Dual-Path Mechanism for Catalytic Oxidation of Hydrogen on Platinum Surfaces

S. Völkening, K. Bedürftig, K. Jacobi, J. Wintterlin,* and G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany

(Received 9 November 1998)

The catalytic formation of water from adsorbed hydrogen and oxygen atoms on Pt(111) was studied with scanning tunneling microscopy and high resolution electron energy loss spectroscopy. The known complexity of this reaction is explained by the strongly temperature dependent lifetime of the product H_2O molecules on the surface. Below the desorption temperature water reacts with unreacted O adatoms to OH_{ad}, leading to an autocatalytic process; at higher temperatures sequential addition of H adatoms to O_{ad} with normal kinetics takes place.

PACS numbers: 82.65.Jv, 61.16.Ch, 68.10.Jy

In July 1823, Döbereiner informed his minister, J. W. Goethe, about his observation that platinum caused hydrogen to react with oxygen to give water at room temperature "by mere contact." This report [1], together with similar observations in other laboratories, prompted Berzelius to introduce the term "catalysis" in order to classify this mysterious class of chemical phenomena [2]. In view of its fundamental importance this reaction has been the subject of numerous investigations, but despite its seeming simplicity its mechanism has remained obscure. On a Pt(111) single crystal surface the reaction was found to take place even at 120 K [3], although below the desorption temperature T_{des} of H_2O at about 170 K [4] water production will be terminated after the H_2O concentration reaches full coverage. H_2 and O_2 are known to chemisorb dissociatively, and hence a mechanism comprising sequential addition of adsorbed hydrogen to oxygen atoms is suggested:

$$O_{ad} + H_{ad} \rightarrow OH_{ad}\,, \tag{1}$$

$$OH_{ad} + H_{ad} \rightarrow H_2O_{ad} \qquad (\rightarrow H_2O_{gas})\,. \tag{2}$$

The experimental data indicate, however, that such a simple mechanism is incorrect. It was found, for example, that the activation energy is much higher above 300 K (0.52 to 0.69 eV [5,6]) than for $T < 170$ K ($\sim$0.13 eV [7]), and that an induction period exists at low temperatures [7] which is absent at higher temperatures [8]. Several modifications and extensions of the simple reaction scheme (1) and (2) have since been proposed [7–14]. They are, however, largely based on indirect (i.e., kinetic) evidence. Additional uncertainty was caused by controversial reports about the spectroscopic identification of OH_{ad} as reaction intermediate [3,10,11]. We report here on a study in which direct microscopic information was obtained by the combination of scanning tunneling microscopy (STM) and high resolution electron energy loss spectroscopy (HREELS). A reaction mechanism will be presented that includes an autocatalytic effect of the reaction product, which leads to a change of the mechanism at the desorption temperature of H_2O.

The STM and HREELS experiments were performed in two separate ultrahigh vacuum systems, both of which routinely achieve base pressures of $<1 \times 10^{-10}$ mbar. The variable temperature STM and the preparation procedure of the Pt(111) sample were described before [15]. The HREEL spectrometer was of the latest Ibach design (Delta 0.5, Vacuum Science Instruments); the resolution was below 2 meV. The experiments started from a surface completely covered with the (2×2) phase of atomic oxygen which was prepared by exposure of the sample to 10 L ($1\ \mathrm{L} = 1.33 \times 10^{-6}$ mbar sec) of O_2 at 90 K and annealing at 225 K for 30 sec.

Previous reports about possible reaction intermediates are conflicting [3,9–11]; their nature is, of course, crucial for establishing the reaction mechanism. According to Ref. [16] OH_{ad} can be prepared by exposing the (2×2)O structure to H_2O below T_{des},

$$O_{ad} + H_2O_{ad} \rightarrow 2OH_{ad}\,. \tag{3}$$

An HREEL spectrum resulting from such a procedure is shown in Fig. 1(*a*). It exhibits mainly the vibrational modes of adsorbed OH [16,17], i.e., reaction (3) leads to a pure OH_{ad} layer, in agreement with Ref. [16]. The corresponding STM images showed mixtures of a $(\sqrt{3} \times \sqrt{3})R30°$ and a (3×3) structure, both of which are clearly different from the known H_2O_{ad} structures [18] and the (2×2)O configuration. The formation of OH_{ad} according to step (3) takes place at temperatures as low as 110 K, consistent with previous findings [19].

If the O_{ad} layer was exposed to hydrogen instead of water the resulting spectrum [Fig. 1(*b*)] was dominated by H_2O and Pt-O modes. Small quantities of OH_{ad} are also present as follows from the two OH_{ad} bending modes; their different intensity ratio compared to Fig. 1(*a*) is attributed to the poorer order at the lower temperature. Hence, O_{ad}, H_2O_{ad}, and OH_{ad} are the only surface species present during the water formation reaction, and the additional intermediates suggested in previous work [9,10] are not observed. (H_{ad} is not detected in these spectra because of its low excitation cross section.) The spectra obtained here are essentially in agreement with the data of Ref. [11], and the differences between the results and Ref. [10] can be traced back to the order of the adlayer.

0031-9007/99/83(13)/2672(4)$15.00

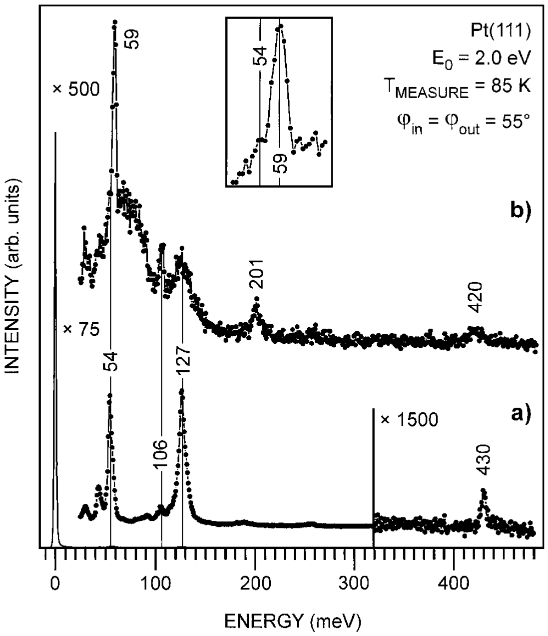

FIG. 1. HREEL spectra from Pt(111), recorded after (*a*) annealing a coadsorbed layer of the (2 × 2)O structure and 1 L of H_2O at 170 K for 60 sec, and (*b*) exposure of 9 L of H_2 on the (2 × 2)O structure at 133 K and quenching to 85 K. (*a*) exhibits the vibrational modes of OH_{ad}: the internal stretch mode (430 meV), the bending modes (127 and 106 meV), and the Pt-OH stretch mode (54 meV). (*b*) shows the main H_2O_{ad} modes (internal stretch at 420 meV, scissors at 201 meV, libration at around 80 meV), the Pt-O stretch of O_{ad} (59 meV), and modes of OH_{ad}. Inset: Detail from spectrum (*b*). E_0 of the primary electrons and sensitivity factors as indicated; the incidence and exit angles φ_{in} and φ_{out} are referenced to the surface normal.

The low intensities of the OH_{ad}-derived features in Fig. 1(*b*) indicate that this intermediate is only a minority species during the reaction which might suggest that reaction (2) is considerably faster than step (1). However, the series of STM images recorded during the reaction (Fig. 2) demonstrates that under identical conditions OH_{ad} is by no means a short-lived surface species. In this experiment a (2 × 2)O layer [hexagonal pattern in Figs. 2(a) and 2(b), with O_{ad} appearing as dark dots [15]] was exposed to a constant H_2 flow. After 625 sec small bright islands had formed between the oxygen atoms [Fig. 2(a)] which grew continuously while the number of O_{ad} atoms decreased simultaneously [Fig. 2(b)]. (Because of their high mobility adsorbed H atoms were not resolved.) After 1175 sec [Fig. 2(c)] these bright islands developed a hexagonal pattern corresponding to a $(\sqrt{3} \times \sqrt{3})R30°$ structure which later partially rearranged into the honeycomb pattern that is characteristic for the (3 × 3) phase [center of Fig. 2(d)]. These two phases are identical to those observed after the $O_{ad} + H_2O_{ad}$ reaction and are hence attributed to OH_{ad}. Further exposure to hydrogen led to additional white patches inside the islands [Fig. 2(e)] which in separate OH/H_2O coadsorption experiments were identified with adsorbed H_2O. Finally the whole surface became converted into a water layer (not shown here). OH_{ad} was thus identified as reaction intermediate by both HREELS and STM, but the STM data suggest that the O_{ad} layer is first completely converted into OH_{ad}, before water is formed.

How can this contradiction between the conclusions reached from the two methods be resolved? The answer is provided by STM images recorded on a larger scale. Figure 3 shows a 1650 Å × 1420 Å image taken during the reaction at 134 K. The area with the small bright dots at the right of the image represents the largely unreacted O_{ad} phase with small OH_{ad} islands [cf. Fig. 2(a)]. The large patches at the left arise from an H_2O_{ad} island (top) and mixed H_2O_{ad}/OH_{ad} islands (bottom), similar to those in Fig. 2(e). The speckled region in between represents a zone with a high density of OH_{ad} islands [cf. Figs. 2(b)–2(d)]. On this large scale the three species O_{ad}, OH_{ad}, and H_2O_{ad} are seen to exist at the same time, but in separate areas.

Time resolved experiments on this larger scale demonstrate that the reaction proceeds by propagation of the OH_{ad} zone into the oxygen covered area. This was easier to follow at somewhat lower temperatures, where the OH_{ad} zone is narrower and propagates more slowly. In Fig. 4 (111 K) the OH_{ad} zone appears as a ring of bright dots, which grows from one terrace (a) to the two neighboring terraces (b). The area around the ring is largely O_{ad} covered with small OH_{ad} islands (bright dots); the interior area is covered with H_2O_{ad}, which was not resolved in this case. (H_2O_{ad} was often shifted away with the tunneling tip and was not always detected.) Obviously, the OH_{ad} zone represents a reaction front, the motion of which transforms the O_{ad} areas into H_2O_{ad} covered regions. Since the size of the images of Fig. 2 (taken at 133 K) is smaller than the width of the reaction front at that temperature (Fig. 3), these snapshots erroneously suggest a uniform transformation of the adlayer. However, the OH_{ad} concentration becomes high only directly within the reaction front, whereas it is low if averaged over macroscopic areas. This explains the difference between the small scale STM images and the HREEL spectra.

Reaction fronts are not compatible with the simple sequence of reaction steps (1) and (2) but suggest the operation of an autocatalytic (nonlinear) effect. That an autocatalytic reaction step participates is also indicated by the variation of the local OH_{ad} concentration [Fig. 2(f)]. It shows an induction period of about 600 sec, followed by a rapid increase of OH_{ad} production, qualitatively similar to the report in Ref. [11]. An autocatalytic process is readily provided by reaction (3): The initially formed H_2O molecules which are mobile at low temperatures [20] decompose by reaction with neighboring O_{ad}. As we have shown above, this process is fast. This creates two OH_{ad} molecules per H_2O molecule which then may react with H_{ad} according to step (2). (The qualitative argument remains valid also for the different stoichiometry of reaction (3) found by Creighton and White [21].) Once initiated, the reaction is carried on by

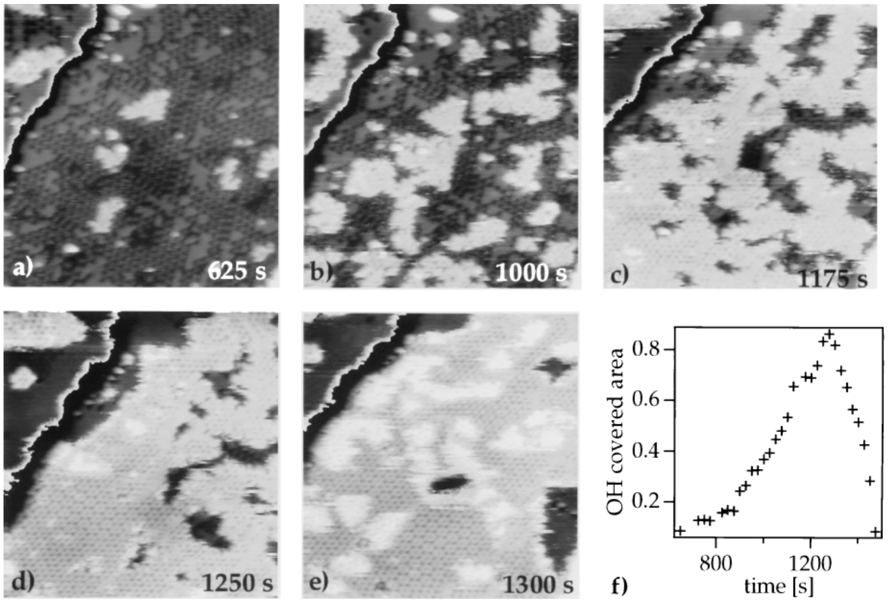

FIG. 2. (a)–(e) Series of STM images, recorded during hydrogen adsorption $[P(H_2) = 8 \times 10^{-9}$ mbar] on the (2×2)O covered Pt(111) surface, at $T = 131$ K. The black-and-white line at the left is an atomic step. Tunneling parameters: -0.45 V (sample potential), 0.8 nA, 170 Å × 170 Å. (f) OH_{ad} covered area as function of time.

cyclic repetition of steps (2) and (3), provided a continuous supply of hydrogen, and as long as there are sufficient O adatoms around. A cycle of the autocatalytic process converts each initial OH into two OH groups. The process is terminated when locally all O atoms are consumed, and the remaining OH_{ad} is transformed into H_2O through step (2). Reaction (1), which is presumably a slow step, is needed to initiate the autocatalytic process, but since trace amounts of H_2O will always be present, it is very likely that step (3) primarily plays this role.

H_2O_{ad} will be stable only if all neighboring O_{ad} atoms have been converted into OH_{ad} which effect, if integrated over the whole surface, is expected to lead to an (average) induction period for water formation at low temperature, in agreement with previous kinetic measurements [7]. Because of its positive feedback effect it is further expected that intentional addition of water accelerates the reaction which is again consistent with a previous report [9].

The idea of an autocatalytic contribution of water at low temperatures had actually been suggested previously. In order to explain the induction period Ogle and White [7] suggested that small H_2O clusters act as autocatalytic centers but later rejected the idea [9]. Verheij *et al.* [13,14] also proposed a kinetic model, in which, below the desorption temperature of H_2O, the initially formed water molecules decompose again. However, the key role in this model is played by surface defects. At $T < T_{des}$ these defects become covered by H_2O islands which requires complex transport processes between the defects and the perimeters of the growing H_2O islands. Our STM observations provide, however, no evidence that surface defects are important at $T < T_{des}$. If at all, they may play a role as nucleation centers for the reaction fronts, and sometimes atomic steps affect the spreading direction of a front, but the fronts may also run across steps (Fig. 4). Because the fronts travel over the whole surface, the two reaction steps (2) and (3) that occur within the fronts and propagate the reaction must be independent of defects of the metal surface. Another kinetic model for the low temperature regime [11] explained the induction period by reaction at O_{ad} island perimeters. However, the $(2 \times 2)O_{ad}$ islands, or the vacancies in the O_{ad} layer [e.g., Figs. 2(a) and 2(b)], are not seen to play a special role. The characteristic dimensions of these structures (on the order of 10 Å) are much smaller than those of the spatial structures formed by the reaction (the ring diameter in Fig. 4 is about 1000 Å, and the front widths in

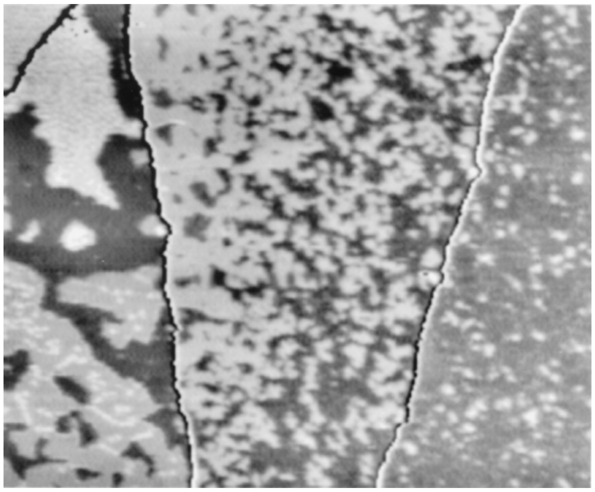

FIG. 3. STM image of Pt(111), after exposure of 2 L of H_2 on the (2×2)O covered surface at 134 K. Black-and-white stripes are atomic steps. -0.45 V, 0.17 nA, 1650 Å × 1420 Å.

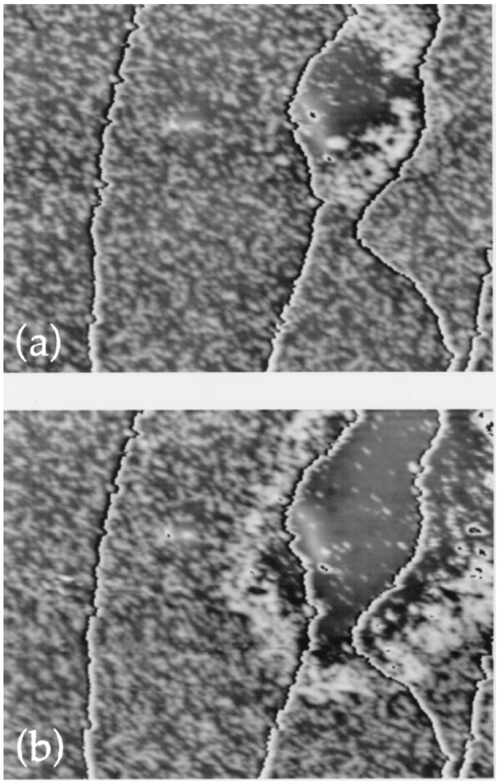

FIG. 4. STM images of the oxygen covered Pt(111) surface during hydrogen adsorption $[P(H_2) = 8 \times 10^{-9}$ mbar$]$ at $T =$ 111 K, recorded at (a) $t = 0$, (b) $t = 625$ sec. -1 V, 0.17 nA, 2100 Å × 1760 Å.

Figs. 3 and 4 are between 100 and 1000 Å). The unique reaction kinetics at low temperatures and the mesoscopic inhomogeneities are sole effects of the autocatalysis coupled to surface diffusion.

The proposed reaction mechanism is no longer operative if there is not sufficient H_2O remaining on the surface, because water is required for reaction (3). This reaction together with step (2) generates the autocatalytic process. Under UHV conditions the critical water coverage is reached roughly at the water desorption temperature $T_{des} \approx 170$ K. Above this temperature water can be formed only by the consecutive H addition reactions (1) and (2) so that above T_{des} a change in the reaction rate should be observed. Exposure of a (2×2)O layer at 200 K to 100 L H_2 left the HREEL spectra of O_{ad} almost unchanged, indicating that no significant reaction took place. Corresponding STM images show that at the beginning of the H_2 dosing, a number of O atoms disappear, which is probably associated with surface defects. However, the reaction then terminated and did not continue even after long H_2 exposures. A similar behavior had been found before in (macroscopic) kinetic measurements between 220 and 250 K [13]. This shows that reaction (1) must be a slow step and determines the reaction rate at higher temperatures, whereas steps (2) and (3) must be fast according to the low temperature results.

In conclusion, the mechanism of the catalytic oxidation of hydrogen on platinum is crucially determined by the presence of the reaction product water on the surface, which is a function of temperature and pressure. In the presence of sufficient H_2O_{ad} this species acts autocatalytically, whereas at small concentrations "normal" kinetics with consecutive steps applies. Although we do not rule out more complex mechanisms, particularly at high temperatures [8,12,13], this is the major effect that explains most of the existing observations, such as the transition from low to high activation energy or the disappearance of an inducation period above T_{des}. However, the desorption temperature of water marks this transition only for experiments under UHV conditions. At "real" catalytic pressures the surface concentration of adsorbed water will not be negligible even at higher temperatures so that the autocatalytic mechanism will then presumably still be important.

---

*Corresponding author.
Electronic address: wintterlin@fhi-berlin.mpg.de

[1] J. W. Döbereiner, Schweigg. J. **39**, 1 (1823).
[2] J. J. Berzelius, Jber. Chem. **15**, 237 (1837).
[3] G. B. Fisher, J. L. Gland, and S. J. Schmieg, J. Vac. Sci. Technol. **20**, 518 (1982).
[4] G. B. Fisher and J. L. Gland, Surf. Sci. **94**, 446 (1980).
[5] J. N. Smith, Jr. and R. L. Palmer, J. Chem. Phys. **56**, 13 (1972).
[6] A. B. Anton and D. C. Cadogan, Surf. Sci. **239**, L548 (1990).
[7] K. M. Ogle and J. M. White, Surf. Sci. **139**, 43 (1984).
[8] J. L. Gland, G. B. Fisher, and E. B. Kollin, J. Catal. **77**, 263 (1982).
[9] G. E. Mitchell, S. Akhter, and J. M. White, Surf. Sci. **166**, 283 (1986).
[10] G. E. Mitchell and J. M. White, Chem. Phys. Lett. **135**, 84 (1987).
[11] T. A. Germer and W. Ho, Chem. Phys. Lett. **163**, 449 (1989).
[12] B. Hellsing, B. Kasemo, and V. P. Zhdanov, J. Catal. **132**, 210 (1991).
[13] L. K. Verheij, M. Freitag, M. B. Hugenschmidt, I. Kempf, B. Poelsema, and G. Comsa, Surf. Sci. **272**, 276 (1992).
[14] L. K. Verheij, Surf. Sci. **371**, 100 (1997).
[15] J. Wintterlin, R. Schuster, and G. Ertl, Phys. Rev. Lett. **77**, 123 (1996).
[16] G. B. Fisher and B. A. Sexton, Phys. Rev. Lett. **44**, 683 (1980).
[17] G. Gilarowski, W. Erley, and H. Ibach, Surf. Sci. **351**, 156 (1996).
[18] M. Morgenstern, J. Müller, T. Michely, and G. Comsa, Z. Phys. Chem. **198**, 43 (1997).
[19] J. R. Creighton and J. M. White, Surf. Sci. **136**, 449 (1984).
[20] M. Morgenstern, Ph.D. thesis, Universität Bonn, 1996.
[21] J. R. Creighton and J. M. White, Surf. Sci. **122**, L648 (1982).