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Operando SXRD : a new view on catalysis

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V Atomic Steps as a Motor for Reaction Oscillations

Atomic steps on catalyst surfaces are often considered as special, active sites for heterogeneous catalytic reactions [85]. Due to the reduced coordination, the metallic atoms at step sites can offer enhanced binding to reactant molecules [3,86,87] and exhibit enhanced activity for bond breaking [88-91]. Here we show that steps on surfaces may also play a role by changing the stability of the catalytically active phase. Our high-pressure Surface X-Ray Diffraction (SXRD) experiment on a palladium model catalyst shows that a high density of steps strongly alters the conditions required for the formation of the thin palladium oxide film that serves as the active phase for the catalytic oxidation of carbon monoxide. With high-pressure Scanning Tunneling Microscopy (HP-STM) we further observe how, under steady-state conditions, reaction-induced variations in the step density lead to the periodic removal and (re)formation of this active surface oxide. We show that this new mechanism is at the heart of the well-known reaction rate oscillations during the catalytic oxidation of carbon monoxide at atmospheric pressure [75,92].

5.1: Introduction

The experiments described in the previous chapters and recent publications of both experimental and theoretical work have shown that atomically thin oxide layers form on the surface of late transition metals such as Ru, Pt, Pd and Rh at elevated temperatures and atmospheric pressure under oxygen-rich conditions [6,9,28,62,93]. In catalytic CO oxidation experiments under realistic pressure and temperature conditions these ultra thin oxide layers have been found to be catalytically much more active than the reduced, gas-covered metallic surfaces [9,62]. The reason for the formation of these thin oxide layers is simply that at high oxygen pressures it is thermodynamically more favorable to incorporate oxygen atoms into the surface in the form of oxides, rather than in the chemisorption structures typical for low oxygen pressures [94]. The growth and thickness of these oxide layers is under these circumstances kinetically limited [93]. Because of this kinetic limitation, these oxide layers only grow under high pressure *and* temperature conditions.

The combination of the chemical potential of the surrounding gasses and the free energy of the surface determines whether it is thermodynamically preferable for the surface to be oxidized or not. For a catalyst operating in a mixture of oxidizing and reducing (reactant) gasses, the combination of the different chemical potentials, the surface free energy and the adsorption energy of the different reactant gasses will determine whether the surface prefers the reduced state, with one or both reactants adsorbed to it, or the formation of an oxide layer [28].

The transition of the catalyst surface from the metallic phase to the oxidized phase can offer a fully new path for the catalytic reaction mechanism. On a metallic surface one or more reactants first adsorb to the surface, and then react to form the product, which subsequently desorbs from the surface, leaving a free site for new reactant molecules to adsorb (Langmuir-Hinshelwood or Eley-Rideal mechanism). This is a very simplified version of a full catalytic reaction, as many intermediate steps are often needed to go from adsorption of the reactant gasses to the desorption of the reaction product. Even in CO oxidation, which is a fairly simple catalytic reaction, this process is composed of more steps than mentioned above, as e.g. the oxygen molecules also have to dissociate after having been adsorbed on the surface.

On the oxidized surface, the oxygen atoms stored *within the oxide layer* serve as a supply of atomic oxygen, which can be easily extracted by the other reactant, in this case CO. After the oxide layer has been locally reduced, the resulting oxygen vacancy is refilled with oxygen from the gas phase in a process which is analogous to the Mars - Van Krevelen mechanism [4] (see chapter 2, figure 6). In this chapter we show that there is an important influence of the roughness (i.e. the density of atomic steps) on the stability of the oxide phase, and thereby on the catalyst's performance. Combining the effect of the roughness on the stability of the oxide layer with the effect of the oxide on the catalysts performance, we can also link the formation and removal of atomic steps, or more generally 'roughness' to so-called self-sustained reaction oscillations [82].

5.2: Experimental

All Surface X-Ray Diffraction (*SXRD*) experiments presented below were performed at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF) in a combined ultrahigh vacuum - high pressure *SXRD* chamber (10^{-10} mbar – 2 bar), which has a volume of ~ 1 liter and is equipped with a 360° beryllium window for entrance and exit of the X-Rays [48]. The chamber was mounted on a z-axis diffractometer with the crystal surface in a horizontal plane. We have used a focused beam of monochromatic, 17 keV X-Ray photons, impinging on the surface at a grazing angle of typically 1° .

5.2.1: Surface roughness and the metal-to-oxide transition

Figure 1 shows an experiment of CO oxidation on Pd(001), in a mixture of CO, CO₂ and O₂ at approximately 700 mbar total pressure and 485 K. This experiment is already extensively described in chapter 4. Figure 1(a) shows the partial pressures of CO, O₂, and CO₂ in the reaction chamber during CO oxidation experiments at a temperature of 485K. Panel (b) shows a series of rocking scans around the surface normal at one of the anti-phase position of a Pd(001) Crystal Truncation Rods (CTR). The scans have been recorded around $(h\ k\ l) = (1\ 0\ 0.2)$ and repeated as a function of time, simultaneously with a measurement of the partial gas pressures.

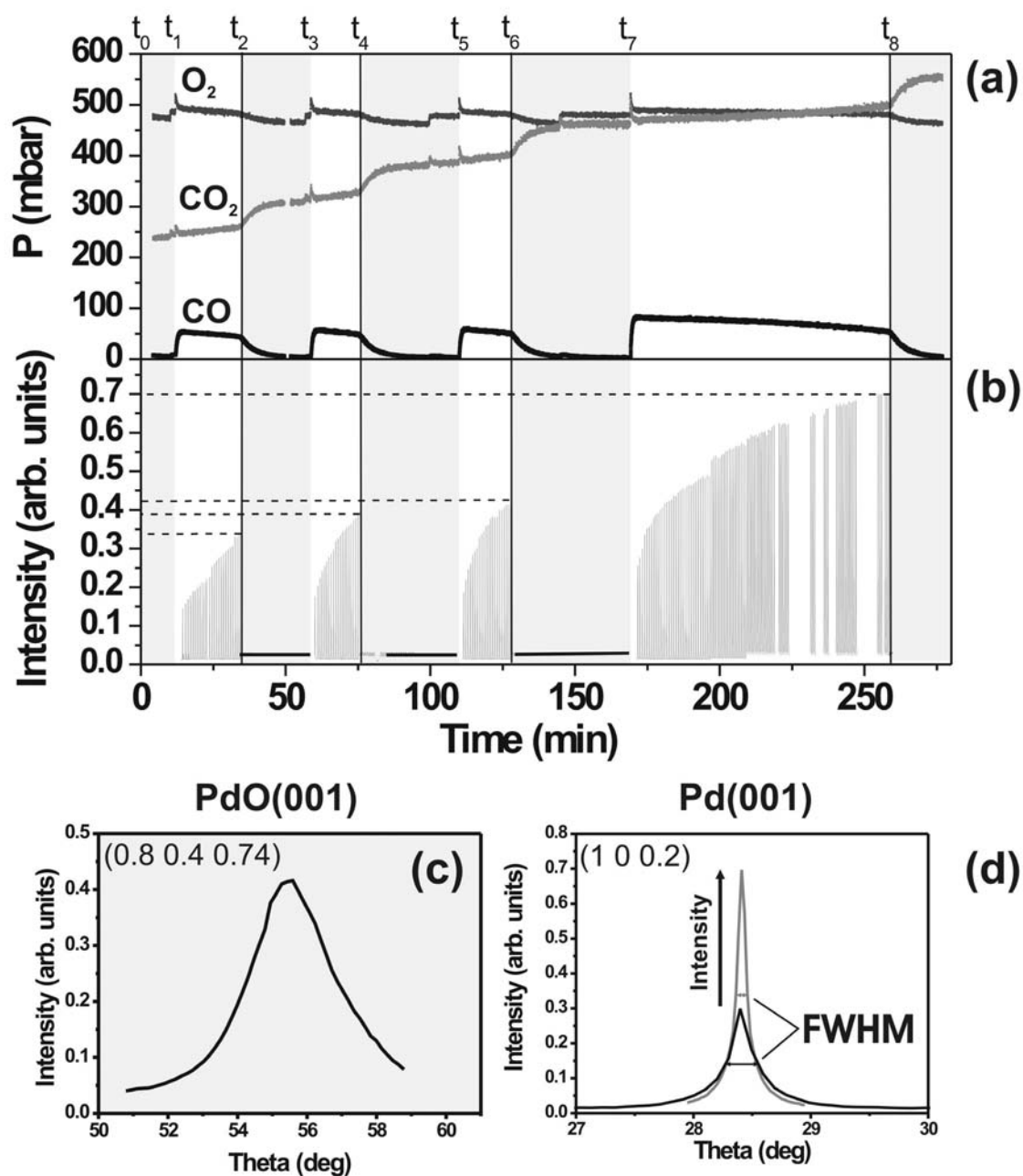


Figure 1: Cycles of oxidation and reduction of the Pd(001) surface during CO oxidation at 460 K. **(a):** Partial pressures of the reactants CO and O_2 and the reaction product CO_2 . **(b):** Series of rocking scans of the Pd(001) surface diffraction peak at $(h k l) = (1 \ 0 \ 0.2)$. **(c):** Rocking scan of the PdO(001) peak of the oxidized palladium surface after reacting 60 mbar of CO to CO_2 (data taken from an earlier part of this experiment, not shown here, see Figure 4). **(d):** Two individual rocking scans of the $(1 \ 0 \ 0.2)$ crystal truncation rod of Pd(001) taken at t_7 and t_8 showing both the increase in intensity already visible in panel (b) and the decrease in FWHM.

The reaction chamber was operated in batch mode, which means that we added a pulse of CO at t_1 , t_3 , t_5 and t_7 ⁱ. By also adding well controlled amounts of O₂ in between the CO pulses we kept the same oxygen pressure at the start of every CO pulse throughout the experiment. The reaction product CO₂ gradually accumulates in the chamber. Also the temperature was kept constant by adjusting the amount of heating after every pulse of CO. This was necessary to correct for the higher gas pressure in the chamber, and hence the higher thermal conductance to the (relatively) cold wall of the reactor.

The experiment started at t_0 in 475 mbar O₂ and 230 mbar CO₂, left over from a previous reaction cycle. Under these conditions we observed a diffraction peak at (0.8 0.4 0.74) corresponding to a commensurate palladium oxide layer, previously identified as PdO(001) (see figure 1c and / or chapter 4). There was no intensity at the metal Pd(001) position (1 0 0.2). At $t = 10$ minutes (approximately 90 seconds before t_1) we added O₂ to the chamber through a leak valve to increase P_{O_2} to 485 mbar. At t_1 52 mbar of CO was added to the chamber. Immediately the CO started reacting with the present O₂ under formation of CO₂, as shown by the linear decrease of the CO and O₂ pressures and the increase in the CO₂ pressure in the upper panel for $t_1 < t < t_2$. Panel (b) shows that as soon as we introduced the CO at t_1 the Pd(001) diffraction peak appeared at (1 0 0.2). The PdO peak had vanished completely (not shown here). The immediate conclusion on the effect of the CO pulse is that the CO/O₂ ratio has changed the gas phase from an oxidizing to a reducing environment. This has completely reduced the PdO oxide layer and stabilized a metallic surface, hence inducing what we later refer to as an ‘oxide-to-metal transition’.

From panel (b) we see that in the metallic phase the height of the Pd(001) peak increases with time. When plotting the diffracted intensity as a function of q (diffraction angle) instead of as a function of time, we see that the increase in height is combined with a decrease in Full Width at Half Maximum (*FWHM*), while the integrated intensity of the peak remains constant (figure 1d). The *FWHM* of the Pd(001) diffraction peak is inversely proportional to the coherence length of the Pd surface structure which in the case of this simple, bulk terminated surface is equivalent to the average terrace width. The *FWHM*

ⁱ Note that whenever we introduced gas to the chamber there were transients in all the mass spectrometer signals at $t = 10, 12, 56, 60, 98, 107, 140, 169$ minutes. These transients are related to our gas sampling and detection and not to the reaction kinetics.

of this rocking scan at the anti-phase of the Pd(001) CTR is therefore a direct measure of the step density. The decrease of the *FWHM* with time reflects a gradual smoothening of the Pd(001) surface by reduction of the step density [95].

At t_2 the Pd(001) diffraction peak spontaneously disappears on the timescale of less than one second. This can be explained because in the batch reactor the two reactants are slowly converted to CO_2 , thereby reducing the ratio between P_{CO} and P_{O_2} . This goes on until the O_2/CO ratio is such that the gas phase is sufficiently oxidizing again, that the surface is ‘re-oxidized’. In this reaction cycle we recorded only the diffraction peak of Pd(001) at (1 0 0.2), but from other cycles not shown here we know that at t_2 the intensity of the PdO(001) layer at (0.8 0.4 L) instantly reappears. Simultaneously with this metal-to-oxide transition we observe an increase in the CO_2 production rate of approximately a factor 13. The metal surface had continued smoothening during all the time spent in the metallic phase, until the metal-to-oxide transition took place. After all CO from this pulse had been consumed by the reaction, we added oxygen to restore the initial O_2 pressure, and corrected the temperature and heating for the increased pressure.

This closes one full oxide-metal-oxide cycle induced by one single CO pulse. After the pulse is fully converted to CO_2 we are back in the *exact* same conditions in both temperature and oxygen pressure as before the CO pulseⁱⁱ.

This initial pulse described above is followed by a 55 mbar CO pulse at t_3 , by which a second oxide-metal-oxide cycle is started. These cycles were repeated with increasingly large pulses of CO. At each CO pulse we start in the same condition: A pure O_2/CO_2 environment ensures that we are in oxidizing conditions, and the surface of the Pd(001) is indeed covered with a several monolayer thick PdO oxide layer. The surface is then exposed to a pulse of CO, carefully chosen to be large enough to fully reduce the oxide layer on the surface, and the CO oxidation reaction now takes places on the metallic surface. The surface though is left with much residual roughness from the oxidized state

ⁱⁱ *The only real difference is the CO_2 pressure inside the reactor, which rises due to each CO pulse. The CO_2 in the gas phase being the product of the catalytic CO oxidation reaction. It has, as far as we could determine no influence on either the oxidation or the reduction process of the Pd surface. Its presence is hence often neglected in the description of the gas composition inside the reactor during the experiment.*

it was in before the induced oxide-to-metal transition. During this metallic phase, the rough metal surface slowly smoothen as we determine from the decreasing *FWHM* of the (1 0 0.2) diffraction peak. The reduction in step density had no measurable effect on the reaction rate. This smoothing of the surface after switching from the oxide to the metallic state has previously been reported for a high pressure STM experiment in similar conditions [10].

The effect of administering ever larger pulses of CO to the reactor, is that the catalyst takes more time to convert enough CO to CO₂ to return to a sufficiently high O₂/CO ratio for the surface to switch back to the oxidized state. This allows the surface more time in the metallic state and hence more time to smoothen out the roughness introduced from the oxide-to-metal transition. This implies that the surface roughness at the metal-to-oxide transition is lower for larger CO pulses. The amount of CO administered to the reactor in one single pulse hence gives us a tool to vary the surface at the metal-to-oxide transition.

5.2.2: Switching point: P_{CO} vs. Roughness

The effect of the change in surface roughness at the metal-to-oxide transition is illustrated in figure 2. The data shown in this figure have been gathered from the four oxide-metal-oxide cycles shown in figure 1 and two, smaller preceding pulses (not shown). The combination of the critical *FWHM* value of the (1 0 0.2) diffraction peak and the critical CO pressure at the metal-to-oxide transitions define the metal-oxide phase boundary in figure 2.

Figure 2 shows that there is a clear variation in the CO pressure P_{CO}^* at which the metal-to-oxide transition takes place as a function of the step density. From figure 2 we see that P_{CO}^* is lower for higher step densities. Thermodynamically, the first-order metal-to-oxide transition of a smooth, step-free surface takes place when the free energies of the two competing structures, namely the metal surface with a chemisorbed layer of reactants and the oxide surface, are equal. The presence of steps may shift this balance because steps on both phases cost different amounts of (free) energy. This shift can go either way, but there are two arguments why steps could work in favor of the metal phase and make it stable down to a lower CO pressure (or up to a higher O₂ pressure) in the presence of many steps. First, on many metal surfaces CO molecules adsorb significantly more strongly at steps than on terraces [3,86,87]. For a metal surface in contact with CO, this reduces the effective step free energy and under

special circumstances can even lead to the spontaneous formation of steps [96]. We anticipate that this enhanced bonding effect is stronger for CO molecules than for O atoms adsorbed at steps on Pd(001) [97]. Secondly, steps make the metal surface a bad template for the commensurate PdO(001) structure, since they lead to dislocations in the oxide. The effect of the step density on the metal-to-oxide transition is reminiscent of the role of steps in the phase transition from the 7x7 surface reconstruction to the 1x1 phase on Si(111), for which the transition *temperature* depends on step density [59].

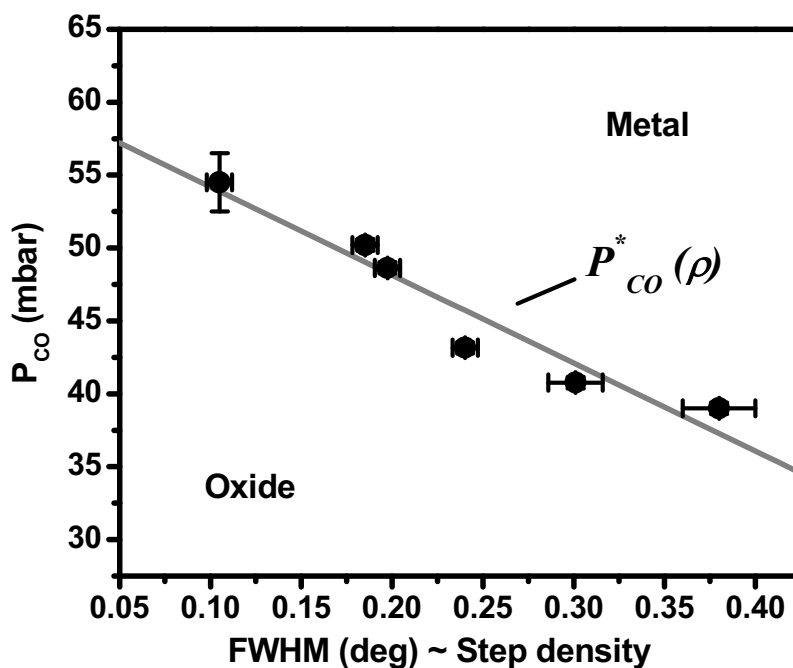


Figure 2: Phase boundary of the Pd(001) surface measured with surface X-ray diffraction. Measurements were performed at a temperature of 460 K in a CO/O₂ gas mixture with a fixed oxygen partial pressure of 480 mbar. The parameter along the horizontal axis is the full width at half maximum (FWHM) of the diffraction peak on the metal surface at (1 0 0.2) immediately prior to the metal-to-oxide transition. This peak width is a sensitive measure of the density of steps on the metal surface. We clearly see that the critical CO pressure P_{CO}^* varies approximately linearly with the step density on the metallic surface. All data were taken from the experiment shown in Figure 1.

5.3: Self-Sustained Reaction Oscillations: Roughness Model

Although the effect of steps on the metal-to-oxide transition may seem to merely shift the catalyst's working conditions, the combination of this effect with the two different reaction mechanisms and reaction rates can have dramatic consequences for the steady-state operation of a catalyst. This is illustrated in figure 3, which shows a High Pressure STM experiment performed by Hendriksen *et al.* in which the CO oxidation rate on Pd(001) in a constant reactant flow at atmospheric pressure spontaneously oscillates between two distinct levels, R_{oxide} and R_{metal} . The oscillations in the CO pressure in the reactor are in anti-phase with the variations in CO₂ production and are caused by the difference in CO consumption at the two reaction rates. Figure 3 also shows STM images that were recorded during these self-sustained reaction oscillations. In earlier High Pressure STM studies Hendriksen *et al.* had already found that the oscillations are the periodic switching between the low-activity metal phase and the high-activity oxide and these changes in structure can also be recognized in figure 3 [9,10,77]. From the changes both in the reaction rates and in the STM images we see that the metal-to-oxide and oxide-to-metal transitions take only a fraction of a second, while the period of the oscillations can be many minutes.

We propose that the essential element that governs the long oscillation period is the slow variation of the surface roughness. We have observed with both *SXRD* and STM measurements that during the catalytic CO oxidation in the metallic phase the surface slowly smoothens, while it slowly roughens when the reaction runs in the oxide phase.

It is plausible that during the Mars - Van Krevelen mechanism on the oxide a small fraction of the metal atoms in the oxide becomes sufficiently strongly undercoordinated with oxygen to become mobile and diffuse out of their original positions until they are re-oxidized and immobilized on top of the oxide [6,9] (see chapter 3, figure 5).

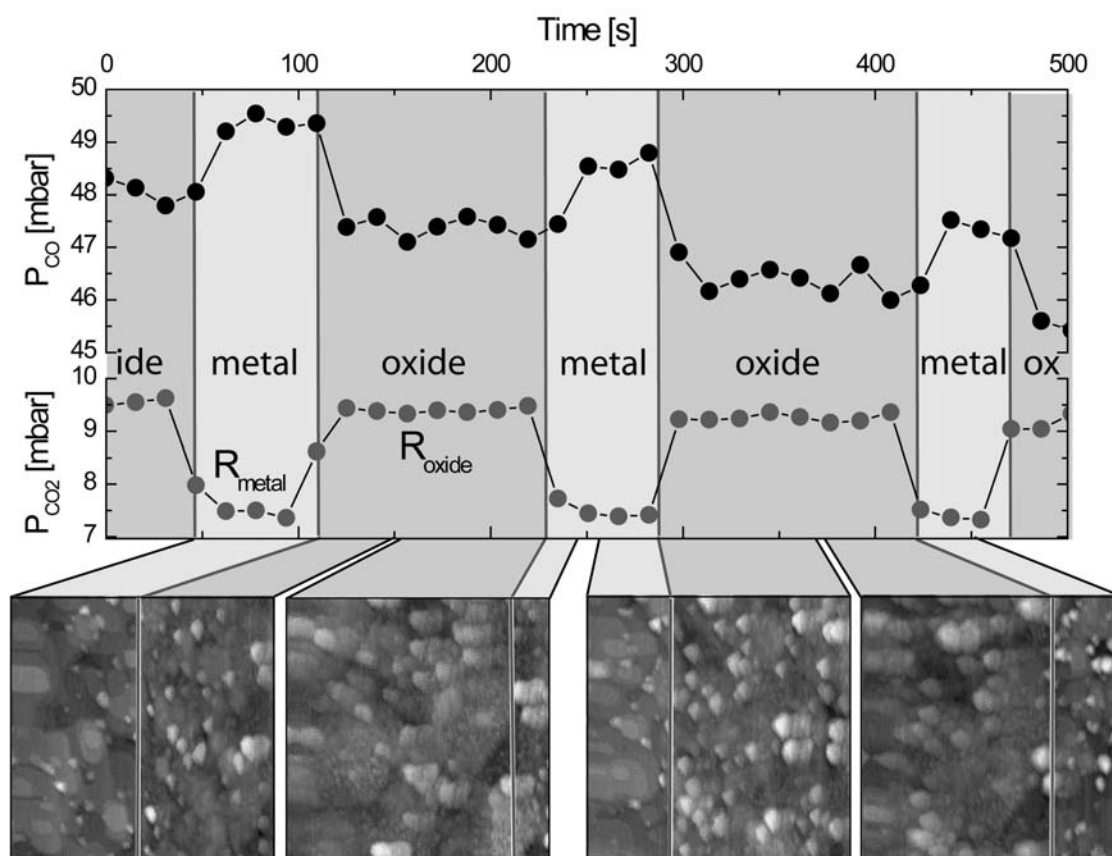


Figure 3: Spontaneous oscillations in the CO oxidation rate on Pd(001). The top panel shows the reaction rate (red) and the CO pressure (black), observed in a flow reactor at a constant oxygen pressure of 1200 mbar and a temperature of 408 K. The scanning tunneling microscopy images (image size: 100nm×100nm) have been recorded simultaneously with the CO_2 and CO pressures and show that the oscillations are accompanied by the oxidation and reduction of the Pd surface. The metal phase exhibits characteristic terrace-and-step configurations with the well-defined step height of Pd(001), while the oxide is rougher and shows no such order. These high-pressure scanning tunnelling microscopy measurements were performed in a dedicated ‘Reactor-STM’, which combined preparation and characterisation of the surface under ultrahigh vacuum conditions with STM experiments in an integrated flow-reactor cell at temperatures up to 500 K and pressures up to 5 bar [9, 23,78].

The lack of mobility within the oxide layer at the temperature of our experiments prevents the resulting roughness from decaying before further roughness is added by the same process. Figure 4 shows that in the oxide phase the roughness of the PdO layer gradually increases as a function of the total amount of CO converted to CO₂. Within the attainable window of roughness during one of our “CO pulse experiments” we see that the roughness varies roughly linearly with the total amount of produced CO₂. This is in good agreement with the assumed model of the roughness being induced by the CO oxidation reaction. On the contrary, in the metallic phase we observe high surface mobility and the reaction does not cause further roughening as it no longer runs through the Mars - Van Krevelen mechanism, so that the surface roughness slowly decays with time (see figure 1b, or chapter 4, figure 6).

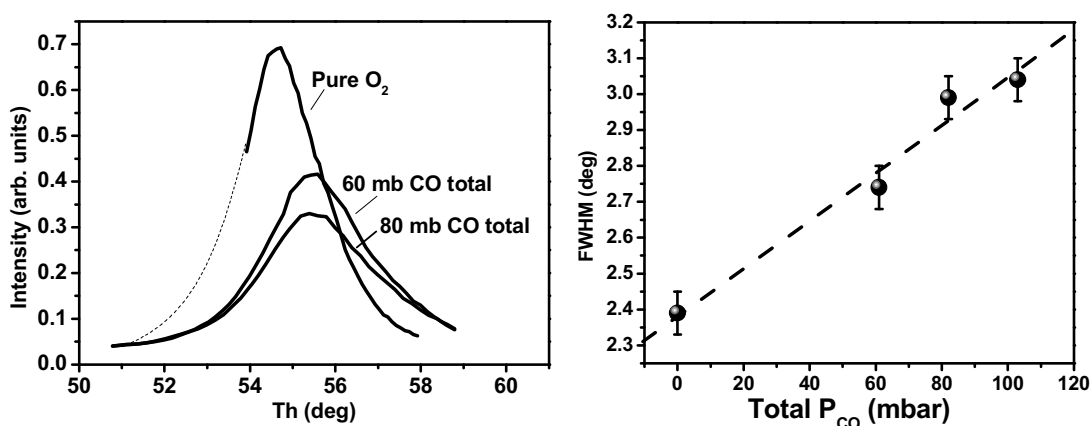


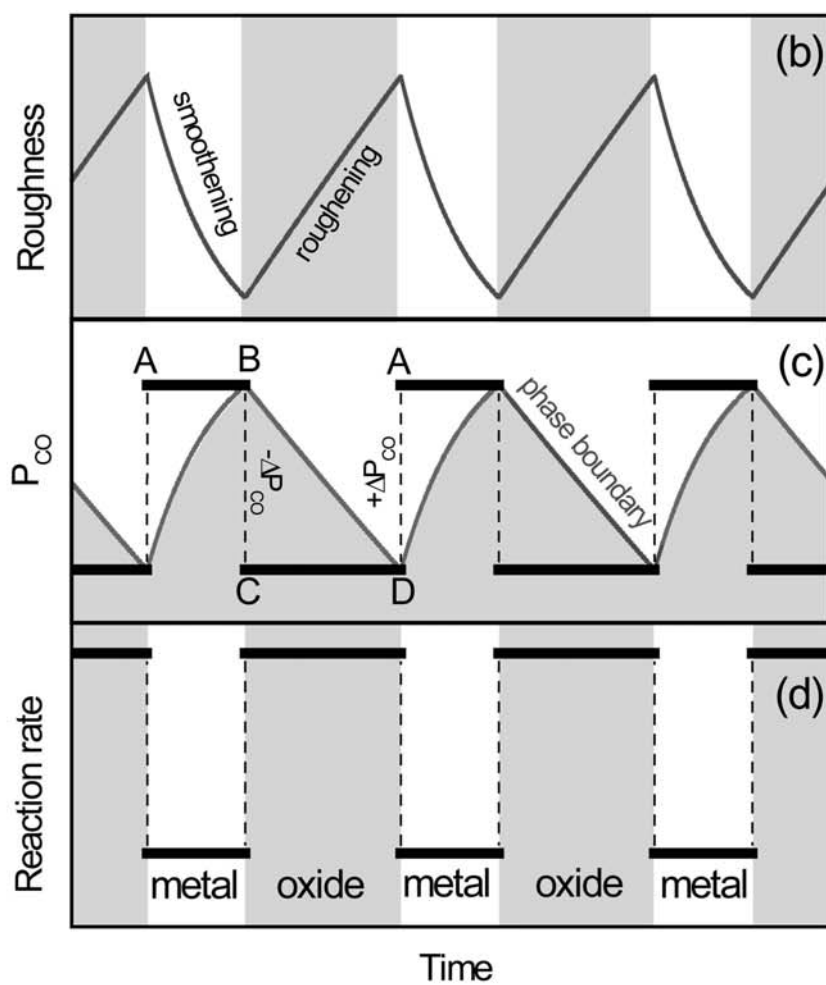
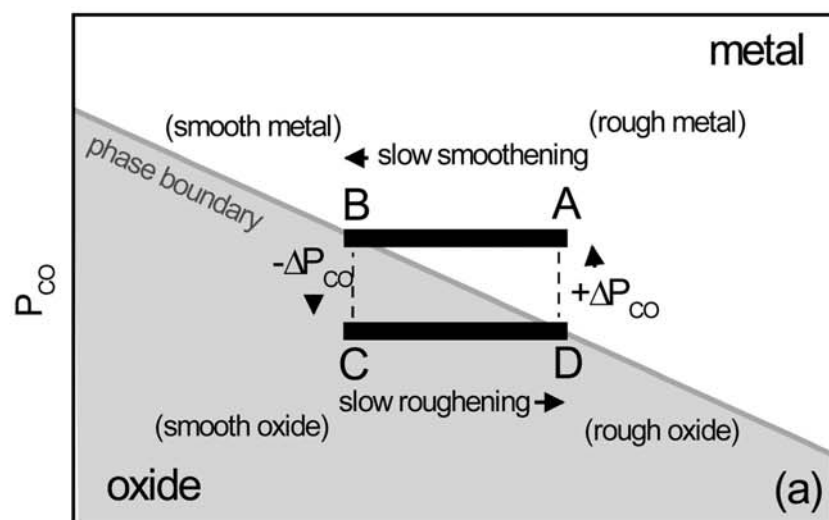
Figure 4: *Left panel:* Rocking scans around the surface normal of the diffraction maximum of PdO at (0.4 0.8 0.72). The scan made directly after forming the PdO layer in pure O₂ has the lowest FWHM, showing the most ordered PdO layer. After the surface has converted respectively 60 and 80 mbar of CO into CO₂, the rocking scans show a clear increase in FWHM, corresponding to a roughening of the surface due to the catalytic conversion of CO to CO₂. **Right panel:** Increase in FWHM as a function of the total conversion of CO. This roughening confirms the assumption of a Mars - Van Krevelen mechanism for this reaction on the thin PdO layer. The dashed line (right panel) is the lowest order fit for this measurement, indicating a linear increase in roughness due to CO oxidation.

Together with the influence of the step density on the metal-oxide transition, this accumulation and decay of roughness leads to a simple scenario for the self-sustained reaction oscillations (figure 5). Each cycle is composed of four steps or transitions, and four surface states: **(A)**→**(B)**→**(C)**→**(D)**→**(A)**. Each oscillation cycle follows these four steps:

(A)→(B): *smoothing metal*. The cycle starts with a rough metal surface (state **(A)**), as we find it immediately after the oxide-to-metal transition. The reaction follows the Langmuir-Hinshelwood reaction mechanism (gas adsorption and subsequent reaction), resulting under these conditions in a low reaction rate R_{metal} . In the metal phase the surface smoothens, which shifts the conditions towards the metal-oxide phase transition (P_{CO}^* increasing towards P_{CO}).

(B)→(C): *metal-to-oxide transition*. On the now smooth metal surface (state **(B)**) the step density has become low enough that $P_{CO}^* = P_{CO}$ and the surface ‘spontaneously’ oxidizes in a fraction of a second (state **(C)**). The reaction changes abruptly to the Mars - Van Krevelen mechanism (oxide reduction and re-oxidation) with the high reaction rate R_{oxide} . Now that more CO is being consumed, P_{CO} is reduced by ΔP_{CO} , which further stabilizes the oxide.

Figure 5: Generic model for the reaction rate oscillations. Each cycle takes the surface through stages **(A)** rough metal, **(B)** smooth metal, **(C)** smooth oxide, and **(D)** rough oxide, after which the next cycle starts again at **(A)**. Panel (a) shows the metal-oxide phase diagram (cf. figure 1), in which the phase boundary is determined by the roughness and the CO partial pressure P_{CO} . Per cycle ABCD the surface crosses this boundary twice (at B and at D). Panels (b)-(d) show the variations in roughness, P_{CO} , and reaction rate ($\sim P_{CO_2}$) during three complete cycles. While in the oxide phase, the surface becomes progressively rough, whereas it smoothens in the metal phase (panel b). As can be read off from panel (a), these variations in roughness introduce corresponding variations in the value of the metal-oxide transition, which are indicated by the green line in panel (c). At points B and D in the cycle, this critical P_{CO}^* value becomes equal to the actual CO pressure P_{CO} (black lines in panel c) and the phase transition takes place. Since the reaction rate on the oxide is higher than that on the metal (panel d), the CO pressure in the reactor switches up or down by $\pm \Delta P_{CO}$ every time the surface is reduced or oxidized (black lines in panel c). The period of the oscillation is determined by the magnitude of ΔP_{CO} and by the smoothing and roughening rates in the metal and oxide phases.



(C)→(D): *roughening oxide*. The Mars - Van Krevelen reaction mechanism leads to a slow build-up of surface roughness, creating a rough oxide surface. This, in turn, reduces P_{CO}^* towards P_{CO} .

(D)→(A): *oxide-to-metal transition*. When the oxide has become sufficiently rough that $P_{CO}^* = P_{CO}$ (state **(D)**) the system switches back to a (rough) metal surface (state **(A)**). The reaction changes abruptly to the Langmuir-Hinshelwood mechanism again, reducing the reaction rate to R_{metal} , thus increasing P_{CO} by ΔP_{CO} and further stabilizing the metal phase. This restores the starting conditions and closes the cycle.

All ingredients in this scenario (oxide roughening and metal smoothening, the dependence of P_{CO}^* on roughness, the different reaction mechanisms and rates and the resulting changes in local P_{CO}) are based on experimental observations.

5.3.1: Numerical model

We have tested the scenario in a simple numerical calculation, in which we modeled the roughness evolution and the dependence of P_{CO}^* on roughness with first-order differential equations. Details of this calculation are given below. Although the model is too crude to faithfully describe all details of the CO oxidation reaction on Pd(001) and produce an accurate fit to measured reaction oscillations, it fully captures the essence of the observed oscillations, such as the influence of P_{CO} on the oscillation period and on the ratio between the metal and oxide parts of the oscillations.

In our model, each of the two phases of the surface, metal and oxide, is characterized by two rates, namely the reaction rate of CO oxidation and the rate of change of the surface roughness. These rates are summarized in the table 1.

The reaction rate R_{metal} on the metal (equation 1) corresponds to the ‘text-book’ Langmuir-Hinshelwood kinetics in which O_2 adsorbs dissociatively and CO molecularly onto the surface. The amount of free positions on the surface is normalized to 1, and the oxygen needs two free adjacent positions to adsorb dissociatively. The constants k_1 and k_2 are ratios of the rate constants for adsorption and desorption of O_2 and CO respectively.

	Reaction rate	Rate of change in roughness
Metal phase	$R_{metal} = \frac{\sqrt{k_1 P_{O_2}} k_2 P_{CO}}{(\sqrt{k_1 P_{O_2}} + k_2 P_{CO} + 1)^2} \quad (1)$	$\frac{d\rho}{dt} = -a\rho \quad (2)$
Oxide phase	$R_{oxide} = k_3 P_{CO} \quad (3)$	$\frac{d\rho}{dt} = b(1-\rho)(R_{oxide})^n \quad (4)$

Table 1: Rate equations for the mathematical model describing self-sustained oscillations caused by formation of roughness in the oxide phase.

On the other hand the reaction rate on the palladium oxide surface in these conditions (equation 3) is proportional to the CO pressure and independent of the oxygen pressure, as observed in chapter 4.

We express the roughness of the surface in a dimensionless parameter ρ , which can vary between 0 (completely smooth surface) and 1 (maximally rough surface). On the metal surface there are several competing diffusion mechanisms that reduce the step density, each with its own non-trivial scaling behavior with time. In the *SXRD* experiments on Pt(110) under these temperature and pressure conditions however, we find that the net result is very well described by an exponential decay of the roughness with time (see chapter 2 of this thesis). In the model this is introduced by making the rate of roughness change proportional to $-\rho$ in the metallic phase (equation 2). On the oxide, roughness is observed as a ‘by-product’ of the reaction. In chapter 2, we have argued that in general the formation rate of the roughness should scale with the reaction rate $(R_{oxide})^n$. For the oxide on Pt(110) we have determined that the rate of production of roughness is best described with a model in which $n = 3$. For the oxide layer on Pd(001) however, we have only determined the total amount of roughness produced as a function of the total amount of CO converted to CO₂ (see chapter 4 of this thesis and [78]). As no further data is available, we have assumed n to be 1 in (equation 4) for the model describing the oscillations on Pd(001). Although this choice might result in a numerical difference between the model and the observed oscillations for Pd(001), it does not affect any of the intrinsic properties of the model. The extra factor $(1-\rho)$ in the

oxide's roughening rate limits the roughness to the interval $[0;1)$. The constants a and b in equations (2) and (4) are both positive.

An important element in the model is the change $\pm\Delta P_{CO}$ in local CO pressure when the surface switches from oxide to metal or vice-versa. As the CO flow is kept constant throughout all the STM experiments in which oscillation have been observed, this can only be caused by the change in reaction rate. The change in CO pressure is hence directly proportional to the change in reaction rate:

$$\Delta P_{CO} = c(R_{oxide} - R_{metal}) \quad (5)$$

where c is a positive constant. For oscillations under steady-state conditions R_{oxide} and R_{metal} are constant and so is ΔP_{CO} .

Finally and most importantly, we need to specify the relation between the CO pressure P_{CO}^* at which the metal-oxide phase transition takes place and the surface roughness ρ . As we have seen experimentally (figure 2) we can describe this by a linear relation

$$P_{CO}^*(\rho) = P_{CO}^*(0) - e\rho, \quad (6)$$

where e is a positive constant. When P_{CO} is higher than $P_{CO}^*(\rho)$, the surface is in the metallic phase with the reaction rate and roughness variation being prescribed by equations (1) and (2). When it is below $P_{CO}^*(\rho)$, the surface is in the oxide phase and the rates are given by equations (3) and (4).

Together, equations (1) to (6) successfully describe the characteristics of the self-sustained oscillations experimentally observed under steady-state reaction conditions as well as the transient oscillations observed during slow ramps in the CO partial pressure. The numerical scheme, based on equations (1) to (6) and that was used to calculate the reaction rate oscillations of figure 3, is shown in figure 6.

The reaction oscillations discussed here are *not* due to some non-linear type of dynamics, which forms the basis of all previously proposed models for

oscillatory oxidation reactions [77,82]. Also, there is *no* element of bi-stability in our model. The seeming bi-stability, both oxide and metal being stable under the same (T, P_{O_2}, P_{CO}) conditions, is removed when we also specify the roughness ρ . At each $(T, P_{O_2}, P_{CO}, \rho)$ combination only one of the two phases is stable.

Based on this model and simple diffusion and reaction-rate considerations, we predict that the oscillation period should be a strong function of temperature, with higher temperatures leading to much shorter periods. Another important element is hidden in the design of the reactor and, in particular, in the flow resistance of the gas line between the CO pressure regulator and the reactor, since this resistance determines the strength ΔP_{CO} of the pressure variations. This quantity dictates how wide or narrow the window is of pressures P_{CO} for which the system will exhibit spontaneous reaction oscillations and it also has a direct influence on the oscillation period. This aspect may be responsible for the

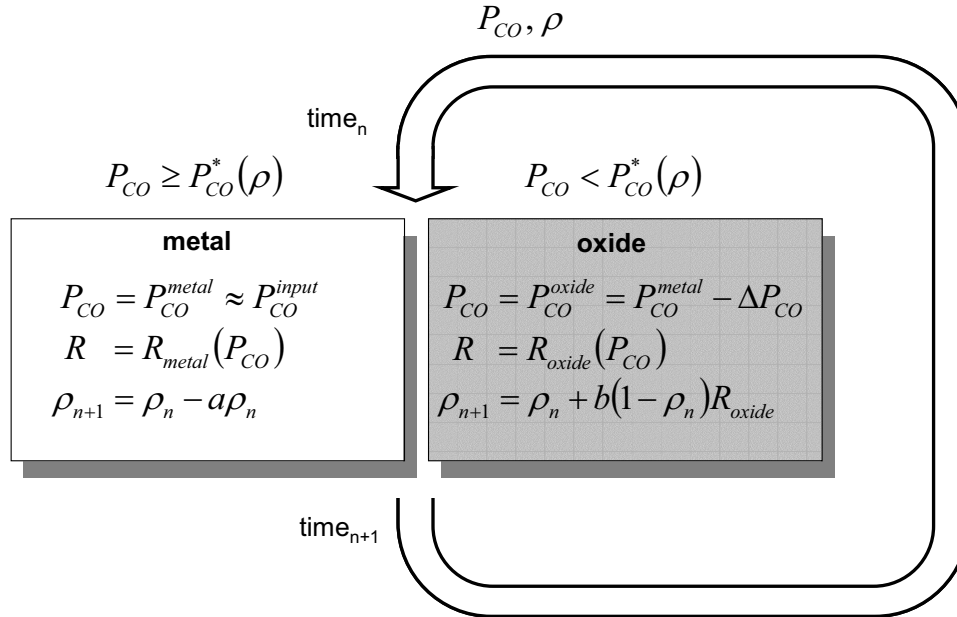


Figure 6: Scheme of the numerical model for self-sustained oscillations at constant oxygen pressure. At the beginning of each numerical time step the local CO pressure P_{CO} and the roughness ρ (through $P_{CO}^*(\rho)$) determine whether the surface is in the metal phase or in the oxide phase. If the system is in the metal phase the local CO pressure is equal to P_{CO}^{metal} , close to the partial pressure of CO in the supplied gas flow, the reaction rate follows equation (1), and the roughness decreases from ρ_n to ρ_{n+1} according to equation (2). In the oxide phase the local CO pressure is reduced by ΔP_{CO} as a result of the high reaction rate, $P_{CO}^{oxide} = P_{CO}^{metal} - \Delta P_{CO}$, the reaction rate follows equation (3), and the reaction induced roughness increases proportional to the reaction rate given by equation (4).

large variation in oscillation behavior found for the same reaction systems between different instruments or different research groups [92].

5.4 Conclusions:

Our scenario presents a new mechanism for oscillatory oxidation reactions at atmospheric pressure. It is not specific for Pd(001); we have observed similar oscillations in CO oxidation on several other Pd and Pt surfaces. As can be seen in chapters 2 to 4, the behavior of all the investigated single crystal surfaces of Pd and Pt is extremely similar with respect to reaction rate in the metallic and oxidized states, and the formation and removal of roughness in these respective states. Equivalent oscillation mechanisms, again involving the role of steps, may be at play in other catalytic reaction systems, e.g. other oxidation reactions or reactions involving the formation of other surface species, such as carbides, sulphides or nitrides.

The new role identified here for roughness in heterogeneous catalysis may serve as a specific target for future catalyst design; e.g. in the form of structural promoters that inhibit the formation of steps or enhance surface mobility and thus increase the decay rate of the roughness.

