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

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Traveling reaction fronts in the oxidation of hydrogen on a Pt(111) surface were investigated by means of scanning tunneling microscopy (STM). The fronts were observed during dosing of the oxygen covered surface with hydrogen at temperatures below 170 K. The fronts represented 10 to 100 nm wide OH-covered regions, separating unreacted O atoms from the reaction product H2 O. O atoms were transformed into H2 O by the motion of the OH zone. Small scale STM data showed the processes within the fronts on the atomic scale. Experiments on larger scale revealed the velocity and the width of the fronts as a function of temperature. A simple reaction–diffusion model has been constructed, which contains two reaction steps and the surface diffusion of water molecules, and qualitatively reproduces the experimental observations. A lower bound for the front velocity was also derived analytically. For a quantitative comparison between experiment and theory the rate constants of the two reaction steps and the diffusion coefficient of H2 O were determined by STM and low energy electron diffraction experiments. With these parameters, the front velocities predicted by the model are approximately one order of magnitude smaller than those determined by STM. The predicted front widths are, depending on the temperature, between two and three orders of magnitude larger than the experimental values. We conclude that these deviations result from the inability of the reaction–diffusion system to describe the complex chemical processes and structure changes within the fronts. The atomically resolved STM data indicate attractive interactions between the particles that in particular affect the diffusion of the H2 O molecules.


I. INTRODUCTION

In a recent letter1 we reported about STM investigations of propagating reaction fronts in the catalytic oxidation of hydrogen on a Pt(111) surface. The central point in Ref. 1 was that STM allowed to monitor both, the reaction fronts on a mesoscopic, 10 to 100 nm scale, and the chemical reactions between the adsorbed particles on the atomic scale. Reaction fronts belong to spatio-temporal patterns that can occur in nonequilibrium systems as a consequence of nonlinearities in the kinetics. Such phenomena have been studied particularly well in a number of catalytic reactions on single crystal surfaces2 that, under certain conditions, display mesoscopic dynamic patterns in the distribution of the adsorbed species.3 The patterns are traditionally modeled by reaction–diffusion (RD) equations,4,5 in which the individual particles are replaced by concentrations, i.e., by continuum variables. An analysis on the basis of an RD description was also performed for the present system that reproduced the qualitative behavior of the fronts, as is often the case with RD models. However, the front velocities and widths, predicted with RD kinetic parameters obtained in independent experiments deviated significantly from the experimentally measured values. We concluded1 a breakdown of the RD description, caused by the complex chemical processes and structure changes elicited from the atomic scale STM data that are not included in simple RD models. The present paper gives a complete account of this investigation.

The experiments were performed in an ultrahigh vacuum (UHV) chamber, in which a Pt(111) surface was first dosed with oxygen. Then H2 was introduced into the chamber. The hydrogen molecules dissociated on the surface, and the adsorbed H atoms reacted with the adsorbed O atoms to give water. OH was formed as reaction intermediate.6,7 Fronts were observed below the desorption temperature of H2 O (~170 K). The following reaction mechanism was proposed.6,7

\[ \text{OH} + \text{H} \rightarrow \text{H}_2\text{O}, \quad (\text{II}) \]

\[ 2 \text{H}_2\text{O} + \text{O} \rightarrow 3 \text{OH} + \text{H}. \quad (\text{III}) \]

(All species are absorbed on the surface.) This sequence is autocatalytic, because if two OH molecules enter step (II), forming two H2 O molecules, step (III) leads to the formation of three OH molecules. The mechanism was supported by several other observations: (i) The previously observed induction period in the formation of water at low temperatures8 is consistent with the autocatalytic acceleration contained in (II)/(III); (ii) step (III) has been known to be a fast reaction at low temperatures;9,10 (iii) by increasing the temperature to >170 K the reaction rate for the H2 O productions surprisingly decreased.6,7 However, the finding is a natural consequence of the desorption of H2 O (\( T_{\text{max}} = 170 \text{ K} \)) because

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H₂O is required to connect the two steps; (iv) preadsorption of H₂O, which takes part in the autocatalytic cycle reduced the induction period for the H₂O formation. ¹¹ (An autocatalytic reaction sequence has been discussed before, ¹²,¹³ but the prominent role of “active sites” in the proposed model is not consistent with our data.)

The autocatalytic process is either started by small amounts of OH, formed by the reaction

\[ \text{O} + \text{H} \underset{k_1}{\rightarrow} \text{OH} \]  

(I)

or by traces of H₂O adsorbing from the residual gas in the vacuum apparatus. Reaction (I) is slow at low temperatures and can be neglected compared to (II) and (III) after ignition of the autocatalytic reaction.

The unexpected 2:1 stoichiometry of H₂O and O in step (III) was first found by Creighton and White ¹⁴ in TPD (temperature programmed desorption) experiments and later confirmed by Bedürftig et al., also by TPD. ⁷ A 2:1 stoichiometry was also supported by the STM data. ⁷ To account for the observed second order rate law, ¹⁴ reaction (III) has to consist of two steps, the comproportionation of one H₂O and O to give OH, which is rate limiting, and the fast dissociation of the second H₂O molecule.

The reaction sequence is in general agreement with recent theoretical investigations by Michaelides and Hu. ¹⁵,¹⁶ Their density functional theory (DFT) calculations revealed low activation energies for steps (II) and (III), ¹⁶ explaining the low temperature at which the reaction occurs, and an activation energy of approximately 1 eV for step (I), confirming that it is slow at the low temperatures considered here. On the other hand, the authors found that reaction (III) is endothermic, because the H atom binds with a lower energy to the Pt surface than to an O atom. It was concluded that in reaction (III) only one of the two H₂O molecules reacts with O to give OH. The other H₂O molecule remains intact and becomes incorporated into the ordered OH surface phase that is formed by the reaction. Consequently, the (v3×v3)R30° structure observed by STM ⁷ would consist not of pure OH (coadsorbed with H), but of one OH and one H₂O per unit cell. ¹⁵ In addition to the (v3×v3)R30° structure smaller areas with a (1×1) structure were observed by STM that are interpreted as a pure OH phase. The alternative reaction according to Refs. 15 and 16 becomes

\[ 2 \text{H}_2\text{O} \rightarrow \text{O} + \text{OH} + \text{H}_2\text{O} \]  

(III*)

Denoting the product of (III*) as OH/H₂O/OH, the resulting alternative reaction mechanism of the hydrogen oxidation is formulated as follows:

\[ \text{OH}/\text{H}_2\text{O}/\text{OH} + 2 \text{H} \rightarrow 3 \text{H}_2\text{O}, \]  

(II*)

\[ \text{H}_2\text{O} + \text{O} \rightarrow 2 \text{OH}, \]  

(III*,a)

\[ 2 \text{OH} + \text{H}_2\text{O} \rightarrow \text{OH}/\text{H}_2\text{O}/\text{OH}. \]  

(III*,b)

Similarly as for the originally considered reaction (III), one would have to assume that (III*) consists of two steps. (III*,a), the formation of OH, would account for the observed second order rate law, ¹⁴ and (III*,b), the incorporation of the second H₂O molecule, would be a fast reaction. Michaelides and Hu found that a one-step reaction (III*), simultaneously involving both H₂O molecules, would be connected with an even lower activation energy. ¹⁶ However, because such a mechanism would represent a tri-molecular reaction, it will not be considered in the following.

One problem with the alternative mechanism is that the vibrational spectra, recorded after adsorption of H₂O on an O covered surface [reaction (III*)], ⁷ did not show the H₂O scissors mode, which seems to disagree with the presence of H₂O in the (v3×v3)R30° structure. Michaelides and Hu suggested ¹⁵ that the absence of this characteristic H₂O vibrational mode may be caused by the almost flat adsorption geometry of the H₂O molecule in the mixed phase. The results of the STM experiments do presently not provide a basis for deciding between the two structure models for the intermediate phase. Fortunately the RD models for both mechanisms proved to be identical, so that this problem does not affect the present analysis (Appendix C). As the original mechanism is notationally simpler, the following presentation will be based on the mechanism (II)–(III).

In the following, STM data are presented from which the front velocities and widths were obtained as functions of temperature. In further STM experiments and by means of low energy electron diffraction (LEED) measurements the rate constants \( k_2 \) and \( k_3 \) of steps (II) and (III) and the diffusion constant \( D \) of H₂O were determined. In the modeling section an RD system is formulated and is solved numerically. Finally, the experimentally determined front velocities and widths are compared with those predicted by the simulations.

II. EXPERIMENTS

A. Experimental conditions

The STM experiments were performed in a UHV chamber at base pressures \( \leq 1 \times 10^{-10} \) mbar. The STM could be operated at sample temperatures between \( \approx 60 \text{ K and } 300 \text{ K} \), which was achieved by simultaneous liquid He cooling and radiative heating by a filament. The Pt(111) crystal was prepared using standard UHV techniques as described previously. ¹⁷ The cleanness and structural perfection of the sample were checked with STM, LEED, and Auger electron spectroscopy. After preparation atomic terraces were several hundred angstroms wide, and residual contaminants were \( \approx 1\% \). Gases were dosed by refilling the chamber, exposures (pressure×time) are given in Langmuirs (L), with 1 L = 1.33×10⁻⁶ mbar s. The experiments on the reaction fronts were typically performed by first preparing a complete (2×2) structure of atomic oxygen. This was achieved by adsorption of 10 L O₂ at 90 K, followed by annealing at 250 K in order to dissociate the adsorbed O₂ molecules and to order the O atoms. The sample was then brought to the desired reaction temperature, scanning was started, and the chamber was filled with H₂ at pressures between 5 ×10⁻⁹ mbar and 1 ×10⁻⁷ mbar. Experimental conditions in the measurements of the kinetic parameters are described.
in Sec. II C. The LEED experiments were performed in a separate UHV chamber with another Pt(111) crystal, which was prepared similarly as the first one.

B. Reaction fronts

Figure 1 shows a series of large scale STM frames (2200 Å × 2200 Å), recorded during dosing of the O covered surface with hydrogen at 112 K. The circular, white structure is a reaction front consisting predominantly of OH that propagates across the surface. The area outside of the ring is covered by O atoms and small OH clusters (bright dots), the area behind the front is covered by H₂O (not resolved here), the thin, approximately vertical lines are monoatomic steps. Image size 2200 Å × 2200 Å, tunneling voltage = 0.8 V, tunneling current 0.17 nA. The front velocity was determined from panel (f), showing the positions of the front in successive images. The frames were recorded one after the other, at 62 s per frame. The error introduced by the finite recording speed of the STM (approximately one order of magnitude faster in the slow y-direction than the front velocity), was minimized by averaging the velocity over several directions. At higher temperatures the fronts become faster, and the error due to the finite recording speed becomes larger.

FIG. 1. Series of successive STM images, recorded during dosing of an O covered Pt(111) surface with hydrogen (p = 2 × 10⁻⁸ mbar, T = 112 K). The circular white structure is a reaction front consisting predominantly of OH that propagates across the surface. The area outside of the ring is covered by O atoms and small OH clusters (bright dots), the area behind the front is covered by H₂O (not resolved here), the thin, approximately vertical lines are monoatomic steps. Image size 2200 Å × 2200 Å, tunneling voltage = 0.8 V, tunneling current 0.17 nA. The front velocity was determined from panel (f), showing the positions of the front in successive images. The frames were recorded one after the other, at 62 s per frame. The error introduced by the finite recording speed of the STM (approximately one order of magnitude faster in the slow y-direction than the front velocity), was minimized by averaging the velocity over several directions. At higher temperatures the fronts become faster, and the error due to the finite recording speed becomes larger.

Adsorbed H₂O is mobile and readily shifted away by the tunneling tip and could often not be resolved. On the other hand, we did not detect major tip effects on the front propagation. One observation was that the propagation of the fronts did not depend on the scanning direction of the tip. Furthermore, experiments were performed in which hydrogen was dosed for some time in the absence of the tip. After the dosing was interrupted the STM was approached to the surface. Fronts were observed that were fixed (because hydrogen was no longer supplied) but were otherwise indistinguishable from those imaged during reaction conditions in the presence of the tip.

The thin lines in the images are atomic steps of the Pt(111) surface. The round feature in the lower half of the image is a one layer deep hole which apparently acted as nucleation center for the front. However, nucleation at defects was not generally observed. Moreover, in the later stages the front moved across the steps without significant interference which was similarly observed in other experiments. Surface defects do thus not appear to be essential for the progress of the reaction, in contrast to previous suggestions. Defects were therefore neglected in the model.

Figure 1(f) displays the positions of the front in successively recorded images. The first two frames were recorded without H₂ dosing, so that the front occurs at the same location. After introducing H₂, the front moved by approximately equal distances between successive frames, indicating a constant front velocity (average value in this experiment 15 ± 3 nm/min). The front profile (in a one-dimensional cross section) remained unchanged as the front traveled across the surface (width approximately 17 nm). Hence, the OH ring fulfills the two criteria that are characteristic for reaction fronts in autocatalytic RD systems: constancy of velocity and shape. The fact that the velocity does not depend on the
curvature indicates that the radius of the ring already exceeds some critical value.

Under other conditions the H₂O behind the fronts could be resolved (Fig. 2). Like in the experiment of Fig. 1 the area is initially mainly O covered, again with small OH clusters (small bright dots). The front, which moves to the center of the area, is still clearly visible, but not as distinctly marked as in Fig. 1. In this case, H₂O islands forming behind the front are seen as large bright patches. The H₂O islands are much larger than the OH clusters. At larger distances behind the front the islands dissolve again, indicating that there still was some tip effect on the water molecules, though less strong than in the case of Fig. 1.

Front velocities and widths could be measured between 108 and 134 K. The data (Figs. 3 and 4) show that both, velocity and width, increase with temperature. At higher temperatures the fronts became too fast to be resolved by our STM technique. The diagrams also include experiments with D₂, but possible isotope effects remained smaller than the experimental error limits.

The atomic processes in the fronts could be resolved in small scale STM data [Fig. 5 (Ref. 6)]. At the temperature in this experiment (131 K) the front is by one order of magnitude wider than the 170 Å frames, so that the series shows the processes at one location of the surface, but no concentration gradients. The hexagonal pattern of dark dots in the first two frames is the (2×2)O structure (Fig. 6).
The front arrives \( \approx 600 \) s after starting the \( \text{H}_2 \) dosing (first frame), indicated by the first formation of the bright \( \text{OH} \) islands. After \( 1250 \) s the islands have coalesced, the ordered structures correspond to the \((\sqrt{3} \times \sqrt{3})\text{R}30^\circ\text{OH}\) and \((3 \times 3)\text{OH}\) phases (Fig. 7). Because of the similarity of the two \( \text{OH} \) structures and their identical \( \text{OH} \) coverages, we will not discriminate between them in the kinetic model. As already mentioned, an alternative model has been proposed for the \((\sqrt{3} \times \sqrt{3})\text{R}30^\circ\) structure, in which one of the two \( \text{OH} \) molecules in the unit cell is replaced by \( \text{H}_2\text{O} \). The very bright, frizzy stripes occurring at \( \approx 1300 \) s are caused by \( \text{H}_2\text{O} \) (Fig. 8).

Two additional observations from Fig. 5 are important for the kinetic model. The first, \( \text{H}_2\text{O} \) is the only mobile oxygen containing species under these experimental conditions. The strong fluctuations of the bright \( \text{H}_2\text{O} \) stripes and the large water islands seen in Fig. 2 indicate the high mobility of water. Oxygen atoms only become mobile at temperatures higher than 200 K. The \( \text{OH} \) islands do not show fluctuations, indicating that \( \text{OH} \) is immobile.

The second, the first two frames in Fig. 5 show that, as the first \( \text{OH} \) islands nucleate and start to grow, they are not surrounded by areas depleted from oxygen. If \( \text{OH} \) would be formed by direct reaction of \( \text{O} \) with \( \text{H} \) [reaction (1)], the number of oxygen containing species would locally remain constant. In this case, the formation of \( \text{OH} \) islands would necessarily be connected with the formation of bare surface areas in order to compensate for the increasing oxygen density from \( 1/4 \) for the \((2 \times 2)\text{O} \) phase to \( 2/3 \) for the \((\sqrt{3} \times \sqrt{3})\text{R}30^\circ \) phase (Figs. 6 and 7). However, the \( \text{OH} \) islands almost exactly fill the areas initially covered by \( \text{O} \), corresponding to a local density increase by a factor of \( 8/3 \). Furthermore, the initially formed \( \text{OH} \) islands display some flat parts which can be interpreted as areas with the \((1 \times 1)\text{OH}\)
The local density increase is thus even higher and amounts approximately a factor of 3. This observation provides further evidence that OH is indeed produced by reaction (III) [or (III*)] and not by reaction (I). With the stoichiometry of step (III) [or (III*)], the local coverage of oxygen containing species can increase from 1/4 to 3/4, if the H₂O molecules come from an external source. This is exactly what is achieved by the suggested mechanism: Behind the front water builds up. However, the H₂O molecules are mobile and can diffuse from behind the front into the O covered area ahead of the front. The same argument explains why at \( \approx 1250 \) s (Fig. 5), the OH layer almost covers the complete area originally covered by O, despite the immobility of the OH. Coupling of H₂O diffusion with reaction (III) can thus explain the local density increase by a factor of 3. The atomic structure changes in the front are thus in agreement with the three processes underlying the suggested mechanism, diffusion of H₂O molecules into the O covered area, reaction of H₂O with O to give OH, and reaction of OH with H to give H₂O.

Figure 9 shows the OH covered area from Fig. 5. At the maximum, the OH phase covers 85% of the area, equivalent to a local OH coverage of \( \Theta = 0.57 \). The value is lower than \( \Theta = 3/4 \), because the average initial O coverage was somewhat lower than 1/4. Note that, because the front propagates with constant speed and shape, Fig. 9 also reflects the spatial OH concentration profile of the front.

C. Kinetic parameters

The two reaction steps (II) and (III) forming the autocatalytic cycle in the hydrogen oxidation can also be investigated separately, allowing to measure their reaction constants \( k_2 \) and \( k_3 \). To determine \( k_2 \) an OH layer was prepared by exposure of the O covered Pt surface to H₂O, which reacts to give OH by reaction (III). This is a known procedure to prepare adsorbed OH. Excess water was desorbed by flash annealing to 180 K. As hydrogen did not adsorb on completely OH covered surfaces, the preparation was started with O coverages <1/4, leading to incomplete OH layers.
The STM showed islands of \((\sqrt{3} \times \sqrt{3})R30^\circ/(3 \times 3)OH\) phases and an otherwise empty surface. Then a constant hydrogen pressure was adjusted, and the formation of H\(_2\)O by reaction (II) was monitored as a function of time. The STM showed that the OH islands transformed into the incommensurate H\(_2\)O structure, details of which will be presented elsewhere. The kinetics was formulated as a second order rate law, ignoring that OH and H\(_2\)O form islands. Assuming that the hydrogen adsorption on the empty Pt between the islands was sufficiently fast and not rate limiting, the H coverage can be treated as a constant (for simplicity, we set [H] = 1) and the kinetics of (II) simplifies to a pseudo-first-order rate law. On these assumptions, we obtained the pseudo-first-order rate constants \(k_2 = 4.3 \times 10^{-4}\) ML\(^{-1}\) s\(^{-1}\) and \(5.5 \times 10^{-3}\) ML\(^{-1}\) s\(^{-1}\) for 133 K and 149 K, respectively. Whereas these individual values seem to be realistic, the corresponding Arrhenius parameters \(E_2 = 0.27\) eV and \(\nu_2 = 8.7 \times 10^6\) ML\(^{-1}\) s\(^{-1}\) are only crude estimates. However, the fact that the DFT calculations\(^{16}\) revealed a similar value for \(E_2 (0.2\) eV) indicates that an activation energy of this size is not unreasonable.

For reaction (III), Creighton and White\(^{10}\) found a second order rate law by using secondary ion mass spectroscopy (SIMS). This suggests that (III) consists of two steps

\[
\begin{align*}
H_2O + O & \rightarrow 2 OH, \\
H_2O & \rightarrow OH + H,
\end{align*}
\]

in which the first step determines the rate, and the second step is fast. The second step is not easily rationalized, as H\(_2\)O alone does not dissociate on Pt. Somehow dissociation must be induced by the OH already present. According to the alternative reaction mechanism (III\(^*\)) the second step would be an incorporation of the H\(_2\)O molecule into the OH structure, rather than a dissociation, but would also have to be fast to account for the second order rate law.

The Arrhenius parameters obtained by Creighton and White were \(E_3 = 0.44 \pm 0.03\) eV and \(\nu_3 = 6.9 \times 10^{-1} \pm 1.4\) cm\(^2\) molecules\(^{-1}\) s\(^{-1}\), which equals \(1.0 \times 10^{15} \pm 1.4\) ML\(^{-1}\) s\(^{-1}\) if we define 1 ML as a coverage of 1 particle per Pt atom. Time-resolved STM experiments to determine \(k_3\) were not possible, because shielding effects prevented the adsorption of water under the tip.

A set of kinetic measurements with LEED were performed instead. First, the \((2 \times 2)O\) structure was prepared (\(\Theta_0 = 1/4\)) and a constant temperature was adjusted by liquid N\(_2\) cooling and simultaneous counter-heating. H\(_2\)O was then adsorbed in a sharp pressure peak to obtain a well-defined starting point of the reaction. In order to nevertheless control the amount of water exposed and to start the experiment with a stoichiometric quantity of water, a separate volume in the gas dosing system was filled with H\(_2\)O vapor, and then rapidly expanded into the chamber by opening a valve. The pressure in the volume (measured by a Pirani gauge) was calibrated such that the \((2 \times 2)\) spots at the end of the reaction just completely disappeared, corresponding to a stoichiometric reaction. In order not to disturb the adsorption process, the LEED electron beam was turned on only 5 to 10 seconds after the exposure, and the spot intensities were recorded as a function of time by means of a video camera. Figure 10 (data for \(T = 137\) K) shows that the \((2 \times 2)\) spots disappear, and that at the end only \((\sqrt{3} \times \sqrt{3})R30^\circ\) spots of the OH phase remain. \(k_3\) was obtained by fitting the decay of the \((2 \times 2)\) spot intensities that are proportional to the \((2 \times 2)O\) coverage to a second order rate law (for the derivation see Appendix A):

\[
I_{(2 \times 2)}(t) \propto \frac{[O]_0}{1 + 2k_3 [O]_0 t}.
\]

It was found, however, that part of the reaction was caused by the LEED electron beam. At 105 K, which is below the low temperature limit of the reaction (\(\approx 110\) K), the LEED pattern still showed some reaction. The effect was taken into account by measuring the rate constant between 105 and 111 K where the reaction was assumed to be exclusively induced by the LEED electrons, and subtracting the averaged rate constants from the values at the higher temperatures. The Arrhenius plot of the resulting \(k_3\) data between 115 and 155 K (Fig. 11) revealed an activation energy \(E_3 = 0.20 \pm 0.09\) eV and a pre-exponential factor \(\nu_3 = 6.0 \times 10^6 \pm 2.4\) ML\(^{-1}\) s\(^{-1}\). The deviations from the Arrhenius parameters obtained by Creighton and White are appreciable, which might be due to the small temperature ranges in both studies. Like for \(k_2\) the obtained Arrhenius parameters should only be regarded as crude estimates. The absolute \(k_3\) values are in relatively good agreement with the data of Creighton and White, e.g., at 133 K they only deviate by a factor of 8, at 144 K by a factor of 2. The activation energy for the rate limiting step (III\(^*\),a) from the DFT calculations\(^{16}\) is \(= 0.3\) eV,\(^{48}\) which is in the same range as the experimental data.

The surface diffusion coefficient of H\(_2\)O is the third constant entering the RD model. For H\(_2\)O molecules on a bare Pt surface the diffusion barrier is low, 0.13 eV according to calculations,\(^{16}\) which accounts for the high mobility of water.
at low temperatures, which has also been observed in previous experiments. However, the H$_2$O molecules also have to travel through, or across, the densely OH covered region as they move towards the front from the water covered area. This process is presumably connected with H transfer via H$_2$O + OH → OH + H$_2$O between H$_2$O molecules attached to OH islands or formed within them. Like the diffusion on the area behind the front this is also a fast process.

By contrast, the diffusion of H$_2$O molecules into the O covered area ahead of the front is relatively slow. This process is necessary for the propagation of the front. That it actually occurred was revealed by atomic scale data (Fig. 5), showing a local density increase in the O covered area. Because H$_2$O forms hydrogen bonds to adsorbed O atoms, this process must be associated with a larger activation energy. This diffusion process was accessible to STM experiments. After dosing small quantities of H$_2$O on the (2×2)O covered surface in the absence of the tip, islands with the typical (ν3×ν3)R30° structure of OH could be detected afterwards (0.27 L H$_2$O, Fig. 12). The formation of islands means that the water molecules do not directly upon adsorption react with the O atoms, but that they can diffuse on the O covered surface until colliding with other H$_2$O molecules or existing OH clusters. They are then immobilized by hydrogen bonds and react to give OH. The density of the OH islands therefore contains information about the diffusion length of the water molecules on the oxygen covered surface. If we assume that the islands on defect-free terraces were formed by homogeneous nucleation with a critical nucleus of one H$_2$O molecule, an expression derived for the density of islands in epitaxial growth can be applied,

$$N^3 = \frac{3R\Theta}{D}. \quad (4)$$

$N$ denotes the island density, $R$ the H$_2$O adsorption rate, and $\Theta$ the total dose of H$_2$O. From a 720 Å×720 Å image with 254 islands a diffusion constant $D = 8.0 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$ was thus obtained. With the usual pre-exponential factor for surface diffusion ($D_0 = 10^{-3} \text{ cm}^2 \text{s}^{-1}$), this value corresponds to a diffusion barrier of $E_D = 0.21 \text{ eV}$. Because the diffusion of water on the oxygen covered area limits the overall mobility of water, these parameters were used in the simulations of the RD model.

III. MODELING

A. Reaction–diffusion model

Based on the experimental findings, the following RD system was derived for the hydrogen oxidation reaction consisting of steps (II) and (III):

$$\frac{\partial}{\partial t} [\text{O}] = -k_3[\text{H}_2\text{O}][\text{O}], \quad (5)$$

$$\frac{\partial}{\partial t} [\text{H}_2\text{O}] = -2k_3[\text{H}_2\text{O}][\text{O}] + k_2[\text{OH}][\text{H}] + D \Delta [\text{H}_2\text{O}], \quad (6)$$

$$\frac{\partial}{\partial t} [\text{OH}] = 3k_3[\text{H}_2\text{O}][\text{O}] - k_2[\text{OH}][\text{H}]. \quad (7)$$

Reaction terms according to reaction (I) were neglected, because this process is slow at the low temperatures considered here. The terms $k_3 [\text{H}_2\text{O}][\text{O}]$ occurring in all three equations take the finding by Creighton and White into account that reaction (III) follows a second order rate law. The terms $k_2 [\text{OH}][\text{H}]$ in Eqs. (6) and (7) are due to reaction (II). They could be simplified by the fact that, because of the adsorption rate and the high mobility of the adsorbed hydrogen atoms, the H coverage could be assumed to be spatially constant and independent of time. We set

$$[\text{H}] = 1. \quad (8)$$

Deviations from a coverage of unity could be considered negligible compared to the much larger uncertainty of $k_2$ (only terms with products $k_2 [\text{H}]$ occur). For the same reason...
we did not have to include an equation for $[H]$ as a fourth variable. Equations (5) and (7) do not contain diffusion terms, because O and OH were found to be immobile on the experimental time scale. Only the diffusion of adsorbed $H_2O$ molecules was included in Eq. (6).

For convenience, new variables were defined for the concentrations

$$b := [O],$$

$$u := [H_2O],$$

$$v := [OH].$$

With $t$ in units of the characteristic time $\tau$ and the spatial variables in units of the characteristic length $L_D$, with

$$\tau = 1/k_3,$$

$$L_D = \sqrt{D/k_3},$$

and with the ratio of reaction constants $\kappa$,

$$\kappa = \frac{k_2}{k_3},$$

the RD system was transformed into dimensionless form

$$\frac{\partial b}{\partial t} = -uv,$$  \hspace{1cm} (15)

$$\frac{\partial u}{\partial t} = -2uv + \kappa v + \Delta u,$$  \hspace{1cm} (16)

$$\frac{\partial v}{\partial t} = 3uv - \kappa v.$$  \hspace{1cm} (17)

**B. Numerical simulations**

The system of partial differential equations (15)–(17) was numerically integrated in one and two dimensions. The two-dimensional simulations (Fig. 13) were performed with a grid of $512 \times 512$ points $(i,j)$, with $i,j=1, \ldots, 512$. The 512 points in one direction represent the system size $L_S$. In the simulations, $L_S$ was a parameter and is given in units of the characteristic length $L_D$ (13). Because the reaction scheme consisting only of steps (II) and (III) requires some OH or $H_2O$ for ignition, an initial $H_2O$ nucleus was defined. In the physical system the presence of $H_2O$ traces on the surface is very likely and can result from adsorption from the residual gas, or from the slow reaction (I) followed by (II). The starting configuration was thus

$$b(i,j) = \begin{cases} 0 & \text{for } (i-i_0)^2+(j-j_0)^2 \leq R^2, \\ b_0 & \text{otherwise}, \end{cases}$$

$$u(i,j) = \begin{cases} u_0 & \text{for } (i-i_0)^2+(j-j_0)^2 < R^2, \\ 0 & \text{otherwise}, \end{cases}$$

$$v(i,j) = 0.$$  \hspace{1cm} (18)

$b_0$ and $u_0$ are the coverages of the perfect O and $H_2O$ phases, i.e., $b_0 = 1/4$, $u_0 = 2/3$, and $R$ is the radius (in units of $L_D$) of the initial $H_2O$ nucleus centered at $(i_0, j_0)$. In the beginning, the surface is completely covered with O except for the $H_2O$ nucleus, the $H_2O$ coverage is maximal in the nucleus and zero elsewhere, the OH coverage is zero on the entire surface.

The evolution of this initial configuration is shown in Fig. 13, displaying one-dimensional cross sections through $(i_0, j_0)$ along the x axis. $H_2O$ starts to diffuse into the oxygen covered area, where it reacts with O to produce OH. The $H_2O$ concentration in the nucleus decreases, and an OH peak develops at the O/$H_2O$ interface (second frame). In the following, $H_2O$ permanently diffuses from the inner area into the oxygen covered area and reacts to give OH [step (III)], thereby causing the interface between O and OH to move outward. Subsequently, OH reacts with H to give $H_2O$ [step (II)], by which the OH coverage decreases and water builds up, causing the OH/$H_2O$ interface to follow the motion of the O/OH interface. As a result, a circular front spreads out that consists mainly of OH. The simulations thus demonstrate that the RD system indeed describes reaction fronts.

Figure 14 shows concentration profiles for different values of $\kappa$. The profiles are from one-dimensional simulations with a grid of 1024 points $(i=1, \ldots, 1024)$, from time instants at which the fronts had already developed a constant shape. For small values of $\kappa$ the OH concentration in the front is large, becoming smaller with increasing $\kappa$. This trend can be understood from the fact that for small values of $\kappa$ the OH producing step (III) is fast compared to the OH consuming step (II), so that the OH coverage in the front is large.

Figure 15 shows how the OH concentration at the maximum varies with $\kappa$. Experimentally, the OH coverage in the
not occur. It was eliminated by the transformation and is contained in the rescaled spatial coordinates. Hence, the only effect of a variation of $D$ is a rescaling of the $x$ axis, whereas the shape of the front profiles (Fig. 14) remains unaffected. As the physical length $x_{\text{phys}}$ is obtained from the dimensionless spatial coordinate $x_{\text{num}}$ used in the simulations by

$$x_{\text{phys}} = x_{\text{num}} \sqrt{\frac{D}{k_3}},$$

the width of the front at constant $k_3$ is proportional to $\sqrt{D}$. A large mobility of water results in broad fronts.

Figure 15 also shows the front width as a function of $k$. The width was measured between the two points at which the OH concentration in the front was 10% of the maximum value. Up to $\kappa = 0.1$, the width decreases with increasing $\kappa$, which is caused by the decreasing OH concentration in the reaction front (Fig. 14). The increase of the interface width for larger values of $\kappa$ results from changes in the water concentration profile with $\kappa$.

C. Analytic derivation of a lower bound for the front velocity

The system of RD equations (15)–(17) has planar wave front solutions, with fronts traveling at constant speed. For such solutions the dynamics can be reduced to the evolution in the coordinate system that moves with the wave velocity. Note that a front propagation of a stable, stationary state (here the water covered surface) into an unstable one (here the oxygen covered surface) also occurs in the Fisher model. Assuming sufficiently localized initial conditions Kolmogorov et al. derived for this model the front velocity selected by the system from a linear analysis around the unstable uniform stationary state. Later, this concept was generalized in the leading edge approach. The main idea is that the motion of the front is governed by its leading edge, i.e., the evolution equations can be linearized around the unstable state. In this way a lower bound to a continuous spectrum of velocities is obtained. For some specific systems it could be shown that this minimum front velocity is indeed the only velocity that is also absolutely stable (see, e.g., Ref. 25). In general, however, the front velocity that is actually selected must be determined by numerical simulation.

In order to describe steady front solutions of Eqs. (15)–(17) the new coordinate

$$\xi = x - ct$$

is introduced where $c$ is the constant velocity of the front (dimensionless, measured in units of $L_D / \tau = \sqrt{D k_3}$). By this transformation into the comoving coordinate system, the partial differential equations (15)–(17) become reduced to a set of ordinary differential equations

$$-c b' = -u b,$$

$$-c u' = \kappa u - 2 u b + u'',$$

$$-c v' = -\kappa v + 3 u b,$$

where the primes denote derivatives with respect to the new variable $\xi$. 

FIG. 14. Concentration profiles from one-dimensional simulations of the RD system (15)–(17), for different values of $\kappa = k_2 / k_3$. The diagrams are from late stages when the fronts have developed a constant shape; $L_s = 200$, other parameters as in Fig. 13.

FIG. 15. Front width, in units of $L_D = \sqrt{D k_3}$, and maximum OH concentration in the front as functions of $\kappa$, from numerical integration of the one-dimensional RD system (15)–(17).
The systems of Eqs. (15)–(17) and (23)–(25) have two uniform stationary states,

\[
\begin{bmatrix}
    b \\
    u \\
    v
\end{bmatrix} = \begin{bmatrix}
    0 \\
    b_0 \\
    0
\end{bmatrix},
\]

which corresponds to the \(\text{H}_2\text{O}\) covered surface, and

\[
\begin{bmatrix}
    b_0 \\
    0 \\
    0
\end{bmatrix},
\]

which corresponds to the \(\text{O}\) covered surface. The initial (and final) coverage of oxygen containing species is \(b_0\). The stationary state \(\tilde{X}_1\) is stable with respect to uniform perturbations, \(\tilde{X}_2\) is unstable. Note that a steady front solution traveling with a constant velocity \(c\) from Eqs. (15)–(17) corresponds to a heteroclinic orbit between the stationary states \(\tilde{X}_1\) and \(\tilde{X}_2\) in Eqs. (23)–(25).

In the leading edge approach the system of Eqs. (23)–(25) was linearized around the unstable uniform stationary state \(\tilde{X}_2\), and an equation for a lower bound of the front velocity \(c\) was derived. For details see Appendix B.

Figure 16 shows the resulting lower bound for the front velocity as a function of \(\kappa = k_2/k_3\) (solid curve), together with results from one-dimensional numerical integration of Eqs. (15)–(17) (circles). It was found that for sufficiently large values of \(\kappa\) the two curves agree within numerical errors. For \(\kappa<0.1\) the analytically obtained front velocities become more than 10% smaller than the numerical values. Such systems with fronts propagating into an unstable state that display larger than the minimal front velocity have been reported previously (e.g., Ref. 29).

IV. COMPARISON BETWEEN THEORY AND EXPERIMENT

For comparison with the experiment, the dimensionless front velocities and widths obtained from the numerical integration of the model (15)–(17) were transformed into measurable quantities. The measurable front velocity is given by

\[
c_{\text{phys}} = c_{\text{num}}(\kappa) \sqrt{D k_3},
\]

where \(c_{\text{num}}(\kappa)\) is the dimensionless velocity.

The temperature dependence is obtained by substituting Arrhenius relations for \(D\), \(k_2\), and \(k_3\) into Eq. (28):

\[
c_{\text{phys}}(T) = c_{\text{num}}(\kappa(T)) \sqrt{D_0 v_3 \exp \left[ \frac{-(E_D + E_3)}{k_B T} \right]},
\]

where

\[
\kappa(T) = \frac{v_2}{v_3} \exp \left[ \frac{-(E_2 - E_3)}{k_B T} \right].
\]

With the experimentally determined Arrhenius parameters (Sec. II C), the RD model can thus be used to make predictions about the front velocity and its temperature dependence (line in Fig. 3). We emphasize that this model curve does not contain any free fit parameters. Furthermore, the experimental points and the model curve are from completely independent data sets. Figure 3 shows that the model nicely reproduces the experimental trend, even if no quantitative agreement is achieved.

The physical front width, \(l_{\text{phys}}\), is obtained by multiplying the dimensionless front width \(l_{\text{num}}(\kappa)\) by the spatial unit \(L_D\) [Eq. (13)]. The temperature dependence again follows by assuming Arrhenius behavior of the parameters

\[
l_{\text{phys}}(T) = l_{\text{num}}(\kappa(T)) \sqrt{D_0 \frac{v_3}{v_1} \exp \left[ \frac{-(E_D - E_3)}{k_B T} \right]},
\]

The result is shown in Fig. 4. The model predicts front widths that exceed the experimental values by three orders of magnitude at 108 K and by two orders of magnitude at 134 K. The variation with temperature is different; in the experiments the fronts become wider with increasing temperature, in the model a weak decrease is predicted.

How significant are these deviations, and how can they be understood? One obvious explanation for the deviations is that the Arrhenius parameters entering the simulations have large errors. On the other hand, it was pointed out that the rates themselves are relatively reliable, and, as the kinetic constants were determined in the same temperature range in which the front velocities and widths were measured, inaccurate Arrhenius parameters were not expected to lead to large extrapolation errors. We have tried to improve the agreement by modifying the Arrhenius parameters within limits that appeared reasonable for the individual quantities. For example, perfect agreement for the front velocity was obtained by either increasing \(v_2\) by two orders of magnitude (to \(8.7 \times 10^8 \text{ ML}^{-1} \text{s}^{-1}\)) or by lowering \(E_2\) from 0.27 eV to 0.22 eV, which clearly is within the range of experimental errors. In both cases the agreement for the front width improved only moderately. The deviation at low temperatures was still two orders of magnitude and one order of magnitude at the high temperature limit. At the same time, the OH peak height was rendered incorrect. From the experimental peak height \(\kappa\) should be lower than \(10^{-2}\) (at 131 K) whereas with the altered \(v_2\) or \(E_2\) \(\kappa\) becomes about 0.3. With a lower
$E_D$ (0.15 eV) than the experimental value of 0.21 eV the agreement for the front velocity improved, too, but it worsened for the front width. Better agreement for the front width was obtained by increasing $E_D$ to 0.27 eV, which led to deviations below one order of magnitude over the whole temperature range, but the front velocity then decreased even further, to values two orders of magnitude below the experimental values. With the Arrhenius parameters of Creighton and White\textsuperscript{10} the agreement for both quantities was worse than in Figs. 3 and 4. To summarize, we have not been able to find a set of Arrhenius parameters that led to a satisfactory simultaneous agreement between the data from the RD model and both experimental data sets. In most cases an improved fit to either the front velocity or the width even caused greater deviations for the other quantity. It appears that errors in the reaction or diffusion constants are insufficient to explain the deviations.

Another possible reason for the lack of quantitative agreement is that the RD description applied here is inadequate for describing the atomic processes in the fronts. The STM data indeed show effects that are not consistent with an RD model that implicitly assumes a random occupation of adsorption sites and a coverage independent diffusion constant of H$_2$O. H$_2$O forms islands (Fig. 2), caused by the strong attractive interactions with other H$_2$O molecules through hydrogen bonds (Fig. 8), and hydrogen bonds are also effective in the OH structure (Ref. 7 and Fig. 7). In particular, the diffusion of H$_2$O will be affected by attractive interactions with OH or other H$_2$O molecules. Even without these interactions, or assuming they were summarily covered by the diffusion coefficient, the surface transport of H$_2$O remains complex. As already pointed out, due to hydrogen bonds, the mobility of H$_2$O molecules on the O covered areas is expected to be much lower than on the empty surface. With the measured value $E_D = 0.21$ eV for the oxygen covered surface and the DFT value of 0.13 eV for the bare Pt,\textsuperscript{16} the ratio of the respective diffusion constants is between $3 \times 10^{-7}$ and $5 \times 10^{-6}$ in the temperature range $T = 108$ K to 134 K. Hence, as H$_2$O molecules travel from behind the front into the oxygen covered region, they are considerably slowed down. Previous studies of front propagations into unstable states\textsuperscript{30–32} have shown that a state dependent diffusion coefficient can alter the front propagation mode. A transition from pulled to pushed fronts can be induced,\textsuperscript{32} with considerable consequences for the speed and the shape of the front.

Moreover, in a more realistic model the mentioned H$_2$O transport process via H$_2$O$+$OH$-$OH$+$H$_2$O should be taken into account. This fast transport process is expected to be important in the interface region, where the local coverage of OH molecules is high (close to 3/4), leading to almost complete site blocking. Finally, it is expected that, because of the small length scales investigated here, fluctuations become important.\textsuperscript{51}

These deviations from the assumptions underlying simple RD models like the one applied here may be accounted for by constructing a mesoscopic model\textsuperscript{55} by coarse graining the microscopic master equations.\textsuperscript{33,36} Such a mesoscopic model would describe the dynamics of continuous coverages, taking into account internal fluctuations in a system of stochastic partial differential equations. Similar models have been constructed previously to explore mechanisms for the formation of nanoscale patterns in reacting systems with strong attractive lateral interactions between the adsorbates.\textsuperscript{53–36} A mesoscopic model for the present reaction has been developed recently, and a detailed analysis is in preparation. As expected, the inclusion of strong attractive lateral interactions causes water to form clusters behind the front, and the transport processes are modified, thus affecting the interface velocity and the width. It should be mentioned, however, that, in a strict sense, such a mesoscopic approach can only provide a qualitative description, because the hydrogen bonds that influence the diffusion of H$_2$O molecules extend only to nearest neighbors. In the mesoscopic model it is assumed that the lateral interactions extend over a sufficiently large number of neighbors.\textsuperscript{33} Furthermore, many particle correlations (necessary for capturing the crystalline structure of the adsorbate layer) are not included in the mesoscopic approach. A complete quantitative description can only be achieved by kinetic Monte Carlo simulations, which, however, have so far been limited by the problem of the very disparate length scales.\textsuperscript{53} Hybrid models combining local MC simulations with large scale mean-field models\textsuperscript{33,34} or the use of finite elements with locally coarse grained dynamics\textsuperscript{45} may solve this problem.

V. SUMMARY

We have investigated traveling reaction fronts that occur during the catalytic oxidation of hydrogen on a Pt(111) surface by means of scanning tunneling microscopy. The STM data revealed both, the atomic processes in the interior of the fronts, and the width and velocity of the fronts on mesoscopic length scales. The investigations could be performed over a temperature range from 108 K to 134 K. The data were compared with simulations based on a simple RD model. The model contains two reaction steps, the reaction of hydrogen atoms with adsorbed OH to give H$_2$O [reaction (II)] and the comproportionation of H$_2$O with oxygen atoms to give OH [reaction (III)], and the surface diffusion of H$_2$O. The model has solutions with traveling fronts, which consist of OH regions separating unreacted oxygen from the reaction product H$_2$O, in full qualitative agreement with the experimental observations. The profile, width, and velocity of the front depends on the rate constants of the two reaction steps and on the diffusion coefficient of H$_2$O. It was also possible to derive a lower bound for the front velocity analytically.

For a quantitative comparison between the experiment and the RD model the rate constants $k_2$ and $k_3$ of the two reaction steps and the diffusion coefficient $D$ of water were determined in additional experiments. The first step, the reaction of H atoms with adsorbed OH to give H$_2$O, was investigated by dosing preadsorbed OH layers with hydrogen and monitoring the formation of H$_2$O with the STM. The second step, the comproportionation of H$_2$O and O to give OH, was investigated by LEED, by recording the disappearance of the $(2 \times 2)$ structure after dosing H$_2$O on the oxygen covered surface. For both rate constants approximate Arrhenius parameters were determined by measurements over temperature ranges of 16 K and 40 K, respectively. The
diffusion constant of the adsorbed H$_2$O on the O covered surface was determined by an analysis of STM images of OH islands formed by dosing water on the (2×2)O phase.

With the values for $k_3$, $k_4$, and $D$, the model allowed to make quantitative predictions of the front velocity and width that did not contain any free fitting parameters. It was found that the front velocity from the model showed the same temperature dependence as the experimentally determined velocity, but that the absolute values were about one order of magnitude lower. The front width predicted by the model was between two and three orders of magnitude larger than the experimental width, depending on the temperature. By varying the Arrhenius parameters of $k_3$, $k_4$, and $D$, which have large experimental errors, good agreement could be achieved for either the front velocity or the width, but it was not possible to achieve simultaneous agreement with the experiment for both quantities.

We concluded that the RD model, though providing a good qualitative description, is inadequate to quantitatively describe the experimental results. The RD model implicitly assumes random occupation of adsorption sites and a coverage independent and thus spatially invariant diffusion constant of water molecules. The atomic scale observations revealed strong deviations from these assumptions. Several physical processes were discussed that should be taken into account in a more realistic model. These include fluctuations, and, as suggested by the formation of OH and H$_2$O islands, strong attractive adsorbate–adsorbate interactions caused by hydrogen bonds between the adsorbed molecules. It was concluded that, in particular, the surface motion of adsorbed H$_2$O molecules is affected. H$_2$O surface diffusion must strongly depend on location, resulting from the different diffusion constants on the oxygen covered areas ahead of the front and on the empty areas behind it, and from interactions with the OH and H$_2$O islands. It was suggested to include such processes in a mesoscopic model or in Monte Carlo simulations.

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APPENDIX A: ANALYSIS OF THE LEED EXPERIMENTS

If reaction (III) consists of two steps

\[ \mathrm{H}_2\mathrm{O}+\mathrm{O}\rightarrow 2\text{OH} \]

\[ \mathrm{H}_2\mathrm{O}\rightarrow \text{OH}+\text{H} \]  

where the first step determines the rate, then the time derivative of the oxygen coverage is given by

\[ \frac{d\left[\text{O}\right]}{dt} = -k_3\left[\text{H}_2\text{O}\right]\left[\text{O}\right] \]  

For stoichiometric starting conditions, [H$_2$O]$_0$ = 2 [O]$_0$, the H$_2$O coverage remains at two times the O coverage during the entire reaction, [H$_2$O] = 2 [O]. Equation (A3) then becomes

\[ \frac{d\left[\text{O}\right]}{dt} = -2k_3\left[\text{O}\right]^2 \]  

having the solution

\[ \left[\text{O}\right](t) = \frac{\left[\text{O}\right]_0}{1+2k_3\left[\text{O}\right]_0t} \]  

APPENDIX B: LEADING EDGE APPROACH AND MARGINAL FRONT VELOCITY

A lower bound for the front velocity is given by the marginal velocity, i.e., all fronts moving more slowly are convectively unstable. The marginal velocity is calculated by the leading edge approach.\textsuperscript{27,28} For this purpose the system of evolution equations (15)–(17) is linearized around the unstable uniform stationary state $\bar{X}_2$ to capture the dynamics in the leading edge of the front. Sufficiently localized initial conditions [Eqs. (18)–(20)] are assumed\textsuperscript{27} in the following. Inserting the ansatz

\[ \tilde{X} = \bar{X}_2 + \delta \tilde{X} \times \exp(\omega t - kx) \]  

into Eqs. (15)–(17) and linearizing yields

\[ \omega(k) \delta \tilde{X} = \mathcal{J}(\bar{X}_2,k) \delta \tilde{X}. \]  

The Jacobian $\mathcal{J}(\bar{X}_2,k)$ at the unstable stationary state is given by

\[ \mathcal{J}(\bar{X}_2,k) = \begin{pmatrix} 0 & -b_0 & 0 \\ -b_0 & -2b_0+k^2 & \kappa \\ 0 & 3b_0 & -\kappa \end{pmatrix}. \]  

The characteristic polynomial for the Jacobian (B3) at $\bar{X}_2$ is

\[ \rho(\omega,c) = \omega \left( \omega^2 + (\kappa + 2b_0-k^2)\omega - \kappa(b_0+k^2) \right). \]  

According to the leading edge approach,\textsuperscript{27,28} the marginal velocity $c_{\text{min}}$ is determined by the general conditions

\[ c_{\text{min}} = \frac{\Re \omega(k_0)}{\Re k_0}, \]  

\[ c_{\text{min}} = -\frac{\left. \frac{d\omega}{dk} \right|_{k_0}}{\left. \frac{d\omega}{dk} \right|_{k_0}}. \]  

In the present case, the coverages cannot oscillate around the uniform stationary state $\bar{X}_2$ in the leading edge, because $u$ and $v$ would assume unphysical negative values.
Therefore, the wave number \( k \) and hence also the growth rate \( \omega(k) \) have to be real. The conditions (B6)–(B8) reduce to

\[
c_{\text{min}} = \frac{\omega(k_0)}{k_0}, \quad (B9)
\]

\[
c_{\text{min}} = \frac{d\omega}{dk}(k_0). \quad (B10)
\]

The marginal velocity \( c_{\text{min}} \) and the critical wave number \( k_0 \) are uniquely determined by these two conditions. From condition (B9) the critical wave number becomes

\[
k_0 = \frac{c_{\text{min}}}{3} \left( (1 - \bar{\kappa}) + \sqrt{(1 - \bar{\kappa})^2 + 3(\bar{\kappa} + 2 \bar{b}_0)} \right), \quad (B11)
\]

where

\[
\bar{\kappa} = \frac{\kappa}{c_{\text{min}}^2}, \quad (B12)
\]

\[
\bar{b}_0 = \frac{b_0}{c_{\text{min}}}, \quad (B13)
\]

The minimum velocity of stable traveling wave fronts is obtained by inserting (B11) into (B10). Because \( k_0/c_{\text{min}} \) is completely determined by the reduced parameters \( \bar{\kappa} \) and \( \bar{b}_0 \), (B10) can be expressed in terms of these two parameters. With the new parameter combination \( \theta = \bar{\kappa} + 2 \bar{b}_0 \), (B10) reduces to the cubic equation

\[
0 = 12 \theta^3 + \left( 3 + 21 \bar{\kappa} - \frac{177}{4} \bar{\kappa}^2 \right) \theta^2 + \left( -6 \bar{\kappa}^4 + \frac{171}{2} \bar{\kappa}^3 \right. \\
\left. - 45 \bar{\kappa}^2 + 6 \bar{\kappa} \right) \theta - \frac{81}{4} \bar{\kappa}^4 - 6 \bar{\kappa}^2 (1 - \bar{\kappa})^3. \quad (B14)
\]

Denoting with \( \theta_0(\bar{\kappa}) \) a solution of this cubic equation, the minimum velocity of the front can be obtained from the universal equation

\[
2 \bar{b}_0 = \theta_0(\bar{\kappa}) - \bar{\kappa}. \quad (B15)
\]

For given \( b_0 \) and \( \kappa \), the dimensionless minimum velocity is given by \( c_{\text{min}} = \sqrt{\kappa / \bar{\kappa} b_0} \), where \( \bar{\kappa} \) is the unique positive real solution of the cubic polynomial

\[
P_3(\bar{\kappa}) = 6(1 - \beta) \bar{\kappa}^3 + \left( -\frac{177}{4} \beta^2 + \frac{171}{2} \beta - \frac{153}{2} \right) \bar{\kappa}^2 \\
+ (12 \beta^3 + 21 \beta^2 - 45 \beta + 18) \bar{\kappa} - 6 + 3 \beta^2 + 6 \beta
\]

(B16)

with \( \beta = 1 + 2 b_0 / \kappa \). The solid curve shown in Fig. 16 has been obtained from a numerical calculation of \( \bar{\kappa} \) as a root of the polynomial (B16). Note that this solution only represents a lower bound for the front velocity. All steady fronts that are slower are convectively unstable. However, in general, there is a continuum of solutions that are faster than the marginal front. This fact is reflected by Fig. 16. For small \( \kappa \) values, the velocity obtained in the numerical simulations is larger than the prediction from the linear analysis performed here.

APPENDIX C: REACTION–DIFFUSION MODEL FOR THE ALTERNATIVE REACTION SCHEME

The reaction–diffusion (RD) model for the alternative mechanism (II*)–(III*) is formulated in analogy to the model (5)–(7) for the mechanism (II)–(III*). With \( [H] = 1 \) and the notations \( b = [O] \), \( u = [H_2O] \), \( w = [OH] \), \( m = [OH/H_2O/OH] \) the kinetic equations become

\[
\frac{\partial b}{\partial t} = -k_3^* u b, \quad (C1)
\]

\[
\frac{\partial u}{\partial t} = -k_3^* u b + 3 k_5^* m - k_3^* u w^2 + D \Delta u, \quad (C2)
\]

\[
\frac{\partial w}{\partial t} = 2 k_3^* u b - 2 k_3^* u w^2, \quad (C3)
\]

\[
\frac{\partial m}{\partial t} = k_3^* u w^2 - k_2^* m. \quad (C4)
\]

To account for the second order law for (III*), reaction (III*,b) has to be much faster than the other reactions, so that the system can be reduced to three species by adiabatic elimination of \( w \),

\[
\frac{\partial w}{\partial t} = 0. \quad (C5)
\]

(III*,b) in Eqs. (C1)–(C4) is treated as a third order reaction. Microscopically, this step is probably the bond formation between one OH and one H_2O molecule and therefore more adequately treated as a second order reaction. This leads to the evolution equations

\[
\frac{\partial b}{\partial t} = -k_3^* u b, \quad (C6)
\]

\[
\frac{\partial u}{\partial t} = -k_3^* u b + 3 k_5^* m - k_3^* u w^2 + D \Delta u, \quad (C7)
\]

\[
\frac{\partial w}{\partial t} = 2 k_3^* u b - 2 k_3^* u w^2, \quad (C8)
\]

\[
\frac{\partial m}{\partial t} = k_3^* u w^2 - k_2^* m. \quad (C9)
\]

However, adiabatic elimination of \( w \) leads to the same set of equations as for (C1)–(C4). After the same transformation into dimensionless form as in Sec. III A, Eqs. (C1)–(C4) and (C6)–(C9) reduce to

\[
\frac{\partial b}{\partial t} = -u b, \quad (C10)
\]

\[
\frac{\partial u}{\partial t} = -2 u b + 3 k_5 m + D \Delta u, \quad (C11)
\]

\[
\frac{\partial m}{\partial t} = u b - k_2 m. \quad (C12)
\]

Setting \( m = v/3 \) the system of equations (C10)–(C12) becomes identical to (15)–(17). That means, as for the kinetics, the intermediate \( m = [OH/H_2O/OH] \) plays the same role as three OH molecules in the original mechanism. In other
words, kinetically, the H$_2$O molecule in the intermediate phase acts like an OH molecule. The entire analysis of the RD system (15)–(17) is thus identical for the alternative mechanism.

46 The additional small bright dots on this area have disappeared behind the front and are therefore attributed to a species that participates in the reaction. Probably they are small OH clusters, indicating also some reaction outside of the fronts.
47 We have considered an alternative mechanism that could lead to reaction fronts. In the course of the reaction from O to H$_2$O a homogeneous distribution of oxygen atoms is eventually transformed into an island structure of H$_2$O molecules, caused by the high H$_2$O density in the islands. Consequently, the reaction is connected with the formation of empty areas, formed between the H$_2$O islands. If one assumes that H$_2$ only adsorbs on the empty Pt surface, one can conceive a nucleation and growth process for the reaction that would be connected with a frontlike behavior of the OH/H$_2$O boundary. After nucleation, hydrogen would adsorb on the empty areas developing between the initially formed H$_2$O islands. The nucleus would then grow by reaction of the adsorbed H atoms with oxygen at the boundary to the O covered region. Hydrogen would be permanently replaced on the growing inner region by adsorption from the gas phase. Like with the autocatalytic mechanism OH would only occur at the OH/H$_2$O interface. However, we rule out such a mechanism for the following reasons: (i) Molecular beam investigations (Ref. 37) have shown that the initial sticking coefficient of (thermal) H$_2$ is even slightly higher on the O covered surface than on the empty surface. As the $(2 \times 2)$O structure is an open structure with empty space between the oxygen atoms, this result is reasonable. (ii) By TPD experiments we found that the $(2 \times 2)$O structure can accommodate hydrogen atoms. Complete $(2 \times 2)$O layers were saturated at H$_2$ at 100 K, but no reaction occurred at this temperature, as indicated by the inset $(2 \times 2)$ LEED pattern. Upon annealing without further H$_2$ dosing, desorption of H$_2$O was detected, so that, at 100 K, a layer of H atoms must have existed on the $(2 \times 2)$ phase that reacted to give H$_2$O during the heating ramp. The coverage was approximately 1/4 of a saturated H layer on the bare Pt, demonstrating that H can occupy empty sites between the O atoms. (iii) The mobility of adsorbed hydrogen is expected to be high even at low temperatures [see the rationale for Eq. (8)], so that no concentration gradients of hydrogen are formed and the availability of H is not rate limiting. (iv) Such a mechanism is based on the assumption of a reaction between hydrogen and oxygen at the OH/H$_2$O interface. However, direct reaction of O with H atoms to give OH would represent reaction (I) which we have ruled out above for the low temperatures considered here.
48 The value of 0.3 eV is for the reaction of the first H$_2$O molecule with O. Michaelides and Hu found that when both water molecules simultaneously reacted an even lower energy resulted, but such a process would represent a tri-molecular step.
49 For the diffusion barrier of hydrogen atoms on Pt(111) one experimental work (Ref. 38) reported relatively large values, between 0.5 and 0.3 eV, which, however, were compensated by very large pre-exponential factors ($D_0=3 \times 10^5$ to 0.5 cm$^2$ s$^{-1}$). A more recent investigation found parameters closer to expectation, $E_D=68 \pm 5$ meV and $D_0=1.1 \pm 0.5 \times 10^{-3}$ cm$^2$ s$^{-1}$ (Ref. 39). Calculated values for $E_D$ are $>0.2$ eV (Ref. 40). At low temperatures hydrogen may possibly also diffuse by tunneling.
50 A counter example where a velocity larger than the minimum one was selected has been studied by Saul and Showalter (Ref. 29).
51 See, e.g., Refs. 41 and 42 for effects of fluctuations on the propagation of RD fronts.
52 A more complex reaction mechanism, e.g., one that distinguishes the OH molecules in the $(1 \times 1)$OH structure from those in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ OH structure, can also be readily incorporated into a mesoscopic model.
53 The interaction radius corresponds to a single lattice site (<1 nm), whereas the diffusion length for isolated water molecules on the empty Pt surface probably lies in the micrometer range.