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Bistability and oscillations in CO oxidation studied with scanning tunnelling microscopy inside a reactor

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Abstract

This article focuses on the microscopic origin of oscillations in the rate of CO oxidation at atmospheric pressures on Pt group metals. We start by briefly reviewing several existing models for oscillatory CO oxidation on such surfaces at pressures ranging from ultrahigh vacuum to several bar. We describe our observations for this reaction on Pt(1 1 0) and Pd(1 0 0) at atmospheric pressures, obtained with a scanning tunnelling microscope inside a microflow reactor. The combination of STM movies and the simultaneously determined partial pressures and reaction rate reveals that by switching between a CO-rich flow and an O_2-rich flow, and vice versa, we can reversibly oxidize and reduce the Pt and Pd surfaces. We find that on both surfaces the formation of the oxide, seen in the STM images, is accompanied by a stepwise increase in the reaction rate and a change in the reaction mechanism. The switching between the reduced metal and the surface oxide exhibits significant hysteresis as a function of CO pressure and for both Pt and Pd there exists a CO pressure window in which both the metal and the oxide state are stable. This bistabililty leads to spontaneous reaction oscillations on Pd(1 0 0). Under our atmospheric conditions these oscillations are not due to the 'familiar' bistability in Langmuir–Hinshelwood kinetics, in contrast with common 'wisdom'. Instead, the high-pressure reaction oscillations reflect the periodic switching between the low-reactivity metallic surface and the high-reactivity oxide surface. Our results show further that effects that are held responsible for low-pressure reaction oscillations are not relevant at atmospheric pressure.

Keywords: Models of surface chemical reactions; Scanning tunnelling microscopy; Catalysis; Oxidation; Palladium; Platinum; Carbon monoxide; Single crystal surfaces; Solid–gas interfaces

1. Introduction

1.1. Oscillatory behaviour

CO oxidation on Pt-group metals has gained special attention because the reaction exhibits oscillatory behaviour [1–3]. Studying the kinetics of such oscillating catalytic reactions can yield much understanding of the catalytic mechanism. Oscillations in the reaction rate have been observed on time scales ranging from seconds up to tens of minutes, indicating that the processes that are responsible for the oscillations are slow compared to the elementary steps of the reaction, i.e. adsorption, reaction and desorption. Therefore, the origin of the variations in the reaction rate has often been ascribed to slow structural changes of the surface of the catalyst. Oscillatory CO oxidation has been observed over a wide range of pressures from 10^{-6} mbar to 1 bar. The models that describe the oscillations at low pressures differ substantially from the models for oscillations at atmospheric pressures. Our interest lies in bridging—or more precisely jumping over—the "pressure gap" between low-pressure model experiments and conditions more relevant for applied catalysis in general. We present a review of our in situ STM experiments with which we focus on the relation between structure of a surface and catalytic activity. Based on our results for oscillatory CO oxidation on Pt(1 1 0) and Pd(1 0 0), which are described in this article, we critically review the models existing for such oscillations. We find that

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the oscillations exhibit elements of these models, but they play a different role. Most well-established mechanisms for oscillatory reactions at low-pressures appear to be absent or non-relevant in our experiments. In order to clearly distinguish the similarities and, more importantly, the discrepancies between our findings and existing models it is essential to first briefly review the current (but by no means complete) knowledge of oscillatory CO oxidation in various pressure regimes.

1.2. Bistability in Langmuir–Hinshelwood kinetics

Basically all models describing oscillatory CO oxidation, both at low and high pressures, follow Langmuir–Hinshelwood (LH) kinetics. Two rate equations describe the variations of the surface coverages of CO molecules θ_{CO} and oxygen atoms θ_O, both chemisorbed on the surface.

$$\frac{d\theta_{CO}}{dt} = k_1 P_{CO}(1-\theta_{CO}^q) - k_2\theta_{CO} - k_3\theta_O\theta_{CO} \qquad (1a)$$

$$\frac{d\theta_O}{dt} = k_4(1-\theta_{CO}-\theta_O)^2 - k_3\theta_{CO}\theta_O \qquad (1b)$$

Whereas θ_{CO} is determined by the rate of adsorption (first term of Eq. (1a), with $q > 1$), desorption (second term) and the reaction (third term), θ_O is only set by the dissociative adsorption of oxygen (first term in Eq. (1b)) and the reaction (second term), i.e. oxygen desorption is usually neglected [4–8]. These two ordinary differential equations are coupled in a non-linear fashion through the reaction term $k_3\theta_O\theta_{CO}$. When the reaction significantly affects the surface coverage (i.e. $k_3\theta_O\theta_{CO}$ cannot be neglected) this set of equations has three solutions for the reaction rate $R(P_{CO},P_{O_2}) = k_3\theta_O\theta_{CO}$ over a limited range of P_{CO}. One solution is unstable and two are stable. This scheme thus exhibits bistability at fixed CO and O_2 pressures [4–6,8]. The first stable solution corresponds to a state with a surface which is covered predominantly with CO ($\theta_{CO} \gg \theta_O$). The high CO coverage effectively blocks the adsorption of oxygen, leading to a low value of θ_O and resulting in a low value of the reaction rate $R_1 = k_3\theta_O\theta_{CO}$. The other stable solution corresponds to a state with a surface which has a relatively high oxygen coverage ($\theta_O > \theta_{CO}$). In this case CO adsorption is not inhibited by the high oxygen coverage, which results in a higher value of $\theta_O\theta_{CO}$ than for the CO dominated surface. Therefore, the oxygen dominated surface has a higher reaction rate $R_2 = k_3\theta_O\theta_{CO} > R_1$. The bistability of the reaction rate originates essentially from the inequivalence of the adsorption of carbon monoxide and oxygen.

Although this simple scheme accounts for the bistability, an additional element is required to spontaneously switch between the two stable states, i.e. a feedback mechanism should be introduced, which regulates the observed self-sustained oscillations.

1.3. Feedback mechanisms for oscillations

1.3.1. Reconstructions

At low pressures (10^{-5} to 10^{-3} mbar) the oscillatory switching between the CO-dominated, low-reactivity LH-branch and the O-dominated, high-reactivity LH-branch on the Pt(1 0 0) and Pt(1 1 0) surfaces is caused by the periodic lifting and restoring of the surface reconstruction, i.e. a quasihexagonal (5 × 20)-structure ↔ (1 × 1) unreconstructed surface for Pt(1 0 0) [9–11], and a (1 × 2)-missing row structure ↔ (1 × 1) unreconstructed surface for Pt(1 1 0) [12,13], respectively. The reconstructions are lifted by CO adsorption when the coverage exceeds a critical value and they are restored when the CO-coverage is below another critical value. The unreconstructed (1 × 1) surfaces have significantly higher sticking probabilities for oxygen ($s_{O,1\times1} > s_{O,recon}$), and therefore drive the system back to the O-dominated, high-reactivity LH-branch. The CO-induced restructuring of the surface therefore modulates the oxygen adsorption, which in turn makes the system oscillate between the low-reactivity, CO-dominated, reconstructed surface and the high-reactivity, O-dominated, unreconstructed surface. The Pt(1 1 1) surface, which does not have a surface reconstruction, shows no oscillations but only bistability under similar low-pressure conditions [14].

The periodic lifting and restoring of the reconstruction is mathematically described by a third rate equation (added to the set of Eq. (1)) for the surface fraction (w) of the non-reconstructed (1 × 1) structure, which is assumed to depend solely on the CO-coverage. This modulates the oxygen adsorption through $k_4 \sim s_{O,1\times1}w + s_{O,recon}(1-w)$. In some models, a term which takes the diffusion CO on the surface into account has been added to describe spatial oscillations [10,15].

Strongly linked to the (1 × 2) ↔ (1 × 1) phase transition is the formation of microfacets [16–19] and the formation of roughness [20,21] during kinetic oscillations.

1.3.2. Subsurface oxygen

For oscillations observed on Pd(1 1 0) in the pressure range of 10^{-3} to 1 mbar [22,23], a surface which does not exhibit a surface reconstruction, an alternative mechanism has been proposed to account for the switching between the two LH-branches [24–28]. According to this mechanism, the slow build up of subsurface oxygen causes the decrease of the adsorption rate of oxygen, which leads to a mainly CO covered surface with the correspondingly low reaction rate. The subsurface oxygen species, being regarded as less unreactive than palladium oxide, slowly react with adsorbed CO, bringing the rate of oxygen adsorption back to its initial higher value, which leads to a sudden transition to a mainly oxygen covered surface. In this way, the accretion and removal of subsurface oxygen makes the reaction system periodically switch between the CO-dominated state and the O-dominated state. Based on the results of titration experiments the ‘subsurface’ oxygen mechanism was disputed [27]. The observed formation of a palladium surface oxide at oxygen pressures and temperatures in the oscillatory regime suggests that the oscillations are caused by an oxidation and reduction mechanism instead [28]. It was found that the rate of reduction of the oxide was comparable to that of chemisorbed oxygen and the decomposition of the PdO appears to be very fast, which all indicates that the oxide is weakly bound or unstable [29] and not unreactive, as was commonly assumed.

1.3.3. Subsurface oxygen coupled to reconstructions

In order to explain their photoemission electron microscopy (PEEM) data of spatio-temporal oscillations on polycrystalline platinum [30] and Pt(1 0 0) [31], Lauterbach et al. suggested the formation of subsurface oxygen to play a role when islands of chemisorbed oxygen are heated. On the Pt(1 0 0) surface, subsurface oxygen is thought to form only at the boundary between (1 × 1) islands with chemisorbed oxygen and the hexagonally reconstructed phase. On the Pt(1 1 0) surface subsurface oxygen is thought to only form on the non-reconstructed (1 × 1) phase and to stabilize this (1 × 1) phase [32–34]. The feedback mechanism for the oscillations is again the structure dependent sticking probability of oxygen, but according to this model the structural phase transition is depending on the concentration of subsurface oxygen.

1.4. Oscillatory reaction at intermediate pressure (10^{-3} to 10 mbar)

For pressures in the 10^{-2} mbar range spatial and temporal oscillations on Pt(1 1 1) have been ascribed to periodic oxidation and reduction of the surface [35]. For Pt(1 0 0), the slow deactivation after several cycles of CO-rich and O_2-rich gas flows during CO oxidation at a total pressure of 9×10^{-2} mbar has been ascribed to oxide formation, involving a restructuring mechanism that allows oxygen to penetrate the surface [36]. Oscillatory CO oxidation on a polycrystalline Pt foil has been observed in the mbar regime [37]. Also the oscillations observed during CO oxidation on supported Pt in the pressure range of 1–10 mbar have been ascribed to oxidation–reduction cycles [38].

1.5. Spatiotemporal patterns from UHV to atmospheric pressure

A variety of techniques has been used to investigate spatiotemporal pattern formation from ultrahigh vacuum up to atmospheric pressures [39,40]. At low pressures, under nearly isothermal conditions, adsorbate concentration patterns form as the combined consequence of the chemical reactions and surface diffusion [6]. On the other hand, at atmospheric pressures, temperature differences on the sample, caused by heat release of the reaction, dominate and give rise to thermokinetic waves.

1.6. Oscillatory reaction at atmospheric pressure

Oscillations also occur on supported Pt catalysts, under isothermal conditions at atmospheric pressures [40–42]. These oscillations have been ascribed to a reversible CO-blocking mechanism [43,44]. However, the most widely accepted model for oscillatory CO oxidation on polycrystalline Pt, Pd and Ir catalysts has been proposed by Sales, Turner, and Maple [4,44–46]. In this model, the switching between the two LH branches is induced by the formation of a non-reactive oxide. In the high-reactivity phase an oxide forms slowly because the O-coverage is high. The oxide blocks further adsorption, thereby making the system switch to the low-reactivity state. CO builds up and slowly reacts with this oxide and as soon as the surface is reduced sufficiently the reaction rate switches to the high value again. These elements are represented in the following rate equations.

$$\frac{d\theta_{CO}}{dt} = k_1 P_{CO}(1 - \theta_{CO} - \theta_O - \theta_{Ox}) - k_2\theta_{CO} - k_3\theta_O\theta_{CO} - k_{red}\theta_{CO}\theta_{Ox} \tag{2a}$$

$$\frac{d\theta_O}{dt} = k_4(1 - \theta_{CO} - \theta_O - \theta_{Ox})^2 - k_3\theta_{CO}\theta_O - k_{Ox}\theta_O(1 - \theta_{Ox}) \tag{2b}$$

$$\frac{d\theta_{Ox}}{dt} = k_{Ox}\theta_O(1 - \theta_{Ox}) - k_{red}\theta_{CO}\theta_{Ox} \tag{2c}$$

Here, θ_{Ox} is the surface coverage with oxide. The surface oxidation rate is thought not to depend on the CO coverage, whereas the reduction rate of the oxide depends linearly on the CO coverage [45,47,48].

Oscillations at atmospheric pressure on ‘dirty‘ Pt(1 1 1), Pt(13 1 1) and Pt(1 0 0) surfaces have also been explained by these oxidation–reduction cycles [49]. Direct evidence of periodic oxidation and reduction during oscillatory CO oxidation on SiO_2-supported Pt has come from X-ray diffraction (XRD) [50]. The XRD data were successfully fitted by a distribution of metallic clusters and PtO and Pt_3O_4 clusters. During the oscillatory reaction the Pt(1 1 1) XRD intensity was found to oscillate out of phase with the sample temperature, which is a measure of the reaction rate. In CO oxidation experiments in the hysteretic window, performed on Pt wires, a severe retexturing of the wires has been found and X-ray energy and wave dispersive analysis have revealed the presence of a surface layer of platinum oxide [51]. For ethylene oxidation on platinum, the reaction rate oscillations have been related to the formation of a surface platinum oxide that is less reactive than chemisorbed oxygen [52,53] and a connection was made to the stability of platinum oxide through a dissociation pressure–temperature relationship for PtO_2 [54,55].

Riekert has pointed out that a phase transition by itself, such as the metal–oxide transition, can explain oscillations

[56]. A phase transition implies a discontinuous change of the structure of the catalyst surface and it will cause the rate of the reaction to change abruptly. Under certain conditions, none of the phases, e.g. neither the metal and nor oxide alone is stable. Theoretically, a steady state in such a system can only be obtained by coexistence of the two phases, either in space or in time.

In the remainder of this article we present an in situ scanning tunnelling microscopy study which focuses on the relation between surface structure and the rate of CO oxidation at atmospheric pressures on Pt(1 1 0) and Pd(1 0 0). For Pd(1 0 0), we observe reaction oscillations. We demonstrate that the atomistic models reviewed in this section are inadequate for the interpretation of these high-pressure reaction oscillations.

2. Experimental

For all our experiments we have used a scanning tunnelling microscope (STM) which is integrated in a small-volume (0.5 ml) micro-flow reactor. This instrument allows us to image the surface with STM and simultaneously analyze the gas in the reactor by means of online quadrupole mass spectrometry. The 'leak' from the reactor to the mass spectrometer in UHV is located directly at the reactor, rather than in the gas line downstream, which makes the detection time delay less than 1 s. At the maximum flow of 10 ml/min the reactor contents are refreshed every 3 s. We have studied the Pt(1 1 0) and Pd(1 0 0) single-crystal surfaces, both of which have been prepared by mechanical polishing followed by cycles of 600 eV Ar-ion bombardment, annealing in 1×10^{-6} mbar oxygen, and by a flash to ~1100 K in UHV, until a clear LEED pattern was obtained. The crystals were directly transferred to the high-pressure reactor-STM combination, which is mounted inside the UHV system. The area of the sample surface that is exposed to the reactant gasses is typically 0.4 cm^2 and it is exclusively the surface orientation of interest that makes contact with the gasses. In most experiments, we heated the sample to the operation temperature of about 425 K in a gas flow at a total pressure of 0.5 or 1.25 bar. In our STM, the sample is thermally anchored to the reactor, which keeps the temperature constant within a few K, also during reaction. Gasses with a purity of 99.997% or better were used and these were pre-mixed in a gas manifold system. The gas flow of the gas mixture was controlled by mass flow controllers and the pressure in the reactor was regulated independently by a pressure controller. The time constant for the oxygen feed was about 50 s and the CO line had a time constant of 217 s, which practically means that our gas system cannot induce fluctuations on the time scale of a few seconds. We should note that the gas system did not allow us to maintain a precisely constant mixture over long periods, i.e. most experiments have been performed with a slowly varying gas composition.

3. Results and discussion

3.1. Forced switching of Pt(1 1 0) and Pd(1 0 0)

3.1.1. Pt(1 1 0)

Our results for Pt(1 1 0) are reproduced in Fig. 1 [57]. The upper panel shows a selection of STM images of the Pt(1 1 0) surface in a 3.0 ml/min gas flow of a varying mixture of CO and O_2 at a total pressure of 0.5 bar and a temperature of 425 K [58]. The lower panel depicts the partial pressures of the reactants, CO and O_2 and the reaction product CO_2, which have been measured simultaneously by means of mass spectrometry. Fig. 1a shows the Pt(1 1 0) surface in a nominally pure CO-flow. The surface consists of smooth terraces with the (1 × 1) bulk-terminated structure. The (1 × 2) missing-row structure, which is observed in UHV had been lifted by the CO and did not play any role in the high-pressure experiment. At $t = 502$ s, we switched from the pure CO-flow to an O_2-rich mixture, and the CO-pressure slowly decreased, reflecting the long time constant of our gas system. In the mixture there was a modest CO_2-production, which settled at a constant level indicated by R_{metal}. Fig. 1b illustrates that the change from the CO to the gas mixture and the resulting reaction had no apparent effect on the surface structure, which still consisted of smooth (1 × 1) terraces. Around $t = 1800$ s, several instabilities in the CO_2 production were observed, which finally resulted in a stepwise increase in the CO_2 production by approximately a factor 3 at $t = 2109$ s. There was a small step down in the CO-pressure resulting from this increase in reaction rate. This collective upward step in reactivity occurred during the recording of Fig. 1c (scanning from bottom to top in 65 s) at the location (=time) indicated by the dashed line. The lower quarter of the image corresponds to the surface before the switch in the reactivity. The upper three quarters of the image, corresponding to the surface with the increased reaction rate, still show smooth terraces, with all the steps at the original positions. At higher magnification the STM-images after the switch show a modest change in the surface corrugation. Unfortunately the resolution of our high-pressure STM was not sufficient to atomically resolve a new structure. After the switch to the increased CO_2-production, the surface became gradually rough on the timescale of several minutes (Fig. 1d). The amount of roughness scaled roughly proportionally to the total amount of produced CO_2. The new height variations clearly did not correspond to integer multiples of the step height of Pt(1 1 0). From this we conclude that the composition of the surface had changed, consistent with the scenario that the surface had oxidized. We have performed in situ surface X-ray diffraction (SXRD) experiments at the European Synchrotron Radiation Facility under similar reaction conditions. These experiments show the formation of an ultra thin surface oxide structure, coinciding with the increase in reactivity [59]. We propose that on the oxide surface, CO_2 is produced by reaction of CO molecules with oxygen atoms of the oxide. From the STM

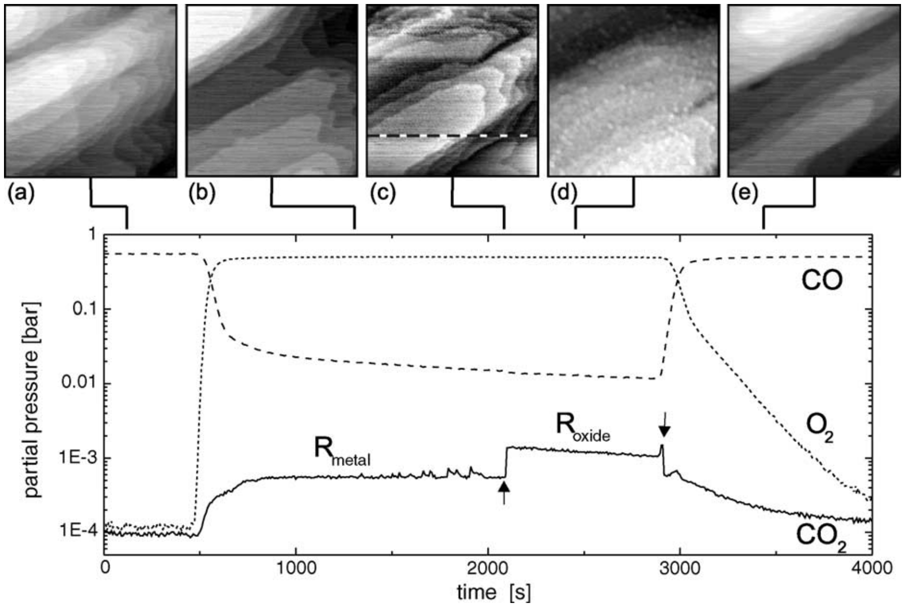

Fig. 1. STM images and mass spectrometer signals measured simultaneously during CO oxidation on Pt(1 1 0) at a temperature of 425 K in a 3.0 ml/min flow of a CO and O_2 gas mixture at a total pressure of 0.5 bar. (Upper panel) A selection of STM images (210 nm × 210 nm, $I_t = 0.2$ nA, $V_t = 80$ mV) from an STM movie [58]. Images (a), (b), the lower part of (c) and image (e) show the metallic, mainly CO-covered Pt(1 1 0) surface. The upper part of image (c) and image (d), represent the oxide surface which gradually roughened. (Lower panel) Partial pressures of the reactant gasses CO and O_2 and the reaction product CO_2. R_{metal} denotes the reaction rate on the metallic surface and R_{oxide} is the rate on the oxide surface. The arrows indicate where the surface switched from metal to oxide and back. (Figure adapted from [57]. Copyright 2002 by the American Physical Society.)

images in combination with the reaction rate we estimate that for roughly every 500 CO_2 molecules formed, a single Pt atom diffused out of the oxide surface, leaving behind a growing density of pits in the oxide and forming an increasing number of new (oxide) islands on top. The roughness had no apparent effect on the reaction rate and we consider it to be a mere by-product of the reaction. This reaction on, or rather with the oxide can be classified as a so-

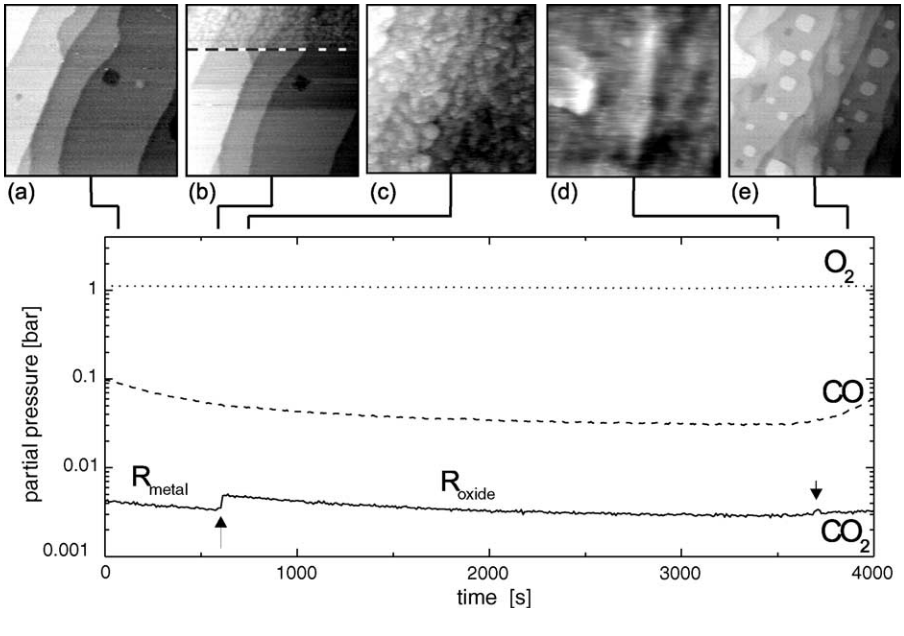

Fig. 2. STM images and mass spectrometer signals measured simultaneously during CO oxidation on Pd(1 0 0) at a temperature of 408 K in a 5.0 ml/min flow of a CO and O_2 gas mixture at a total pressure of 1.25 bar. (Upper panel) A selection of STM images (140 nm × 140 nm, $I_t = 0.2$ nA, $V_t = 112$ mV) from an STM movie [58]. Image (a), the lower part of (b) and image (e) show the metallic, mainly O-covered Pd(1 0 0) surface. The upper part of image (b) and images (c) and (d) represent the oxide surface. (Lower panel) Partial pressures of the reactant gasses CO and O_2 and the reaction product CO_2. R_{metal} indicates the reaction rate on the metal surface and R_{oxide} is the rate on the oxide surface. The arrow pointing up marks the switch from the metal to the oxide, the arrow pointing down marks the switch from the oxide to the metal. (Figure adapted from [63] with permission of Elsevier Science Publishers.)

called Mars–Van Krevelen mechanism, in which one of the reactants (oxygen) actually becomes part of the catalyst (platinum oxide), and the other reactant (CO) reacts with this lattice constituent (the oxygen atoms) [60]. Such a reaction mechanism has also been found to be active in methane oxidation on Pt and Pd catalysts [61,62]. At $t = 2913$ s, we switched back to a CO-rich flow, which reduced the surface back to its metallic state. The reaction rate switched down again to the value R_{metal}, after which it decreased together with the O_2 pressure. Initially the surface still had some residual roughness, but this decayed with time to restore the starting situation of smooth terraces with the (1 × 1) structure, as can be seen in Fig. 1e.

After the initial exposure to high pressures of CO, that lifted the (1 × 2) missing-row reconstruction, we have never observed the reoccurrence of this reconstruction, neither after oxygen exposure, nor during the reaction. In addition, we have never found any indication for the micro-faceting that has been observed at low pressures [16–19]

3.1.2. Pd(1 0 0)

For Pd(1 0 0) we have found a similar type of switching behaviour, as can be seen in Fig. 2 [63]. The upper panel shows a series of images of the same area at the surface of Pd(1 0 0) during an oxidation–reduction cycle at a total pressure of 1.25 bar, at a temperature of 408 K, in an O_2-rich gas flow of 5.0 ml/min. The lower panel depicts again the simultaneously measured partial pressures of CO, O_2, and CO_2. Fig. 2a shows the metallic Pd(1 0 0) surface in the gas mixture at $t = 100$ s. The surface consists of smooth terraces separated by mono- and multi-atomic steps. The CO_2 production on this metallic surface (R_{metal}), which we have found to follow Langmuir–Hinshelwood kinetics [63], decreases together with the CO-pressure until $t = 578$ s, where the surface oxidized and the reaction rate increased stepwise (R_{oxide}). We also observed a small step down in the CO-pressure, which is not visible on the (logarithmic) scale of Fig. 2. The upward step in reaction rate occurred at the dashed line in Fig. 2b, which was scanned from bottom to top in 43 s. The part of the image above the dashed line reveals that the oxidation of Pd(1 0 0) immediately created roughness on the surface in the form of small islands, similar to what Zheng and Altman had found [64]. The formation of palladium oxides on Pd(1 0 0) at atmospheric pressure has also been confirmed by recently SXRD and by first-principles atomistic thermodynamics calculations [65]. After formation of the oxide, the oxide surface became increasingly rough during the reaction (Fig. 2c and d). At $t = 3680$ s, we increased the CO-pressure again, which made the surface switch to the metallic state again, at a CO-pressure that was significantly lower than the CO-pressure at which the metal-to-oxide switch had occurred. Fig. 2e shows several Pd adatom islands that were left at the surface after the reduction. These islands slowly decayed with time.

3.2. Two reaction branches and bistability

If we plot the CO_2-pressure (P_{CO_2}) as a function of the CO-pressure (P_{CO}) for low P_{CO}, the kinetics are seen to be surprisingly simple. Both for Pt(1 1 0) and for Pd(1 0 0) all data fall on two 'reaction branches', as can be seen in Fig. 3. One branch corresponds to the reaction on the metallic surface (R_{metal}), the other corresponds to the reaction of the oxide surface (R_{oxide}). For Pt(1 1 0), the CO_2-production on the metallic surface appears to be independent of P_{CO}, suggesting that this surface is fully saturated with CO. The oxide branch for Pt(1 1 0) is proportional to P_{CO}, which shows that there is sufficient oxygen available at the oxide surface for reaction and that the CO_2-production is either limited by the supply of CO or the reaction between the CO and the oxygen atoms in the oxide. The same is true for the oxide branch of Pd(1 0 0). Remarkably, the slope $\mathrm{d}P_{CO_2}/\mathrm{d}P_{CO}$, which is the rate constant for the reaction on the oxide, is equal for Pt(1 1 0) and Pd(1 0 0). In addition, we have found it not to depend on temperature. This strongly suggests that in both cases the reaction rate was limited by a non-intrinsic process, e.g. the CO supply to the surface. The reaction rate on the metallic surface of Pd(1 0 0) depended on both P_{CO} and P_{O_2}, following standard Langmuir–Hinshelwood kinetics. We have calculated the reaction rate for a varying CO/O_2 ratio using the textbook Langmuir–Hinshelwood equation that includes adsorption and deso-

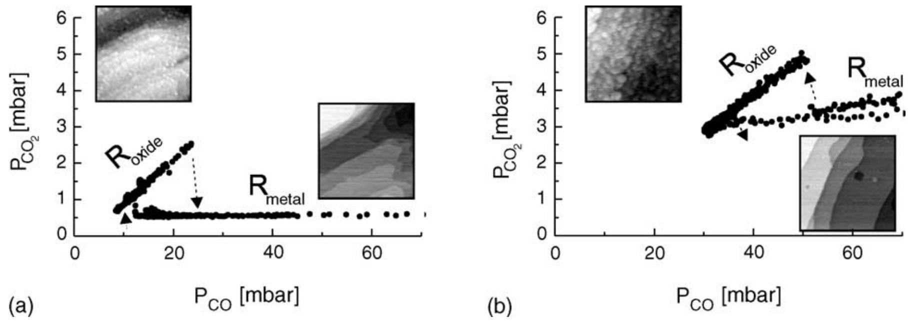

Fig. 3. The CO_2 production P_{CO_2} as a function of the CO-pressure P_{CO} at a nearly fixed oxygen pressure for (a) Pt(1 1 0) at $P_{O_2} = 0.5$ bar and $T = 425$ K and (b) Pd(1 0 0) at $P_{O_2} = 1.2$ bar and $T = 408$ K. In both cases, the data separate into two distinct reaction rate branches, one that corresponds to the reaction on the metal (R_{metal}), and one that corresponds to the reaction on the oxide (R_{oxide}). There is a significant range of bistability. Both plots show a distinct hysteresis, as is indicated by the arrows, which mark where the reactivity switches between the two branches.

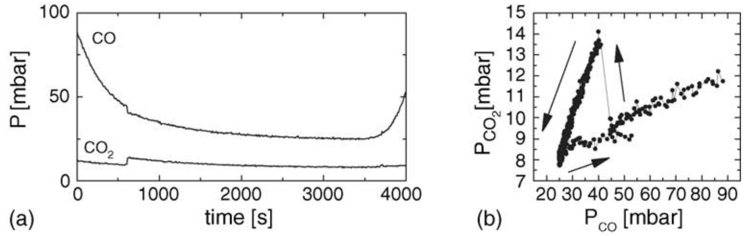

Fig. 4. (a) Partial pressure variations of CO and CO_2 on Pd(1 0 0) at $T = 408$ K and $P_{tot} = P_{CO} + P_{O_2} = 1.25$ bar. Panel (b) shows the same measurement with P_{CO_2} against P_{CO}.

rption of CO (molecular) and O_2 (dissociative) [63]. The experimental partial pressures were used as input, and assuming that the number of empty sites is small at this pressure, the ratio of CO and O_2 adsorption/desorption was essentially the only free fitting parameter. The numerical fit to our reaction rate data showed that for these low CO-pressures the metallic surface is mainly covered with chemisorbed oxygen.

For both surfaces, the metal branch and the oxide branch in Fig. 3 have significant overlap in a P_{CO}-window of roughly 20 mbar. This overlap provides the required bistability for oscillatory CO oxidation, namely, two distinct stable states for a single value of the CO-pressure. However, the observed low-rate metal branch and high-rate oxide branch are fully inconsistent with the low-rate CO-covered state and the high-rate O-covered state of the models for oscillatory CO oxidation described in Section 1. Moreover, the Langmuir–Hinshelwood kinetics observed on the metallic surface of Pd(1 0 0) do not show any bistability under oxygen-rich conditions.

In the traditional models, describing oscillations at atmospheric pressure, the surface is thought to switch back and forth between two metallic states, one mostly CO-covered and the other mostly O-covered, and the formation of a non-reactive oxide actually induces the switching from the O-rich state to the CO-rich state which leads to the oscillations. By contrast, we are forced to conclude that only one of the states, the one with the low reaction rate, is metallic, while the other, with the high rate, is actually the oxide. We thus find that under oxygen rich conditions the surface oxide has a higher catalytic activity than the metal surface. Several earlier experiments had already indicated that oxide formation plays a role in the oscillations on Pt [50,51], but the surface oxide had not been considered as one of the stable states and certainly not as the better catalyst. Recently, also for methane oxidation on Pd catalysts it has been proposed that switching back and forth between the reduced (metal) state and the oxidized state is responsible for oscillatory behaviour [66].

3.3. High-pressure reaction oscillations

When the reaction jumps from the low-rate metallic branch to the high-rate oxide branch, more CO is consumed per second. This leads to a decrease of the local steady-state CO-pressure in the reactor. For Fig. 3 this means that for a switch from the low-rate branch to the high-rate branch, P_{CO_2} steps up and P_{CO} steps down by the same amount, $\Delta P_{CO} = \Delta P_{CO_2}$. Switching from the high-rate branch to the low-rate branch in turn leads to a step down in P_{CO_2} and an equally large step up in P_{CO}. This naturally leads to a modest 'clockwise' hysteresis in the switching pressure P_{CO} between the two branches by the amount ΔP_{CO}, which is typically 10 mbar in our experiments. This additional hysteretic effect is smaller than the 20 mbar overlap of the two branches in CO pressure, typically observed in e.g. Fig. 3. Note that this effect tends to drive the system out of the bistable window in CO pressure, and therefore acts, by itself, against self-sustained oscillations.

There is a striking difference between Pt(1 1 0) and Pd(1 0 0) (Fig. 3a and b), whereas the hysteresis is indeed 'clockwise' for Pt(1 1 0), it is anti-clockwise for Pd(1 0 0). As described above, the clockwise hystersis means that the Pt surface switched to the oxide state at a lower P_{CO} than that at which it switched back to the metallic state. Instead, the oxide on Pd(1 0 0) formed at a higher P_{CO} value than that at

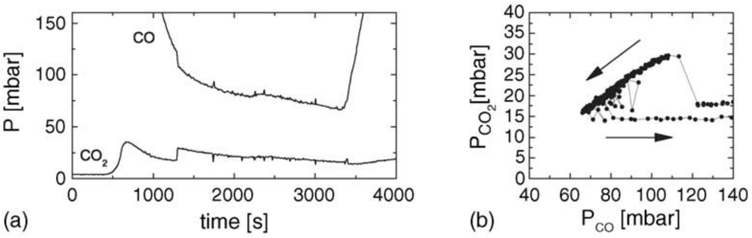

Fig. 5. (a) Partial pressure variations of CO and CO_2 on Pd(1 0 0) at $T = 433$ K and $P_{tot} = P_{CO} + P_{O_2} = 1.25$ bar. The maximum in P_{CO_2} at $t = 680$ s in corresponds to the reaction following Langmuir–Hinshelwood kinetics on the metal surface. The maximum occurs during the transition from the pure CO-flow to the O_2-rich flow. Panel (b) shows the same measurement with P_{CO_2} against P_{CO}.

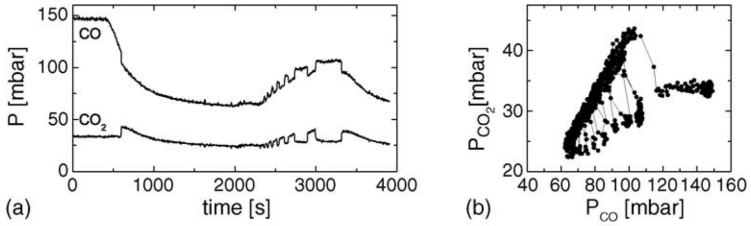

Fig. 6. (a) Partial pressure variations of CO and CO_2 on Pd(1 0 0) at $T = 443$ K and $P_{tot} = P_{CO} + P_{O_2} = 1.25$ bar. Panel (b) shows the same measurement with P_{CO_2} against P_{CO}. (Figure adapted from [63] with permission of Elsevier Science Publishers.)

which the oxide was reacted away. As expected, we find that Pt(1 1 0), having clockwise hysteresis, does not exhibit self-sustained oscillations. However, it did exhibit instabilities on the metal-branch (e.g. Fig. 1 for $1800 \text{ s} \leq t \leq 2109$ s) within the bistability window around $P_{CO} = 15$ mbar (Fig. 3a).

On the other hand, Figs. 5–7 show that the reaction rate on Pd(1 0 0), having anti-clockwise hysteresis, can spontaneously oscillate in time. Like in Fig. 4, the CO partial pressure in Figs. 5–7 was always varied slowly and continuously at constant $P_{O_2} + P_{CO}$. Rapid stepwise variations in the reaction rate, P_{CO_2} and corresponding oppositely directed rapid variations in P_{CO} were fully spontaneous. Figs. 5–7b illustrate that the oscillations in P_{CO_2} (and P_{CO}) correspond to spontaneous switching between the metal branch and the oxide branch. We find that the reaction rate switches between values exclusively on the two branches and not to intermediate values. From this we conclude that the entire surface switches collectively within our time resolution of a few seconds. From experiment to experiment, the shape and period of the oscillations varied substantially, similar to what many authors have already reported [4,44,49]. For example the oscillations in Fig. 5 only consist of short downward spikes in P_{CO_2}, i.e. excursions to the metal-branch for only a single data point, corresponding to a lifetime of the metal phase shorter than 8 s. We emphasize that variations of the mixture coming from our gas handling system could not lead to such short and abrupt steps and spikes in the partial pressures since the time constants (typically 50 s) are significantly larger than 8 s. Whereas in Fig. 5 we find oscillations during the slow downward ramp in P_{CO}, Fig. 6 shows no oscillations during a similar decrease in P_{CO}. The reaction rate, P_{CO_2}, started to oscillate strongly as we slowly increased P_{CO}. P_{CO} exhibited modulations in anti-phase with P_{CO_2}, caused by the rate oscillations. The oscillations had a block-wave character and the period of the oxide phase varied from 35 s, when the oscillations had just started, to 103 s around $t = 2900$ s. The period of the metal phase was 17 s at the beginning and increased to 311 s at the local maximum in P_{CO} around $t = 3150$ s. The oscillations in Fig. 7 also had a block-wave character, and where initially the periods of the oxide and metal phase were comparable (110 and 90 s, respectively), at later times for lower P_{CO} the surface spent less time in the metal phases (31 s) and the oxide phase period decreased only modestly (72 s).

Between experiments on the same crystal in the same setup, we have observed a significant variation in the CO-pressure, or, probably more importantly, the ratio P_{CO}/P_{O_2} at which the metal surface switched to the oxide for the first time. We observed that at higher temperatures, the value of P_{CO}/P_{O_2} at which he metal to oxide transition occurred was also higher ($P_{CO}/P_{O_2} = 0.037$ for $T = 408$ K compared to $P_{CO}/P_{O_2} = 0.11$ for $T = 443$ K). In addition, this ratio seemed to depend on the sample history.

An STM image during half of a spontaneous oscillation cycle is shown in Fig. 8. The lower part is the metallic Pd(1 0 0) surface which contains a high density of high-curvature steps and several large ad-atom islands, similar to what we observed in Fig. 2e. The upper half shows the rough oxide surface. Images during self-sustained oscillations, like Fig. 8, confirm that the oscillations are spontaneous metal–oxide phase transitions. However, there is no obvious change in the image surface structure that could be responsible for the switching from the metal to the oxide and vice versa. STM imaging during the oscillations was difficult for several reasons. First of all, during the oscillations the surface

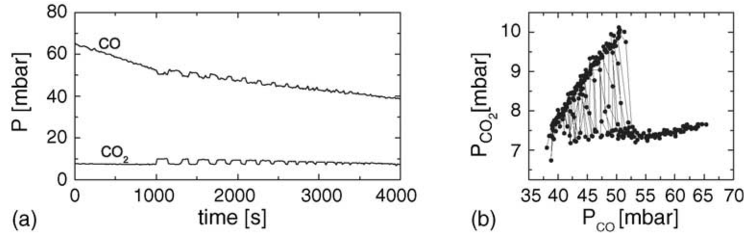

Fig. 7. (a) Partial pressure variations of CO and CO_2 on Pd(1 0 0) at $T \approx 408$ K and $P_{tot} = P_{CO} + P_{O_2} = 1.25$ bar. Panel (b) shows the same measurement with P_{CO_2} against P_{CO}.

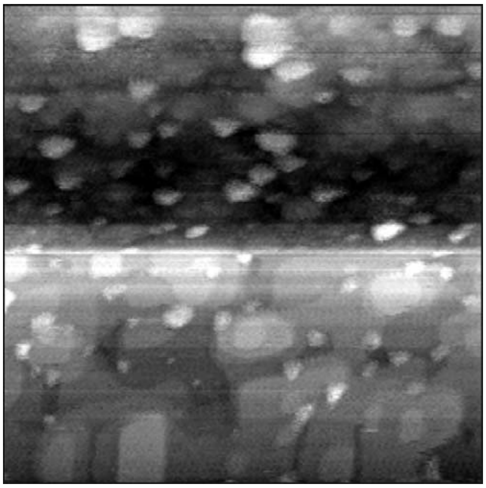

Fig. 8. STM image (100 nm × 100 nm) of the Pd(1 0 0) surface. The imaging was started (from bottom to top) at $t = 1670$ s, just before the fourth oscillation in Fig. 7 and halfway the image, at $t = 1720$ s, the surface switched spontaneously to the oxide. The global height variation from bottom to top is due to change in thermal drift resulting from the switch to the high-rate branch, which caused a small increase in the sample temperature (on the order of 1 K).

became increasingly rough; this made the imaging difficult due to tip convolution effects. Furthermore, the tip did not always remain stable under the varying reaction conditions. Secondly, the phase transition, especially from the oxide to the metal, was accompanied by significant surface diffusion. This made the surface highly dynamic, which resulted in blurred images at the low scan velocities employed here. Finally, the CO oxidation reaction was highly exothermic. The switch to the high-rate branch was therefore accompanied by a rapid, but small, change in sample temperature. This resulted in thermal drift of the STM, which was small enough to still image the surface during the oscillations, but it certainly did not improve the imaging quality.

Reactor-STM and high-pressure SXRD experiments are currently being performed to find out what structural change induces the metal–oxide phase transitions that constitute the reaction oscillations.

4. Summary and conclusions

We have studied the catalytic oxidation of CO at atmospheric pressures on Pt(1 1 0) and Pd(1 0 0) using a high-pressure STM inside a flow reactor. By switching from a CO-rich flow to an O_2-rich flow and vice versa we could reversibly oxidize and reduce the Pt and Pd surfaces. In both cases, the formation of the oxide had a dramatic positive effect on the reaction rate, which increased stepwise at the moment when the surface oxidized.

The CO_2 production, e.g. considered as a function of the CO pressure, shows two distinct reaction branches. The low-reactivity branch corresponds to the reaction on the metallic surface and the high-reactivity branch corresponds to the reaction on the oxide. Our results show that under O_2-rich conditions the oxide is the more catalytically active surface. This observation is at variance with the common belief that these oxides are non-reactive in CO oxidation and that their formation degrades the catalyst performance. The two reaction branches overlapped over a CO-pressure window of a few tens of mbar. The switching from metal to oxide and back exhibited hysteresis in the CO pressure, which was ‘clockwise’ for Pt(1 1 0) and ‘anti-clockwise’ for Pd(1 0 0).

The observed bistability of the reaction for fixed CO and O_2 pressures was found to lead to spontaneous oscillations in the reaction rate for Pd(1 0 0). We have observed that oscillatory CO oxidation on Pd(1 0 0) at atmospheric pressure reflects the periodic switching between the low-reactivity metallic surface and the high-reactivity oxide surface. This observation is fully inconsistent with widely accepted models that describe the oscillations as the switching between two reaction branches on the metallic surface that both follow traditional Langmuir–Hinshelwood kinetics, i.e. the switching between a low-reactivity, CO-dominated surface and a high-reactivity branch, which is mainly covered with chemisorbed oxygen. Regarding the feedback mechanism that regulates the switching from one branch to the other, we stress that we have never found any indication for surface restructuring of the kind that has been observed on Pt(1 1 0) at low pressures, i.e. the $(1 \times 1) \leftrightarrow (1 \times 2)$ phase transition and micro-faceting. We exclude that the slow build-up of a non-reactive oxide is responsible for inducing the oscillations. We have seen that the surface oxide is ‘merely’ one of the stable states and the oxide is not actively involved in further regulating the switching. The slow build-up and slow removal of a hypothetic (second type of) non-reactive oxide or subsurface oxygen population that regulates the oscillations can be ruled out as well, as it is inconsistent with the observation that during an oscillation, the switching from the oxide to the metal occurs instantaneously. The observed oscillations on Pd(1 0 0) vary from short spikes in the CO_2 production of a few seconds to block waves of several minutes. These oscillation characteristics depend strongly on slow variations in the CO pressure, temperature, and the history of the surface. Clearly, a hidden parameter that provides the feedback mechanism, responsible for the spontaneous switching between the metallic and the oxide reaction branches has not been identified yet in this work. Currently, high-pressure STM and SXRD experiments are underway in search for this crucial parameter.

Acknowledgements

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