citation: *The Journal of Chemical Physics* **140**, 104701 (2014); doi: 10.1063/1.4867535

View online: <http://dx.doi.org/10.1063/1.4867535>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/140/10?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Oxidation of C₂H₅OH by NO and O₂ on the surface of stepped Pt(332): Relationship to selective catalytic reduction of NO with hydrocarbons

J. Vac. Sci. Technol. A **27**, 121 (2009); 10.1116/1.3054132

The importance of hydrogen's potential-energy surface and the strength of the forming R – H bond in surface hydrogenation reactions

J. Chem. Phys. **124**, 044705 (2006); 10.1063/1.2159482

Microcanonical unimolecular rate theory at surfaces. III. Thermal dissociative chemisorption of methane on Pt(111) and detailed balance

J. Chem. Phys. **123**, 094707 (2005); 10.1063/1.2006679

Reaction fronts in the oxidation of hydrogen on Pt(111): Scanning tunneling microscopy experiments and reaction–diffusion modeling

J. Chem. Phys. **116**, 5759 (2002); 10.1063/1.1453964

Isothermal study of the kinetics of carbon monoxide oxidation on Pt(111): Rate dependence on surface coverages

J. Chem. Phys. **106**, 4204 (1997); 10.1063/1.473126

Hydrogenation of O and OH on Pt(111): A comparison between the reaction rates of the first and the second hydrogen addition steps

L.-Å. Näslund^{a),b)}

Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

(Received 13 November 2013; accepted 21 February 2014; published online 10 March 2014)

The formation of water through hydrogenation of oxygen on platinum occurs at a surprisingly low reaction rate. The reaction rate limited process for this catalytic reaction is, however, yet to be settled. In the present work, the reaction rates of the first and the second hydrogen addition steps are compared when hydrogen is obtained through intense synchrotron radiation that induces proton production in a water overlayer on top of the adsorbed oxygen species. A substantial amount of the produced hydrogen diffuses to the platinum surface and promotes water formation at the two starting conditions O/Pt(111) and (H₂O+OH)/Pt(111). The comparison shows no significant difference in the reaction rate between the first and the second hydrogen addition steps, which indicates that the rate determining process of the water formation from oxygen on Pt(111) is neither the first nor the second H addition step or, alternatively, that both H addition steps exert rate control. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4867535>]

I. INTRODUCTION

The catalytic reaction to form water through hydrogenation of oxygen on platinum is not only one of the most important fundamental heterogeneous catalytic reactions but also a model system for a surface reaction in general. The catalytic formation of water (H₂O) appears to be very simple—two hydrogen atoms (H) are added to one oxygen atom (O) with a substantially reduced reaction barrier when this occurs on the surface of, e.g., platinum (Pt). Nevertheless, the details behind this surface reaction are still puzzling and an unambiguous explanation for the surprisingly low reaction rate is still to be found.

Model experiments of H₂O formation through hydrogenation of adsorbed O on Pt(111) in ultra high vacuum (UHV) conditions suggest that the formation of Pt-OH species at the first H addition step is the rate-limiting process.^{1–6} Pioneering work by Gland *et al.*¹ proposed that both oxygen- and hydrogen gas adsorb dissociatively and that the interaction between the adsorbed H and O, to produce Pt-OH, is the rate limiting process. Furthermore, formation of H₂O in the presence of O becomes an autocatalytic process where the first hydrogenation step is replaced with the reaction between produced H₂O and coadsorbed O forming two Pt-OH intermediates.⁷ Substituting the first H addition mechanism with an autocatalytic process increases the reaction rate significantly, as shown in a combined scanning tunneling microscopy (STM) and high-resolution electron energy loss spectroscopy (HREELS) study.^{2–4} Based on these experiments, it is highly plausible that the first H addition step of the H₂O formation through hydrogenation of O on Pt is the rate limiting process, and this is still suggested in the liter-

ature today.^{5,6,8} The present report will, however, show that neither the first nor the second H addition step can be the rate limiting process or, alternatively, that both H addition steps exert rate control.

Instead of exposing O/Pt(111) to a H₂ gas flow as performed in earlier studies,^{1–6} hydrogen is made available for hydrogenation of the adsorbed O through photon beam induced breakage of H₂O in a multilayer water film,^{9–11} producing H⁺ that is transported through the film to the surface using the Grotthuss mechanism.¹² By comparing the H consumption for the O and OH hydrogenation at the two starting surface conditions O/Pt(111) and (H₂O+OH)/Pt(111) it should be possible to confirm or contradict the suggestion that the first H addition step is the rate-limiting process in the H₂O formation through hydrogenation of O on Pt(111).

At a temperature below 130 K co-adsorbed H₂O/Pt(111) and O/Pt(111) stays intact. Above 130 K, on the other hand, H₂O/Pt(111) can react with O/Pt(111) and form (H₂O+OH)/Pt(111) where each OH is connected to H₂O through hydrogen bonds (H-bonds) in a saturated network.^{13–17} Without the surrounding water molecules OH decomposes into O and H₂O through a recombination process.^{13,18,19} However, OH formation can also proceed through reaction between co-adsorbed H/Pt(111) and O/Pt(111), where the H addition step results in the formation of one OH/Pt(111) according to

If the hydrogenation of O/Pt(111), on the other hand, proceeds through reaction with H₂O/Pt(111), then two OH/Pt(111) are formed according to

Since reaction (1) can occur at temperatures below 130 K, while reaction (2) only can occur above 130 K¹³ it is

^{a)}Electronic mail: lars-ake.naslund@liu.se.

^{b)}Present address: Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-58183 Linköping, Sweden.

FIG. 1. Schematic illustration showing that the amount of OH on the surface is reduced if hydrogenation of O/Pt(111) occurs through reaction with co-adsorbed H prior to reaction with co-adsorbed H_2O (reaction scheme 2) compared to if hydrogenation occurs only through reaction with co-adsorbed H_2O (reaction scheme 1). Stages A, B, and C show the starting condition, hydrogenation through co-adsorbed H/Pt(111) (only in reaction scheme 2), and hydrogenation through co-adsorbed $\text{H}_2\text{O}/\text{Pt}(111)$ plus desorption of loosely bonded $\text{H}_2\text{O}/\text{Pt}(111)$, respectively. The $\text{H}_2\text{O}/\text{Pt}(111)$ are not shown except those formed through H addition steps in stage B. Co-adsorbed H originating from the irradiation of the water overlayer is colored red.

possible to hydrogenate O/Pt(111) only through reaction (1) even though H_2O is present on the Pt-surface by keeping the system at, e.g., 100 K. Furthermore, hydrogenation of O/Pt(111) can initially proceed through reaction (1) at 100 K for a limited time period and thereafter the hydrogenation of the residual O/Pt(111) can proceed at an elevated temperature, e.g., 165 K, through reaction (2).

The benefit of bringing the system up to 165 K for the post-reaction between the residual O/Pt(111) and co-adsorbed $\text{H}_2\text{O}/\text{Pt}(111)$ is that all H_2O not H-bonded to OH will desorb,^{13,20} including H_2O that is formed in the O hydrogenation process. Hence, each H addition step results in the formation of a vacancy in the H-bonded network of $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ that is formed when all residual O/Pt(111) in the second stage have been hydrogenated through reaction (2) at 165 K. In other words, the amount of formed OH in a post-reaction between the residual O and co-adsorbed H_2O at 165 K is related to the number of H addition steps that has occurred at 100 K.

Figure 1 shows schematically that the amount of formed OH/Pt(111) depends on the two hydrogenation reactions. If hydrogenation of a saturated coverage of $(2 \times 2)\text{-O}/\text{Pt}(111)$ only proceeds through reaction (2) at 165 K the obtained coverage of OH is significantly higher compared to the case where hydrogenation initially proceeds through reaction (1) at 100 K and thereafter through reaction (2) at 165 K. Al-

though the presence of co-adsorbed $\text{H}_2\text{O}/\text{Pt}(111)$ is essential for this system,^{13,18,19} H_2O is not shown in the illustrations in Figure 1. As shown in Figure 1, it is also possible that two subsequent H addition steps at 100 K results in H_2O that desorbs or reacts with residual O according to reaction (2) when the temperature is raised to 165 K leaving two vacancies in the H-bonded network.

Figure 2 shows schematically in stage A, a saturated layer of OH formed through reaction between co-adsorbed $\text{H}_2\text{O}/\text{Pt}(111)$ and O/Pt(111). Additional hydrogenation of OH proceeds through reaction with a H forming H_2O according to

Stage B illustrates hydrogenation of OH at 100 K for a limited time and the formed H_2O will thereafter desorb when the temperature is raised to 165 K, as shown in stage C. If we compare the two situations shown in Figures 1 and 2 (compare reaction schemes 2 and 3) we can see that the number of H addition steps, shown as red bold H in stage B, is the same in both figures. Furthermore, the amount of OH in stage C is also the same in the two situations. It is, thus, possible to directly compare the amount of OH in the last stage of the two situations shown in Figures 1 and 2 to estimate the number of H addition steps occurring in the two starting conditions. The amount of OH in reaction schemes 2 and 3 depends, thus, on

FIG. 2. Schematic illustration showing that the amount of OH on the surface is reduced if hydrogenation of (H₂O+OH)/Pt(111) occurs through reaction with co-adsorbed H (reaction scheme 3). Stages A, B, and C show the starting condition, hydrogenation through co-adsorbed H/Pt(111), and desorption of loosely bonded H₂O/Pt(111), respectively. H₂O in (H₂O+OH)/Pt(111) are not shown. Co-adsorbed H originating from the irradiation of the water overlayer is colored red.

the reaction barrier of the first and the second H addition step, respectively.

Figures 3 and 4 demonstrate different scenarios for four reaction schemes where the outcome depends on the reaction barriers for the first- and the second H addition steps. In Figure 3, the reaction schemes 4 and 5 start with a saturated layer of (2 × 2)-O/Pt(111) and a saturated layer of

(H₂O+OH)/Pt(111), respectively. The reaction barrier for the first H addition step is much higher than the barrier for the second H addition step. In the figure, this is illustrated as when only 10 hydrogenation reactions have occurred in reaction scheme 4 then 27 hydrogenation reactions have occurred in reaction scheme 5 in the same time span. As a consequence, the amount of OH in stage C for reaction scheme 4 has been

FIG. 3. Schematic illustration showing that if the reaction barrier for the first H addition step is much higher than the barrier for the second H addition step the amount of OH on the surface is different in the two reaction schemes. Stages A, B, and C show the starting condition, hydrogenation through co-adsorbed H/Pt(111), and hydrogenation through co-adsorbed H₂O/Pt(111) (only in reaction scheme 4) and desorption of loosely bonded H₂O/Pt(111), respectively. Co-adsorbed H₂O and H₂O in (H₂O+OH)/Pt(111) are not shown. Co-adsorbed H originating from the irradiation of the water overlayer is colored red.

FIG. 4. Schematic illustration showing that if the reaction barrier for the first H addition step is much lower than the barrier for the second H addition step the amount of OH on the surface is different in the two reaction schemes. Stages A, B, and C show the starting condition, hydrogenation through co-adsorbed H/Pt(111), and hydrogenation through co-adsorbed H₂O/Pt(111) (only in reaction scheme 6) and desorption of loosely bonded H₂O/Pt(111), respectively. Co-adsorbed H₂O and H₂O in (H₂O+OH)/Pt(111) are not shown. Co-adsorbed H originating from the irradiation of the water overlayer is colored red.

reduced by 20%, compared to full OH coverage as shown in Figure 1 (reaction scheme 1), while the corresponding OH reduction for reaction scheme 5 is 54%. In Figure 4, on the other hand, the reaction barrier for the first H addition step is much lower than the barrier for the second H addition step, illustrated as when 27 hydrogenation reactions have occurred in reaction scheme 6 then only 10 hydrogenation reactions have occurred in reaction scheme 7 in the same time span. Compared to full OH coverage, the amount of OH in stage C has been reduced by 54% and 20% for reaction scheme 6 and 7, respectively.

The schematic illustrations in Figures 1–4 show that it is possible to find out, through comparison of the OH coverage in the last stage of two experiments, whether the first or the second H addition step is the rate determining process in the formation of H₂O via hydrogenation of O/Pt(111). In the first experiment, the starting surface condition is a saturated layer of O/Pt(111) co-adsorbed with H₂O/Pt(111) and in the second experiment the starting surface condition is a saturated layer of (H₂O+OH)/Pt(111) co-adsorbed with H₂O/Pt(111).

The probing technique that is employed in the present study is the chemical specific and local geometry sensitive high-resolution X-ray photoelectron spectroscopy (XPS). Figure 5 presents the O1s XPS spectra of O/Pt(111) and (H₂O+OH)/Pt(111). The single XPS peak for O/Pt(111) is located at a binding energy of 529.8 eV while the corresponding

peaks for (H₂O+OH)/Pt(111) are located at 530.0 and 531.5 eV for OH and H₂O, respectively. Also included in Figure 5 are asymmetric Voigt functions representing O/Pt(111) and (H₂O+OH)/Pt(111). Resting on a Shirley background the fitted asymmetric Voigt functions match the line shape of the O1s peaks perfectly for both XPS spectra. The combination of

FIG. 5. O1s XPS of (a) O/Pt(111) with one peak at 529.8 eV and (b) (H₂O+OH)/Pt(111) with two peaks that correspond to OH and H₂O at 530.0 and 531.5 eV, respectively.¹³ Included are also asymmetric Voigt functions on top of Shirley backgrounds.

two asymmetric Voigt functions for (H₂O+OH)/Pt(111) show a OH:H₂O ratio of 1:1.

The third reactant, hydrogen, is made available for the hydrogenation of O and OH through photon beam induced breakage of H₂O^{9–11} in a multilayer water film (6 ML) on top of the starting conditions O/Pt(111) and (H₂O+OH)/Pt(111). The produced H⁺ will diffuse through the film to the surface using the Grotthus mechanism.¹² Some of the photon beam produced H⁺ will diffuse to the Pt-surface and promote O and OH hydrogenation. A relevant question is if the H⁺ reacts with O and OH without adsorption to the Pt surface, according to an Eley-Rideal process, or if H⁺ adsorbs to the Pt-surface prior the hydrogenation process, i.e., according to a Langmuir-Hinshelwood process. Unfortunately, the 6 ML water film on top of the layer where the H addition steps to O and OH occur does not allow us to study the hydrogenation process in detail. The H⁺ is, however, small enough to penetrate the first adsorbing layer and can thereafter move freely on the Pt-surface under the water film overlayer.²¹ Once at the Pt-surface, the H⁺ will be involved in the charge redistribution between the surface and the bulk of the Pt,²² i.e., the surface charge neutralization process will generate co-adsorbed H, O, OH, and H₂O on the Pt(111) equivalent to experiments where hydrogenation of oxygen occurs through exposure of H₂ gas onto O/Pt(111). It is therefore more likely that the H addition steps in this study proceeds according to a Langmuir-Hinshelwood process.

II. EXPERIMENTAL

The study was performed at beamline 5-1 at the Stanford Synchrotron Radiation Lightsource (SSRL) located at the SLAC National Accelerator Laboratory in Menlo Park, CA. The XPS spectra were obtained using a Scienta SES-100 electron energy analyzer. The photoelectron binding energy was calibrated against the Pt Fermi level and the total energy resolution for the spectroscopy was better than 0.1 eV.

The Pt(111) crystal, acquired from Surface Preparation Laboratory, was continuously cooled with liquid nitrogen (LN₂). The temperature was controlled by infrared radiation from a 0.15 mm thoriated-tungsten filament mounted approximately 2 mm from the backside of the Pt(111) crystal, monitored using an alumel/chromel thermocouple spot-welded to the side of the Pt crystal, and calibrated against the desorption onset of a D₂O multilayer reported to be 140 K.^{20,23} The cleaning of the Pt(111) crystal was completed using several sputtering-annealing cycles. Sputtering was performed with neon ion bombardments for 3 min at a sputter current of $I_{\text{Ne}} = 5 \mu\text{A}/\text{cm}^2$ and the subsequent annealing temperature was ~ 950 K. During the cooling stage, in the temperature interval 800–400 K, the Pt surface was treated with O₂. The final cycle was completed with a heat ramp to 600 K to remove residual oxygen.

The (2 × 2)-O layer was prepared through an O₂-dose at $T < 100$ K until saturation coverage followed by a heat ramp to 200 K. The initial coverage of the (2 × 2)-O layers was the same for all sets of data, confirmed through the integrated intensity of O1s XPS spectra. The co-adsorbed (H₂O+OH)/Pt(111) monolayer was prepared following the

procedure from Ref. 24. Water was supplied onto the (2 × 2)-O layer at $T < 100$ K until a multilayer was achieved. Subsequent heating to 160 K, with a heat ramp of ~ 0.5 K/s and 5 s delay time before cool-down, desorbed weakly bonded H₂O as confirmed by the chemical shift of the O1s photoelectron peak between multilayer adsorbed H₂O and H₂O/Pt(111).¹³ The nomenclature used in Sec. III will be H, OH, and H₂O. However, all hydrogen used throughout the study was the more irradiation stable isotope deuterium, introduced to the system as deuterium dioxide (D₂O).

Hydrogen is made available for hydrogenation of the adsorbed O or OH through photon beam induced breakage of H₂O in a multilayer water film.^{9–11} To induce the H⁺ production, the irradiation of the water overlayer was performed with photon energy of 535 eV; the difference between the kinetic-energy positions of the Pt Fermi level recorded with the first- and second-order light was used to calibrate the photon energy. The photon beam had a grazing incident angle to the sample of 6°, which gave an illuminated area of about $30 \times 1000 \mu\text{m}^2$ on the sample surface. The irradiation of the multilayer water film was performed on several spots on the sample separated by 500 μm in the direction perpendicular to the photon beam; a spacing of 500 μm was confirmed to be enough. Each set of data is, thus, obtained from a single sample preparation and since the initial (2 × 2)-O coverage for the three data sets presented in this study was the same, the decrease of the integrated intensity of each O1s XPS spectra of the residual amount of OH is proportional to the number of H addition steps with sufficient precision to show a significant difference in the reaction rates between the first and the second hydrogen addition steps; provided that the reaction barriers for the two hydrogen addition steps are larger than the energy barrier for the proton transport from the bulk water to the surface.

III. RESULTS AND DISCUSSION

Figure 6 shows O1s XPS of 6 ML H₂O on top of a saturated layer of O/Pt(111) and (H₂O+OH)/Pt(111) in part (a) and (b), respectively, after a 535 eV photon beam exposure of 0, 600, 1200, and 1800 s. The inset of Figure 6(a), enlarging the binding energy region for O adsorbed on Pt(111), shows a decrease in intensity around 529.8 eV indicating that O is consumed with time. Simultaneously, there is an initial intensity increase around 530.3 eV indicating OH formation, but with longer exposure time the intensity in the whole binding energy region of 529–531 eV reduces which suggests both O and OH consumption. Correspondingly in the inset of Figure 6(b) the decrease in intensity at 530.0 eV indicates OH consumption with photon beam exposure.

In addition to the intensity decrease in the binding energy region of 529–531 eV there is a decrease of the H₂O XPS peak intensity at 532.8 eV, which is a consequence of photon beam induced breakage of H₂O in the 6 ML water film. The products from the photon beam induced fragmentation of the water molecules will diffuse away from the irradiated volume. Some of the fragments will reach the water film surface and desorb or kick out surface H₂O into the vacuum.^{25–29} Water fragments can also recombine back into H₂O, especially if OH-

FIG. 6. O1s XPS of 6 ML H_2O on top of (a) O/Pt(111) and (b) $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$. The multilayer water, with the peak position at 532.8 eV, forms a hydrogen-bonded network for the proton transfer that is initiated through a 535 eV photon beam exposure. The insets enlarge the binding energy region and show that the intensity for O and OH decreases as the H_2O is irradiated for 0, 600, 1200, and 1800 s.

radicals are trapped in the water film matrix.^{28,29} Detectable OH-fractions in the water overlayer are therefore not expected since the delay time between irradiation and XPS recording was more than 15 min. While hydrogen is small and therefore can easily penetrate the first adsorbing layer,²¹ the saturated layer of O/Pt(111) + $\text{H}_2\text{O}/\text{Pt}(111)$ and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ + $\text{H}_2\text{O}/\text{Pt}(111)$ in the two experiments will prevent adsorption of OH that might diffuse toward the Pt-surface after the photon beam induced breakage of H_2O in the multilayer water film.³⁰

The starting surface conditions, i.e., saturated layer of O/Pt(111) + $\text{H}_2\text{O}/\text{Pt}(111)$ and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ + $\text{H}_2\text{O}/\text{Pt}(111)$, imply that areas of uncovered Pt-surface are not a prerequisite for the H addition mechanism: areas of uncovered Pt-surface are, however, necessary when O/Pt(111) or $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ is exposed to a H_2 gas flow since the H addition mechanism needs to be preceded by H_2 dissociation if it is to occur.

Irradiation directly onto the two starting conditions O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$, without the 6 ML water film overlayer, did not show any decrease of the XPS peak intensity for either O or OH. Figure 7 shows O1s XPS of O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ before and after 15 and 30 min irradiation, respectively. The lack of any decrease in the XPS intensity for O at 529.8 eV and OH at 530.0 eV confirms that the starting conditions, O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ in the two experiments, are insensitive to the photon beam exposure and radiation damaging does not occur. The O/Pt(111) does adsorb some H_2O , whereas for $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ a slight decrease in the XPS intensity for H_2O at 531.5 eV indicates desorption of loosely bonded H_2O .

After the photon beam exposure, the multilayer H_2O film is removed through desorption by heating the sam-

ples up to 165 K. For the first experiment, while the multilayer H_2O is desorbing, the residual O on the Pt-surface reacts with neighboring H_2O and forms a H-bonding network of $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$.¹³ For both experiments all H_2O that is not bonded to an OH, including H_2O that is formed in the oxygen hydrogenation process, will desorb at temperatures >160 K.^{13,20} Figure 8 shows O1s XPS spectra of $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ where the integrated intensities for the OH contribution in each case are proportional to the amount of OH that persist after desorption of the H_2O multilayer films for the two starting condition O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$. The amounts of $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ present after the three photon beam exposure time of 600,

FIG. 7. O1s XPS of (a) O/Pt(111) and (b) $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ before and after a 535 eV photon beam exposure for 15 and 30 min, respectively. The irradiation does not alter the amount of O and OH on the Pt-surface.

FIG. 8. O1s XPS of $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ after that the multilayer water film, which has been irradiated for 0, 600, 1200, and 1800 s, has been removed through desorption at 165 K. Starting condition was 6 ML H_2O on top of (a) $\text{O}/\text{Pt}(111)$ and (b) $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$, respectively.

1200, and 1800 s indicate an initially slow response to the photon beam produced H. 600 s irradiation only decreases the XPS intensity slightly for both experiments. After 1200 s irradiation, on the other hand, the decrease is significantly larger and an additional intensity decrease is observed after 1800 s photon beam exposure time. The induction period, i.e., the small initial decrease even though 1/3 of the total irradiation time has passed, is due to a delayed response before steady-state condition is reached. An induction period is expected since the concentration of H at the Pt-surface will increase with time, due to the probability distribution for the H diffusion length from the photon beam induced fragmentation of H_2O . However, with time the H adsorption on the Pt-surface will increase and eventually the H reaction with O and OH can proceed independently of the probability distribution for the H diffusion toward the Pt-surface. After the induction period, the reaction rate of the H addition steps seems to follow a pseudo-first order reaction process, i.e., an exponential decrease of the reaction rate.

Interesting to note is that the decrease of the OH XPS peak is almost the same independent of the choice of starting conditions $\text{O}/\text{Pt}(111)$ or $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$. Table I presents the relative amount of OH, $\theta_{\text{OH}}(t)/\theta_{\text{OH}}^{\text{initial}}$ obtained from the integrated intensity of the OH XPS peak at 530.0 eV using the asymmetric Voigt function that was obtained in Figure 5. Comparing the two experiments, $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111) + 6 \text{ ML } \text{H}_2\text{O}/\text{Pt}(111)$ shows a slightly larger decrease of the OH XPS peak intensity compared to $\text{O}/\text{Pt}(111) + 6 \text{ ML } \text{H}_2\text{O}/\text{Pt}(111)$, although the OH intensity estimation is not precise enough

TABLE I. The relative amount of OH^a, $\theta_{\text{OH}}(t)/\theta_{\text{OH}}^{\text{initial}}$, that remains after 535 eV photon beam irradiation of 6 ML H_2O on top of $\text{O}/\text{Pt}(111)$ or $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ followed by the multilayer H_2O removal at 165 K.

Starting condition	Photon beam exposure time/s			
	0	600	1200	1800
$\text{O}/\text{Pt}(111) + 6 \text{ ML } \text{H}_2\text{O}$	1	0.93 ± 0.02	0.47 ± 0.03	0.32 ± 0.02
$(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111) + 6 \text{ ML } \text{H}_2\text{O}$	1	0.96 ± 0.02	0.42 ± 0.03	0.29 ± 0.02

^aIncluded are also the combined standard deviation of the integrated intensity determination of the initial OH-coverage and the obtained OH-coverage after photon beam exposure.

to differentiate the OH intensity decreases in the two experiments. According to Figures 1–4, the obtained decrease of OH XPS peak intensity observed in the two experiments implies that both H addition steps exert rate control or that neither the first nor the second H addition step is the rate determining process in the H_2O formation via O hydrogenation on Pt(111). In other words, the absence of a significant difference suggests that the energy barriers of the first and the second H addition step must be similar in the present study or at least not too different.

The activation energy, E_a , for the overall H_2O formation process through hydrogenation of $\text{O}/\text{Pt}(111)$ where the H are made available through photon beam induced breakage of H_2O in a multilayer water film can be estimated from the Arrhenius equation

$$k_{\text{obs}} = A \exp(-E_a/k_B T), \quad (4)$$

where k_{obs} is the observed rate constant, A is the Arrhenius frequency factor, k_B is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$), and T is the temperature. For simplicity, assuming a pseudo-first order reaction mechanism where the rate of the H_2O formation is governed by a sole rate determining process, the observed rate constant can be obtained using the integrated rate equation

$$\theta_{\text{OH}}(t)/\theta_{\text{OH}}^{\text{initial}} = \exp(-k_{\text{obs}} t), \quad (5)$$

where $\theta_{\text{OH}}(t)/\theta_{\text{OH}}^{\text{initial}}$ can be estimated from the integrated intensity of the OH XPS peak at 530.0 eV for each photon beam exposure time t . The Arrhenius frequency factor, on the other hand, needs to be approximated using, for example, the frequency of free vibration of molecules, which is given by

$$A = k_B T / h, \quad (6)$$

where h is the Planck's constant ($4.136 \times 10^{-15} \text{ eV s}$).

Figure 9(a) shows $\theta_{\text{OH}}(t)/\theta_{\text{OH}}^{\text{initial}}$ versus photon beam exposure time t for the starting condition $\text{O}/\text{Pt}(111)$ as the photon beam induced fragmentation of water molecules in the 6 ML water film overlayer produces hydrogen for the H addition mechanism on the Pt-surface. For this experiment, the photon flux was increased by a factor of 10 to reduce the induction period and shorten the total experimental time. It was possible to record twice as many data points compared to the previous irradiation experiments. As in the previous experiments the hydrogenation process initially shows an induction period before a region of a higher rate of OH intensity reduction that decreases exponentially. The exponential decrease of

FIG. 9. (a) The relative amounts of OH, $\theta_{OH}(t)/\theta_{OH}^{initial}$, that is formed from the residual O/Pt(111) after a 6 ML water overlayer has been exposed to a photon beam of 535 eV. (b) The decrease of the OH in the 540–1260 s exposure time period follows approximately a first order reaction mechanism and the logarithm of the normalized OH intensities can be fitted with a straight line, which provides the reaction rate constant k . The dashed line extends the fitted line to the y-intercept point.

the reaction rate starts after the inflection point, i.e., between 360 and 560 s, and if we roughly approximate the OH reduction with a pseudo-first order reaction mechanism, according to Eq. (5), then we can estimate k_{obs} through the straight-line equation obtained after taking the logarithm of Eq. (5),

$$\ln(\theta_{OH}(t)/\theta_{OH}^{initial}) = -k_{obs}t, \quad (7)$$

where k_{obs} is the slope of a line with the y-intercept point at $\ln(\theta_{OH}(t)/\theta_{OH}^{initial}) = 0$. Figure 9(b) shows $\ln(\theta_{OH}(t)/\theta_{OH}^{initial})$ versus t together with a fitted straight-line for the data points at 540–1260 s from which k_{obs} is estimated. Since the study is performed at $T = 98 \pm 1$ K the expressions (4)–(6) result in an observed rate constant of $1.44 \pm 0.23 \times 10^{-3} \text{ s}^{-1}$, an Arrhenius frequency factor of $2.04 \pm 0.02 \times 10^{12} \text{ s}^{-1}$, and an activation energy of $0.29 \pm 0.01 \text{ eV}$.

The comparison in Figure 8 shows an unexpected observation because the established understanding is that the formation of the Pt-OH species at the first H addition step is the rate-limiting process. However, since both the approximated frequency factor and the obtained activation energy are of sizes that can be expected for H^+ diffusion in water, it is reasonable to suggest that the insensitivity of the starting condition in the present study is due to a rate-determining proton transfer from the water film to the Pt-surface prior to the H addition steps; the selected approximation of the Arrhenius frequency factor is in the present study the frequency of free vibration of molecules, which is a valid approximation if the H^+ transport in the water film would be the rate-determining process. The first H addition step can then still have a larger activation barrier compare to the second H addition step, al-

though the difference cannot be substantial since both activation barriers have to be smaller than the activation barrier of the proton transfer from the water film to the Pt-surface, i.e., the activation barriers for the H addition steps must be smaller than the obtained value of 0.29 eV. On the other hand, Sachs *et al.*^{3,4} estimated the activation energy for the second H addition step to be 0.27 eV, which in combination with the present study could imply that both H addition steps exert rate control with activation barriers of 0.27–0.29 eV. However, if both H addition steps require the same activation energy, then the reaction rate of the overall water formation would not decrease significantly when reaction (1) is replaced with reaction (2), i.e., when the first H addition step would be the autocatalytic reaction between O and formed H_2O , as indicated in the work by Sachs *et al.*^{3,4} Another question is also if an Arrhenius frequency factor in the order of 10^{12} s^{-1} is appropriate for the overall H_2O formation process, which is a more complex reaction system compare to H^+ diffusion in water. Selecting a smaller Arrhenius frequency factor would give a reduced value of the activation energy in the present study. Therefore, assuming that both H addition steps exert rate control, the obtained activation energy for the observed OH reduction should be viewed as an upper limit for the studied system. A support for a lower value of the activation energy for the overall H_2O formation process is presented in a recent study,³¹ where O/Pt(111) was exposed to a H_2 gas flow at 5–15 K above the water desorption temperature. The activation energy was determined to be 0.20 eV, which further supports the suggestion of that there is no substantial difference in the activation barriers of the first and the second H addition steps.

Hence, the insensitivity of the starting condition in the present study, where hydrogen is made available for hydrogenation of adsorbed O and OH through photon beam induced breakage of H_2O in a water film overlayer producing H^+ that was transported through the film to the surface using the Grotthius mechanism suggests that the rate-determining process most likely is the proton transfer from the water film to the Pt-surface, although the study does not provide evidence against the possibility that both H addition steps exert rate control.

IV. CONCLUSION

The presented XPS study indicates that the rate determining process of water formation through oxygen hydrogenation on Pt(111) is neither the first nor the second H addition step or, alternatively, that both H addition steps exert rate control. O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$ were covered with a water multilayer film and thereafter exposed to a 535 eV photon beam to induce H^+ production. After the water film was removed no significant difference in the amount of OH on the surface was found for either of the two starting conditions O/Pt(111) and $(\text{H}_2\text{O}+\text{OH})/\text{Pt}(111)$. This is possible only if the first and the second H addition steps have near equal reaction rates.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of

Materials Sciences and Engineering, under Contract No. DE-AC02-76SF00515, and was partly carried out at the Stanford Synchrotron Radiation Lightsource, a National User Facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The assistance from Toyli Anniyev, Janay B. MacNaughton, and Hirohito Ogasawara while acquiring the XPS data was very much appreciated. Further appreciation goes to Hirohito Ogasawara and Anders Nilsson for valuable discussions.

- ¹J. L. Gland, G. B. Fisher, and E. B. Kollin, *J. Catal.* **77**, 263 (1982).
- ²S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin, and G. Ertl, *Phys. Rev. Lett.* **83**, 2672 (1999).
- ³C. Sachs, M. Hildebrand, S. Völkening, J. Wintterlin, and G. Ertl, *J. Chem. Phys.* **116**, 5759 (2002).
- ⁴C. Sachs, M. Hildebrand, S. Völkening, J. Wintterlin, and G. Ertl, *Science* **293**, 1635 (2001).
- ⁵Y. Sha, T. H. Yu, Y. Liu, B. V. Merinov, and W. A. Goddard III, *J. Phys. Chem. Lett.* **1**, 856 (2010).
- ⁶Y. Sha, T. H. Yu, B. V. Merinov, P. Shirvanian, and W. A. Goddard III, *J. Phys. Chem. Lett.* **2**, 572 (2011).
- ⁷G. E. Mitchell, S. Akhter, and J. M. White, *Surf. Sci.* **166**, 283 (1986).
- ⁸L. Ou and S. Chen, *J. Phys. Chem. C* **117**, 1342 (2013).
- ⁹K. Mase, M. Nagasono, S. Tanaka, T. Urisu, E. Ikenaga, T. Sekitani, and K. Tanaka, *Surf. Sci.* **390**, 97 (1997).
- ¹⁰K. Andersson, A. Nikitin, L. G. M. Pettersson, A. Nilsson, and H. Ogasawara, *Phys. Rev. Lett.* **93**, 196101 (2004).
- ¹¹B. Brena, D. Nordlund, M. Odelius, H. Ogasawara, A. Nilsson, and L. G. M. Pettersson, *Phys. Rev. Lett.* **93**, 148302 (2004).
- ¹²R. L. A. Timmer, M. J. Cox, and H. J. Bakker, *J. Phys. Chem. A* **114**, 2091 (2010).
- ¹³T. Schiros, L.-Å. Näslund, K. Andersson, J. Gyllenpalm, G. S. Karlberg, M. Odelius, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson, *J. Phys. Chem. C* **111**, 15003 (2007).
- ¹⁴K. Bedürftig, S. Völkening, Y. Wang, J. Wintterlin, K. Jacobi, and G. Ertl, *J. Chem. Phys.* **111**, 11147 (1999).
- ¹⁵C. Clay, S. Haq, and A. Hodgson, *Phys. Rev. Lett.* **92**, 046102 (2004).
- ¹⁶J. R. Creighton, and J. M. White, *Surf. Sci.* **122**, L648 (1982).
- ¹⁷K. Bange, T. E. Madey, J. K. Sass, and J. M. Stuve, *Surf. Sci.* **183**, 334 (1987).
- ¹⁸A. Michaelides and P. J. Hu, *J. Chem. Phys.* **114**, 513 (2001).
- ¹⁹A. Michaelides and P. J. Hu, *J. Am. Chem. Soc.* **123**, 4235 (2001).
- ²⁰G. B. Fisher and J. L. Gland, *Surf. Sci.* **94**, 446 (1980).
- ²¹V. Tripkovic, E. Skúlason, S. Siahrostami, J. K. Nørskov, and J. Rossmeisl, *Electrochim. Acta* **55**, 7975 (2010).
- ²²A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
- ²³S. K. Jo, J. Kiss, J. A. Polanco, and J. M. White, *Surf. Sci.* **253**, 233 (1991).
- ²⁴G. B. Fisher and B. A. Sexton, *Phys. Rev. Lett.* **44**, 683 (1980).
- ²⁵K. I. Öberg, H. Linnartz, R. Visser, and E. F. van Dishoeck, *Astrophys. J.* **693**, 1209 (2009).
- ²⁶T. Hama, M. Yokoyama, A. Yabushita, M. Kawasaki, S. Andersson, C. M. Western, M. N. R. Ashfold, R. N. Dixon, and N. Watanabe, *J. Chem. Phys.* **132**, 164508 (2010).
- ²⁷S. Andersson, C. Arasa, A. Yabushita, M. Yokoyama, T. Hama, M. Kawasaki, C. M. Western, and M. N. R. Ashfold, *Phys. Chem. Chem. Phys.* **13**, 15810 (2011).
- ²⁸C. Arasa, S. Andersson, H. M. Cuppen, E. F. van Dishoeck, and G. J. Kroes, *J. Chem. Phys.* **134**, 164503 (2011).
- ²⁹J. Koning, G. J. Kroes, and C. Arasa, *J. Chem. Phys.* **138**, 104701 (2013).
- ³⁰H. Ogasawara, L.-Å. Näslund, J. MacNaughton, T. Anniyev, and A. Nilsson, *ECS Trans.* **16**, 1385 (2008).
- ³¹L.-Å. Näslund, *Surf. Sci.* **618**, 42 (2013).