

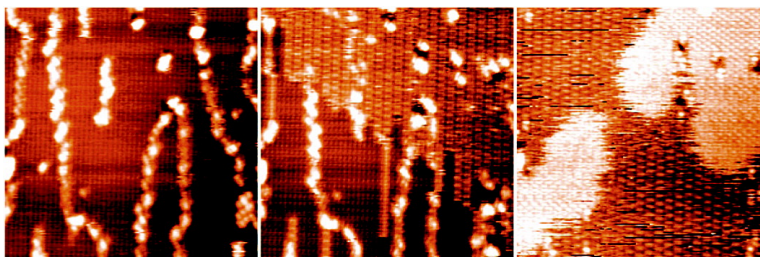
Article

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Water Production Reaction on Rh(110)

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Abstract: By means of scanning tunneling microscopy and density functional theory calculations, we studied the water formation reaction on the Rh(110) surface when exposing the $(2 \times 1)p2mg\text{-O}$ structure to molecular hydrogen, characterizing each of the structures that form on the surface during the reaction. First the reaction propagates on the surface as a wave front, removing half of the initial oxygen atoms. The remaining 0.5 monolayers of O atoms rearrange in pairs, forming a $c(2 \times 4)$ structure. Second, as the reaction proceeds, areas of an intermediate structure with $c(2 \times 2)$ symmetry appear and grow at the expense of the $c(2 \times 4)$ phase, involving all the oxygen atoms present on the surface. Afterward, the $c(2 \times 2)$ islands shrink, indicating that complete hydrogenation occurs at their edges, leaving behind a clean rhodium substrate. Two possible models for the $c(2 \times 2)$ structure, where not only the arrangement but also the chemical identity is different, are given. The first one is a mixed H + O structure, while the second one resembles the half-dissociated water layer already proposed on other metal surfaces. In both models, the high local oxygen coverage is achieved by the formation of a hexagonal network of hydrogen bonds.

1. Introduction

Hydrogen oxidation is one of the most widely studied catalytic reactions since the beginning of catalytic research with Berzelius.¹ Because of its apparent simplicity, this reaction is considered a model system for more complicated processes. Nevertheless, its mechanism on the atomic scale still offers new unknown details, as recently evidenced, for example, on platinum surfaces.^{2,3} The structure of water on metal surfaces itself is currently one of the most debated open questions in surface science, especially concerning a possible partial dissociation of the adsorbed water molecules.^{4–7}

Scanning tunneling microscopy (STM) experiments^{2,8,9} showed that on Pt(111), below the water desorption temperature ($T < 170$ K), the reaction proceeds via a wave front. A ring of an intermediate structure in hexagonal arrangement expands on the surface while maintaining its width. Outside the ring the surface

is still covered by oxygen in the initial (2×2) structure, while inside H₂O islands form. The major pathway to OH formation is not via H + O addition but by water reacting with oxygen in 2:1 stoichiometry, as proved by DFT calculations.³ Nevertheless, this disproportionation reaction is not completed but stops at a mixed OH + H₂O phase, the second water molecule acting only as a catalytic promoter in the dissociation of the first H₂O molecule. It is this mixed OH + H₂O layer that is observed as a reaction intermediate structure in STM, with all molecules in hexagonal arrangement and interconnected by a hydrogen bond network, as confirmed by several theoretical studies.^{3,10,11} The final hydrogenation of the OH + H₂O phase is proposed to proceed by proton transfer: OH groups at the leading edge of the ring are hydrogenated by H atoms, and protons are transferred to the internal edge where the pure water areas form.³ H₂O molecules are easily displaced by the tunneling tip and thus often are not resolved in STM images.²

On Rh(110), the situation is potentially more complicated, as it has been reported that on this surface oxygen induces a variety of reconstructions.¹²

Recently we investigated the water formation reaction on a reconstructed Rh(110) surface, starting from the $(10 \times 2)\text{-O}$ structure.¹³ This surface is characterized by a (1×2) missing row reconstruction and the presence of strain in the topmost

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metal layer, which leads to a nanoscale segmentation. We showed that the reaction proceeds in two distinct steps: in a first step, half of the adsorbed O atoms are removed by a reaction front; this leads to relaxation of the surface strain and to formation of new patches of clean Rh where molecular hydrogen can adsorb and dissociate. These patches act as special sites in the second reaction step, which starts homogeneously on the surface, reacting off all remaining oxygen. In both reaction steps our STM images did not show any evidence of the formation of an intermediate structure.

In this work, we present the results of an STM/density functional theory (DFT) study of the oxygen hydrogenation reaction on the unreconstructed Rh(110). Our approach has been: (i) to characterize by STM the *dynamics* of the overall reaction, which involves the formation of intermediate structures at least on part of the surface; (ii) to generate and study these intermediate structures *statically* (i.e., by preparing them in equilibrium conditions all over the surface), both from the experimental and the theoretical point of view. The starting surface is saturated by 1 monolayer (ML) of oxygen in a $(2 \times 1)p2mg$ structure. This structure is characterized by a *zig-zag* arrangement of O atoms in 3-fold sites along the close-packed $[1\bar{1}0]$ metal rows.¹² The surface is exposed to molecular hydrogen, and the water production reaction is monitored by acquiring series of STM images. We show that a reaction front propagates on the surface, converting the saturated structure to another one with a lower coverage, with a rearrangement of the remaining O atoms, as confirmed by DFT calculations and simulated STM images. At this point, steady-state islands of an intermediate structure form, attracting and capturing all existing O atoms, before being converted from their borders to water, which immediately desorbs. Two hypotheses on the nature of this structure are given.

2. Experimental Section

The rhodium crystal has been prepared by sputtering with Ar^+ ions (1 keV) and annealing to 1200 K. The annealing temperature was chosen to be high enough to dissolve subsurface argon bubbles, which are easily produced at lower temperatures. Then the surface has been further treated by cycles of oxidation and reduction at 770 K: for the first two cycles, 3 L of oxygen followed by 5.4 L of hydrogen were dosed, then the sample was exposed to 1 L of O_2 and 1.4 L of H_2 three times. In all previous studies, the $(2 \times 1)p2mg$ structure was prepared by simply dosing oxygen on the clean Rh(110) surface at temperatures $T \leq 300$ K.^{12,14–18} Nevertheless, we found that, on the atomic scale, adsorption at different temperatures within this range leads to slightly different surfaces. At $T \geq 270$ K, in fact, a well-ordered $(2 \times 1)p2mg\text{-O}$ coexists with a local reconstruction, where metal atoms jump above the topmost layer, leaving one-layer deep holes on the surface, and align in chains, elongated in the $[1\bar{1}0]$ direction. To avoid this reconstruction, O exposure has to be performed at lower temperatures. Even this procedure, though, does not give a perfect oxygen layer, as *chainlike* defects, 0.4–0.7 Å higher than the O structure, appear at domain boundaries. The best compromise turned out to be dosing 6 L

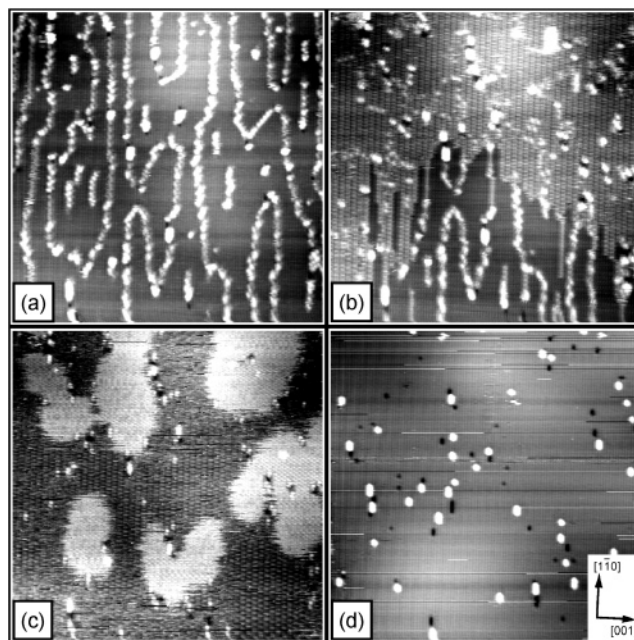


Figure 1. STM images of the water formation reaction on a $(2 \times 1)p2mg\text{-O/Rh(110)}$ surface reacting with H_2 at 260 K ($p_{\text{H}_2} = 5 \times 10^{-9}$ mbar): (a) initial surface; (b) a reaction front propagates over the surface, removing half of the initial O atoms, while the remaining oxygen rearranges in pairs; (c) brighter areas of an intermediate structure nucleating at defects; (d) final, clean surface. Small bright/dark features are ejected rhodium atoms/holes on the metal substrate, already present on the initial surface. Dimensions: 50×50 nm². Scanning parameters: $I = 1.58$ nA, $V_B = +0.14$ V. Time: (a–b) 665 s; (b–c) 175 s; (c–d) 805 s.

of oxygen at 200 K and subsequently annealing the surface to 260 K (see Figure 1a).

The measurements were performed with an Omicron VT-STM, with typical scanning parameters $V_B = 0.14$ V and $I = 1.5$ nA, while exposing the surface to molecular hydrogen with $p_{\text{H}_2} = 5 \times 10^{-9}$ mbar on the surface—corrected for the sensitivity of the pressure gauge and the screening factor of the tip of 5, as estimated in ref 19. The typical acquisition time is 35 s/frame. Several reaction temperatures were checked, and it turned out that 260 K is a good compromise between a reaction on a resolvable time scale and an acceptable induction period (of the order of some minutes).

Low-electron energy diffraction (LEED) measurements were performed in the 50–120 eV electron energy range with a beam current below $2 \mu\text{A}$.

3. DFT Simulations

The Rh(110) surface was mimicked by a five-layer film. The lateral symmetry of the system has been used to reduce the number of atoms per layer in a two-dimensional repeat unit to eight. The two outer layers of the film were fully relaxed in all three dimensions; the distance between repeat units of the supercell in the vertical direction was larger than 1 nm. The Vienna ab initio simulation program was used to determine the atomic positions of adsorbed oxygen and OH on the surface and the ground-state electronic structure.²⁰ To account for the limitation of pseudopotentials, we employed an all-electron scheme, the projector augmented wave method.²¹ On the technical side, we note that the energy cutoff was 400 eV and

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the number of k points varied until the change of their number did not affect the system energy. In total, we analyzed six configurations with 0.5 ML of atomic oxygen and seven configurations with a mixed oxygen and OH coverage following the simulation cycle described below. First the adsorbates were positioned a few angstroms above the surface and allowed to relax to their ground-state positions in an adsorbed configuration. From the electronic ground-state structure, we calculated the ensuing STM images with a tungsten tip contaminated in certain cases by Rh or oxygen. The STM image was then compared to experimental data in view of the distance between features and the absolute height of a structure in the images. To check for the influence of tip–adsorbate interactions we also performed simulations where the tip was mimicked by a tungsten cluster and positioned above the surface. These calculations showed that interactions are not relevant for the obtained adsorption energies and the STM topographs. Here, we present only the final results of this extensive analysis, while other configurations and their simulated STM images²² are omitted.

The adsorption energy per unit cell was calculated in the standard fashion:

(i) For the $c(2 \times 4)$, structure the adsorption energy is the difference between the total energy of the clean Rh(110) surface and two oxygen molecules in the gasphase, reduced by the total energy of four oxygen atoms adsorbed at the surface

$$\Delta E_{c(2 \times 4)} = E_{\text{Rh}(110)} + 2E_{\text{O}_2} - E_{c(2 \times 4)}$$

(ii) The adsorption energy for the two trial $c(2 \times 2)$ structures was determined in a similar way

$$\Delta E_{c(2 \times 2)} = E_{\text{Rh}(110)} + 4E_{\text{O}_2} + 6E_{\text{H}_2} - E_{c(2 \times 2)}$$

In all cases, the Rh(110) unit cell consisted of a five-layer film with eight atoms per layer.

4. Reaction Dynamics: STM Results

When the sample is exposed to molecular hydrogen, after an induction period of about 100–200 s, the reaction starts propagating on the surface as a wave front (Figure 1b). The presence of an ongoing reaction is evidenced by the formation of *paired features*, which gradually cover the whole surface in a $c(2 \times 4)$ structure. Figure 2a shows a zoom on these features, which are 0.3–0.4 Å high, with an internal distance of ~ 2.8 Å.

The reaction then continues with the formation of islands of an intermediate structure, which appear brighter in STM images (Figure 1c). A closer inspection reveals that the islands are made of an hexagonal arrangement of double-peak features, leading to a $c(2 \times 2)$ structure, as shown in Figure 3a,b. The internal distance between the peaks is on average ~ 2.8 Å, and a corrugation of 0.25–0.35 Å is measured between adjacent features in the [001] direction (see the line profile in Figure 3b). The units are 0.3 Å higher than *paired features* in the $c(2 \times 4)$.

The $c(2 \times 2)$ islands nucleate at surface defects, such as in proximity of ejected rhodium atoms and holes in the substrate, both resulting from the preparation of the initial structure, after completion of the $c(2 \times 4)$ structure and grow at its expense: the *paired features* of the $c(2 \times 4)$ structure get disordered in a rim around the $c(2 \times 2)$ islands. This disordered rim expands

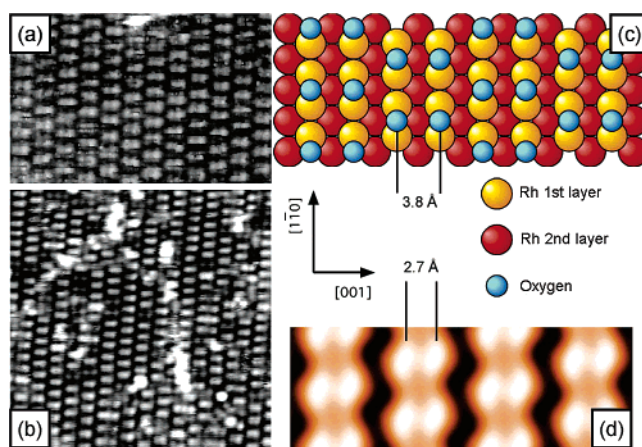


Figure 2. $c(2 \times 4)$ -O structure: (a) zoom on the surface behind the reaction front. Dimensions: 11.5×7.5 nm². Parameters: $I = 1$ nA, $V_B = +0.13$ V. (b) STM image of the structure obtained by dosing 0.6 L O₂ at 100 K and annealing to 270 K. Dimensions: 20×20 nm². Parameters: $I = 1$ nA, $V_B = +0.42$ V. (c) Structural model of the $c(2 \times 4)$ -O. (d) Simulated STM image ($V_B = +130$ eV, $I = 0.05$ nA).

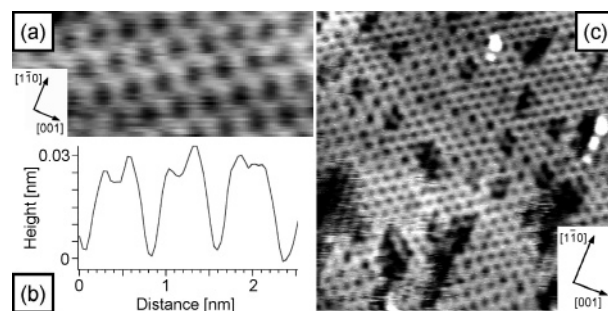


Figure 3. $c(2 \times 2)$ structure: (a) zoom on the reaction intermediate structure. Dimensions: 6.0×2.5 nm². Parameters: $I = 0.6$ nA, $V_B = +0.6$ V. (b) Line profile on the hexagonal structure along [001]. (c) STM image of the surface obtained by dosing water up to saturation at 170 K on 0.35 L O₂ adsorbed at 200 K and annealing the surface to 223 K. Dimensions: 15×15 nm². Parameters: $I = 1$ nA, $V_B = +0.12$ V.

in an anisotropic way, until all *paired features* disappear. Concomitantly, the $c(2 \times 2)$ islands grow and partly merge but never cover the whole surface. From our images on various length scales, we can deduce that they cover about half of the surface at the maximum extension.

Once the maximum extension is reached, the $c(2 \times 2)$ islands start to shrink again, restoring an oxygen-free substrate (Figure 1d).

5. Discussion

We begin the discussion with the first part of the reaction, which leads to the formation of the $c(2 \times 4)$ structure.

The nucleation and propagation mechanism can be traced back to the lack of free space on the initial surface for molecular hydrogen adsorption and dissociation, which is conversely possible at defects (nucleation) and on areas where the reaction has already started, leading to an autocatalytic process: when further O atoms are removed by the reaction front, new free adsorption sites are created, where further H₂ can adsorb and dissociate and the front propagates. A similar explanation for the autocatalytic role in the propagation of a reaction front has already been inferred for the water formation reaction on the reconstructed (10×2) -O/Rh(110) surface.¹³

Regarding the $c(2 \times 4)$ structure, the appearance of paired features on the Rh(110) surface strongly reminds the results of

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ref 23, where low-coverage oxygen atoms were found to arrange in pairs. The height and the internal distance are in good agreement with the present data, even though in that case a $c(2 \times 4)$ disposition was not observed but O pairs were ordered in a (2×3) or a $c(2 \times 6)$ pattern. To confirm that also the $c(2 \times 4)$ structure is a pure oxygen adsorption structure, we dosed 0.6 L of O_2 at 100 K on clean Rh(110) and annealed to 270 K, to see if it was possible to obtain a $c(2 \times 4)$ phase when using slightly higher doses and annealing temperature. The resulting surface indeed displays a clear $c(2 \times 4)$ LEED pattern and the STM images (see Figure 2b) doubtless show the same structure that forms during the water production reaction, thus giving a clear hint for the identification of *paired features* as couples of O atoms.

A model where oxygen atoms sit in short-bridge sites has been proposed for the O pairs in ref 23, despite the apparently shorter O–O distance in STM images, which has been attributed to an electronic rather than to a geometric effect.²⁴

Our DFT results support short-bridge as the actual adsorption site also for O atoms in the $c(2 \times 4)$ structure (Figure 2c). The adsorption energy per atom was found to be 2.6 eV. Simulated STM images (Figure 2d) show remarkable agreement with the STM data, as (i) oxygen atoms appear as protrusions when imaged with a clean W tip; (ii) the apparent O–O distance is ~ 2.8 Å; and (iii) the height of the O pairs is 0.25–0.40 Å. Regarding point (i), it is important to note that, even though oxygen atoms adsorbed on a metal surface usually appear as depressions when imaging with a tungsten tip, recent results for oxygen on Ru(0001) showed that different coverages, as well as the local geometry and the actual electronic structure of the system, can result in a reversed contrast.^{25,26}

The agreement between experiments and simulations strongly suggests that the $c(2 \times 4)$ superstructure is composed of only 0.5 ML of oxygen. This entails that when the reaction front propagates on the surface, removing O atoms from the $(2 \times 1)p2mg$ structure (1 ML), the remaining oxygen immediately rearranges in a lower coverage structure. This sequential reaction dynamics is therefore in remarkable similarity with the one recently found for water formation on (10×2) -O/Rh(110),¹³ with a wave front removing only half of the initial oxygen coverage. During this initial stage of the reaction, no intermediate product can be seen in our images, water forming and desorbing quickly from the surface.

On the less densely O covered $c(2 \times 4)$ surface, conversely, the reaction sequence proceeds slowly, through the formation of an intermediate structure with $c(2 \times 2)$ periodicity. To better characterize the $c(2 \times 2)$ phase, the same structure has been produced also by dosing water on a low-coverage oxygen pre-dosed Rh surface. This procedure generally facilitates partial water dissociation on late transition metals^{27–29} and has already been used to study a reaction intermediate for the water formation reaction on Pt(111).^{27,28} Figure 3c presents an STM

image of the structure obtained after dosing water up to saturation at 170 K on 0.35 L of O_2 , adsorbed on the clean Rh(110) substrate at 200 K, and annealing the surface to 223 K. It clearly displays an hexagonal arrangement due to double-peak features in a $c(2 \times 2)$ disposition, with ~ 2.8 Å internal distance and ~ 0.2 Å corrugation, very similar to the observed reaction intermediate structure.

Before attempting a detailed chemical description of the units forming the $c(2 \times 2)$ phase, we can assume that the bright protrusions in STM images are related to oxygen, either as single atoms or as part of a molecule (OH, H_2O). If we interpret each double-peak feature as composed of two distinct O-containing adsorbates, we can infer a 1 ML coverage for oxygen in the $c(2 \times 2)$. This conclusion, together with the observation that, as discussed in the previous section, $c(2 \times 2)$ islands cover a maximum area of about half of the surface, indicates that, before complete hydrogenation and desorption as water molecules, all the oxygen atoms present on the surface in the $c(2 \times 4)$ -O condense in the $c(2 \times 2)$ structure, implying a constant overall O coverage of 0.5 ML. There must be, therefore, a strong attractive interaction in the latter structure. O pairs can easily diffuse on clean rhodium patches, created as a consequence of the formation of the first $c(2 \times 2)$ nuclei. This statement is based on the observation that $c(2 \times 2)$ islands are surrounded by a region where diffusing species, whose height corresponds to oxygen in the $c(2 \times 4)$, are resolved; moreover, in these areas *paired features* can sometimes be imaged by STM at random positions. When diffusing O pairs get close to a $c(2 \times 2)$ island, they are “trapped” by the strong attractive interaction inside the structure.

From STM images where both the $c(2 \times 2)$ and the $c(2 \times 4)$ phases are present, we can determine the register of the bright $c(2 \times 2)$ protrusions, on the basis of the known position of the O pairs forming the $c(2 \times 4)$ structure, whose model is depicted in Figure 2c. According to this procedure, the oxygen atoms associated to the protrusions in the $c(2 \times 2)$ phase sit in alternate 3-fold sites.

We performed DFT calculations and STM image simulations of the $c(2 \times 2)$ structure for nine different setups, varying not only the chemical composition (OH and H_2O) but also the positions of oxygen atoms (see ref 22 for further details). For an equal number of O and H atoms, the most stable configurations involved a position of the hydrogen atoms between oxygen atoms, so that all atoms are roughly in one plane (the adsorption energy per OH in this case is about 3 eV). However, if a 1:1 stoichiometry is retained, then a full coverage means that areas exist on the surface, where oxygen atoms are next to each other without a bridging hydrogen atom. In this case oxygen–oxygen repulsion should have the effect that the coverage actually decreases: exactly the opposite of the trend observed in the experiments. High coverage can be obtained only if additional hydrogen atoms are bonded to oxygen at the regions of repulsion, but this implies that the layer does not contain oxygen and hydrogen in 1:1 stoichiometry, as in OH groups. In addition, all simulated STM images with “1:1” structural models are in stark disagreement with experimental images.

We therefore suggest a different stoichiometry. If a 3:2 ratio for hydrogen:oxygen atoms in the structure is considered, two minimum configurations are found. In the first configuration (see Figure 4), which we call $c(2 \times 2)A$, oxygen atoms sit in a zig-zag arrangement along close packed Rh rows. As the

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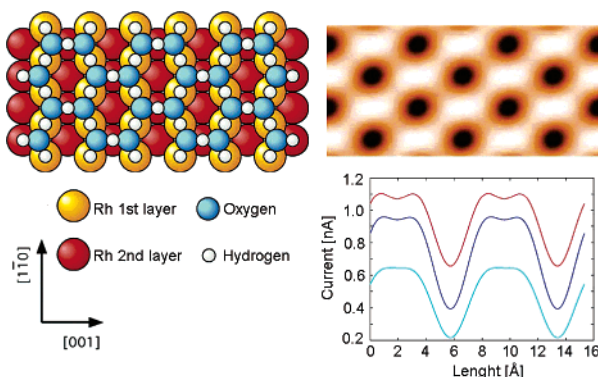


Figure 4. $c(2 \times 2)$ A structure. Left panel: structural model. Right top panel: corresponding simulated STM image ($V_B = +130$ eV, $I = 0.04$ nA). The protrusions correspond to oxygen couples while the depressions are the hollow sites surrounded by O–H complexes. Right bottom panel: simulated current profiles along [001] at decreasing (light blue to red) tip–surface distances.

number of hydrogen atoms attached to oxygen in different simulations is not constant (see text below), the extraction of adsorption energy values is not straightforward. We have therefore divided the total adsorption energy per unit cell by the number of oxygen atoms. In this case the adsorption energy is assigned to oxygen/hydrogen complexes, with a variable number of hydrogen atoms (one to two) per each oxygen atom. The adsorption energy per oxygen/hydrogen complex in this configuration is 2.0 eV. All the adsorption sites are equivalent, 0.578 Å left or right to the short bridge site. The zig-zag is in antiphase between adjacent $[1\bar{1}0]$ rows, thus leading to O–O pairs in the [001] direction with an internal distance of 2.77 Å. The distance between O atoms in the zig-zag is 2.94 Å. The resulting geometry for O atoms is therefore a pseudo-hexagonal arrangement. H atoms are placed exactly in the middle of two adjacent O atoms, sitting either above hollow sites or above on top sites of first-layer Rh atoms, 2.2 Å high from the surface, therefore interacting more with O atoms than with the metal substrate. The short distance between oxygen atoms (especially for [001] O–O pairs) suggests that the configuration is stabilized by an attractive force. According to the presence of H atoms between these O atoms, this force is attributed to hydrogen bonds. The H atom in the hydrogen bond would be located midway between neighboring oxygen atoms instead of being covalently bound closer to one of them. This kind of configuration arises in crystals when the O–O distance is decreased below 2.5 Å, e.g., for ice at high pressure: from the low-pressure molecular phases Ice VIII, where one covalent O–H bond and one $H\cdots O$ hydrogen bond form, first a proton disordered phase, called Ice VII, with protons tunneling along the hydrogen bonds, and then a symmetric nonmolecular Ice X phase are created.³⁰ The O–O distances in our $c(2 \times 2)$ structure are certainly longer, but the surface might play a stabilizing role. In fact it is known that the surface is able to strengthen intermolecular hydrogen bonds³¹ and change the bond length³² and therefore might play a role also in the HB symmetrization in the $c(2 \times 2)$ structure.

Simulated STM images of the $c(2 \times 2)$ A structure, reported in the right top panel of Figure 4, exhibit a hexagonal arrangement. It is important to note that the Bardeen approach we used in our calculations limits their validity to tunneling

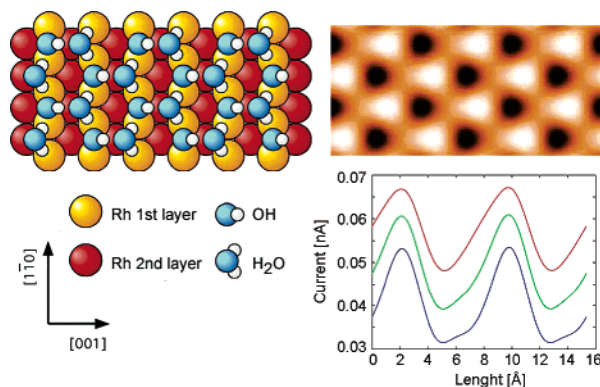


Figure 5. $c(2 \times 2)$ B structure. Left panel: structural model. Right top panel: corresponding simulated STM image ($V_B = +130$ eV, $I = 0.002$ nA). The protrusion maxima correspond to water molecules while the depressions correspond to Rh atoms. Right bottom panel: simulated current profiles along [001] at decreasing (blue to red) tip–surface distances.

currents lower than the experimental ones.^{25,26} To examine the situation at higher currents, we generated simulated current vs position line scans at constant height, for decreasing tip–surface distances (Figure 4 right bottom panel): when approaching the surface, the image maxima clearly show a double-peak structure.

The agreement between this model, with its respective STM image simulations, and the experimental images is very good, both involving an hexagonal arrangement of double-peak features with comparable internal distance (theory value 2.77 Å, experimental value ~ 2.8 Å) and similar corrugation (theory ~ 0.5 Å, experimental value 0.25–0.35 Å).

Another stable configuration with the same 3H:2O stoichiometry exists. This second model, presented in Figure 5 and called $c(2 \times 2)$ B, involves OH groups and water molecules and is very similar to the half-dissociated water layers found on other transition metal surfaces, e.g. Pt(111), where it forms also as an intermediate during the water formation reaction,³ and Ru-(0001),⁴ with the only difference, in this latter case, that no single hydrogen atoms are involved in the structure. Also in our case, in fact, an hexagonal arrangement of molecules interconnected by hydrogen bonds is considered, even though the layer is not flat as on the cited surfaces. O atoms belonging to OH groups sit close to the surface in roughly short-bridge sites with H above them pointing toward the closest H₂O molecule; on the contrary, water molecules are slightly farther from the surface, with O atoms almost above 3-fold sites and H pointing downward to adjacent OH groups. The adsorption energy per oxygen/hydrogen complex in this case is 3.5 eV.

Simulated STM images (Figure 5 right top panel) show the hexagonal arrangement, but it is not possible to reproduce the double-peak features in the line profile (Figure 5 right bottom panel). There is therefore poor agreement with experimental data, even though structure $c(2 \times 2)$ B turned out to be much more stable than $c(2 \times 2)$ A (1.5 eV per oxygen/hydrogen complex). However, we note also that the final step in the reaction, the reduction of the surface oxygen coverage by water desorption, is only exothermic for the $c(2 \times 2)$ A structure (here, the desorption of water leads to a gain of 1.4 eV per molecule), while it is endothermic for the $c(2 \times 2)$ B structure (under the same conditions desorption leads to a loss of 0.6 eV per water molecule).

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Hence, we are not able to definitely identify the $c(2 \times 2)$ structure that forms during the water formation reaction. The simulated STM images point in favor of model $c(2 \times 2)$ A, which DFT predicts to be less stable than $c(2 \times 2)$ B. Furthermore, we calculated the transition energy between the two models and found that there is no barrier. This indicates that the formation of the $c(2 \times 2)$ B phase is not kinetically hindered, i.e., the $c(2 \times 2)$ A should immediately convert to the $c(2 \times 2)$ B. Finally, we cannot find a reasonable explanation for the formation of the less stable structure when water is dosed on an O precovered layer. It is interesting to note that a similar situation, where the most stable structure is not the one experimentally observed, has recently been proposed for the water layer on Ru(0001).³³

The two proposed models for the $c(2 \times 2)$ structure differ mainly in the role of hydrogen atoms: in $c(2 \times 2)$ A, in fact, they do not belong to any specific oxygen but lay in the middle of adjacent O atoms, while in $c(2 \times 2)$ B they are close to specific O atoms to which they are covalently bound, being part of a molecule, either OH or H₂O. However, in both cases hydrogen bonding plays a crucial role. It is interesting to note that a hexagonal hydrogen bond network forms, similarly to the OH + H₂O layer on Pt(111) and Ru(0001), even though the Rh(110) substrate has a rectangular geometry. This observation indicates that the preference of hydrogen bonded systems to form hexagonal adsorption structures, proposed in the theoretical study in ref 28, holds regardless of the substrate geometry.

Further investigations are needed to definitively clarify the structure of the $c(2 \times 2)$ reaction intermediate. More complicated configurations, not considered in our calculations, will have to be tested, e.g., the possibility that the double peak is due to the system switching between two $c(2 \times 2)$ B symmetric configurations, triggered by the absence of a hydrogen atom.

Coming back to the overall reaction, we can now try to depict a complete picture of the second part of the reaction mechanism. The ordered $c(2 \times 4)$ -O surface appears to be unreactive at 260 K: we always see the second step of the reaction nucleating in the proximity of defects, where the first $c(2 \times 2)$ patches appear. This indicates that only close to a defect atomic hydrogen can interact with O atoms, trapping them into an hydrogen bond network. The condensation of oxygen atoms in the new structure creates free rhodium patches where O atoms can diffuse after detachment from the $c(2 \times 4)$ structure, giving rise to the disordered rim. When these diffusing O atoms get close to the borders of a $c(2 \times 2)$ nucleus, they get easily trapped by hydrogen bonds and the island therefore expands into the disordered rim. It is important to note that the presence of free patches between the $c(2 \times 4)$ and the $c(2 \times 2)$ phases is essential to the process, as only mobile oxygen atoms can be incorporated in the hydrogen bond network. Indeed in the STM images we see that at regions where the border between $c(2 \times 2)$ and $c(2 \times 4)$ areas is locally sharp, with negligible rim width, the $c(2 \times 2)$ island does not grow. As a consequence the growth of the $c(2 \times 2)$ islands proceeds asymmetrically on the surface, until all the oxygen originally present in the $c(2 \times 4)$ structure has been incorporated.

Only at this point further water molecules can leave the

surface: complete hydrogenation occurs at the island borders where water molecules desorb, leading to a decrease in the island dimensions. This behavior contrasts the one observed during the reaction on the Pt(111) surface, where water molecules form and condense inside the intermediate structure ring.^{2,8,9} The difference can be due to the fact that on platinum the reaction was carried out below the water desorption temperature. On rhodium, conversely, desorption takes place immediately at the outer border, without allowing proton transfer toward the inside of the hexagonal structure.

As the chosen reaction temperature is lower than the hydrogen desorption temperature,³⁴ H atoms are likely to be present on the final surface, even though they are not visible in the STM images.

6. Conclusions

We studied the water formation reaction on Rh(110) at 260 K, starting from the saturated (1 ML) oxygen layer. STM image series evidenced that upon exposure of the system to molecular hydrogen, after a short induction time a reaction front propagates across the surface, reacting off half of the oxygen atoms and leaving back a $c(2 \times 4)$ structure where the remaining oxygen (0.5 ML) is arranged in pairs.

When the surface is almost completely covered by the $c(2 \times 4)$ structure, areas of a new $c(2 \times 2)$ structure nucleate in proximity of surface defects. We were not able to clearly establish the chemical identity of this structure but on the basis of DFT calculations and STM image simulations two hypotheses are given: in the first model a H + O coadsorption structure is considered, while the second one resembles the half-dissociated water layer proposed on Ru(0001) and Pt(111). Both models involve a 1 ML O coverage and the formation of an hydrogen bond network.

$c(2 \times 2)$ islands grow at the expense of the $c(2 \times 4)$ structure, surrounded by disordered areas, where diffusion of O pairs from the $c(2 \times 4)$ toward the island borders occurs. Here O atoms interact with hydrogen. A peculiar feature of the microscopic reaction mechanism is that during the second stage of the reaction the local oxygen coverage increases, while the overall O coverage decreases or remains constant. The $c(2 \times 2)$ islands reach a maximum extension corresponding to about half of the surface (i.e., an overall coverage of ~ 0.5 ML on the surface), and afterward they contract, due to water desorption from the borders. Finally a clean (or partly hydrogen covered) rhodium surface is restored. A distinct feature of the observed reaction mechanism is that the intermediate $c(2 \times 4)$ structure is unreactive at the temperatures we used, and it needs to be converted into the reactive $c(2 \times 2)$ structure (with no O loss) before the reaction can progress with further water release. This transition requires the formation of a hydrogen-bonded network and the presence of free metal patches for the oxygen to become mobile.

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