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High-pressure STM studies of oxidation catalysis

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Chapter 4

New insights into the oscillatory behaviour of CO oxidation over platinum group metals

In this Chapter the most popular models described in the literature regarding the oscillatory behaviour of catalytic reactions such as CO oxidation are discussed. In order to explain the experimental observation introduced in Chapter 3, of oscillations between a metallic surface and a surface oxide, a new model is proposed. This new model involves two key features: (1) the observation that the oxide surface gradually roughens under reaction conditions and that the metal surface gradually smoothens and (2) the relation between the surface roughness and the CO partial pressure at which the surface switches between metal and oxide (and vice versa).

4.1 Introduction

The discovery by Belousov that during reactions involving HBrO_3 , bromomalonic acid and the redox couple $\text{Ce}^{3+}/\text{Ce}^{4+}$ in solution, the colour of the solution changed periodically under otherwise stable conditions, such as a constant temperature, has constituted the starting point of research of oscillatory chemical reactions [1]. Oscillatory behaviour of chemical reactions is a fascinating phenomenon, which can help in understanding the reaction mechanism of a catalyst and the mechanism of communication between different parts of a catalyst. Knowledge about the oscillatory mechanism may also be useful when trying to prevent potentially dangerous situations in practical, e.g. industrial processes, due for example to the periodic increase in the heat released by the reaction [2]. In addition, oscillations are sometimes deliberately forced onto a catalytic system by varying the reaction conditions. In this way sometimes better average conversion rates or selectivities can be obtained [3]. Sustained oscillatory behaviour has been observed in a large number of oxidation reactions catalysed by transition metals of Groups VIII and I B [4-9]. This behaviour is very well documented for the platinum catalysed oxidation of carbon monoxide [10], hydrogen [11], ammonia [12], ethylene [13], propylene [14], and other hydrocarbons. Oscillations during CO oxidation on Pd and Pt have been observed for a variety of catalyst configurations, e.g. in the form of a single crystal [15], a wire [16], a foil [17] or supported on a pellet [18], under a variety of conditions, involving low and high gas and catalyst

temperatures and (partial) pressures ranging from UHV [19,20] to atmospheric pressures [7,20-22]. In the course of previous attempts to explain the origin of reaction oscillations a large number of mathematical models has been suggested in the literature. In spite of the large number of studies there is no agreement yet on the chemical source of the behavior. It is also not clear whether all observations of catalytic oscillations share the same origin [23]. From the mathematical point of view the description of the oscillatory evolution of the gas concentrations and other relevant aspects of the reaction system can be described by means of an appropriate set of differential equations [24-27]. Often, these differential equations are not linear. As a consequence the oscillatory catalytic systems have been classified as *non-linear* [24-27]. It is well established in the literature that in order to meet the conditions for oscillations the catalytic system should be sufficiently far from thermodynamic equilibrium [28]. In the previous chapter the concept of *bistability* has been introduced. In a system exhibiting bistability, we can have oscillations between the two levels of the reaction rate. A requirement for such oscillations is the existence of a *feedback* mechanism, which allows the periodic transition of the system between the two states [27-30].

In some catalytic systems the oscillatory process is even more complicated. By adjusting the reaction parameters the system can make the transition from one to two to four to eight, etc. levels, which introduces several doublings of the oscillation period. This scenario is illustrated in figure 4.1, which represents the Feigenbaum diagram or *Feigenbaum scenario* to chaos [31]. It shows the rate of the reaction as a function of some suitable reaction parameter λ , which could be the temperature or a ratio of concentrations. The left side of the diagram contains only one branch, corresponding to the conventional situation in linear kinetics. There the reaction system is not too far from the equilibrium state and there is one rate of reaction for each set of reaction conditions. If the system deviates from equilibrium to the point where the reaction parameter exceeds a critical value, the system becomes unstable and oscillates between two states, for example between the two surface structures (reconstructed and unreconstructed) of Pt(110) during CO oxidation. If the reaction parameter exceeds a next critical value, the number of available branches for the rate doubles again and the reaction cycles between four levels. The final transition on the right-hand side of the Feigenbaum diagram is to an infinitely long period and infinitely many levels, a situation referred to as chaos [31].

4.2 Traditional models for reaction oscillations

Since this thesis is mainly devoted to CO interaction with various Pd and Pt single-crystal surface in this section we will summarize the models proposed

previously, in particular for the oscillatory behaviour of CO oxidation over various platinum-group catalysts.

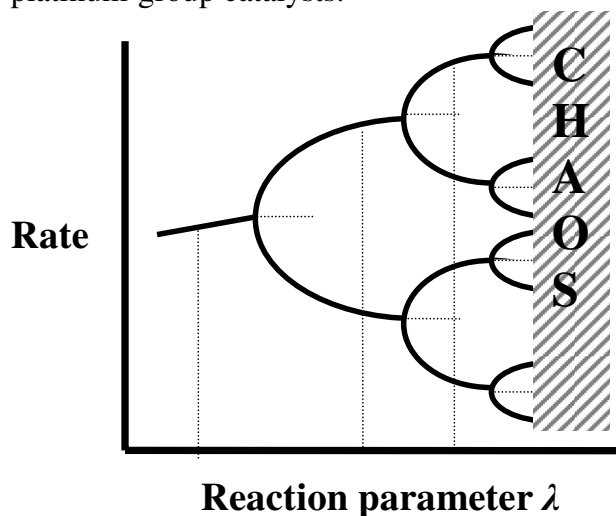


Figure 4.1: Schematic representation Feigenbaum diagram: if the reaction parameter λ deviates sufficiently from equilibrium conditions, the rate of the reaction may develop oscillations between two, four, eight, ... levels. At high deviation from equilibrium the system may behave chaotically. After [29].

Adsorbate-induced surface structural transformation

This model, also known in the literature as the reconstruction model is based on the facts that the topmost metal layers of a single crystal can reconstruct and that different reconstructions show different adsorption behavior. The first kinetic oscillations linked to an adsorbate-induced surface structural transformation have been observed for the (100) surface of platinum. Clean Pt(100) exhibits a quasi-hexagonal reconstruction, which can be transformed into the bulk like, unreconstructed (1×1) structure by the adsorption of a variety of gases. CO oxidation over Pt(100) will be described in detail in Chapter 6. Here, we illustrate the reconstruction model using the example of Pt(110). A freshly prepared, adsorbate-free Pt(110) surface shows the (2×1) periodicity of the so-called “missing row” reconstruction [32-34]. CO adsorption lifts this reconstruction and a phase transition to a (1×1) structure occurs. In spite of the fact that this unreconstructed surface is CO covered and has a low reaction rate, its sticking coefficient for oxygen atoms is twice as high as that on the reconstructed surface. In other words oxygen will adsorb even though CO to some extent inhibits the process. Under oscillation conditions the increased consumption of CO can now make the surface flip to become predominantly O-covered. With no CO to stabilize the surface against the missing-row reconstruction, the surface will reconstruct again. In turn, this surface has a low sticking coefficient for

oxygen. This situation enables CO to take over, so that the surface becomes again CO-covered and it switches back to the unreconstructed phase. This completes one oscillation cycle and sets off the next one [32-34].

Faceting model

Faceting is a process, which causes an initially flat, single-crystal surface to separate into two (or three) other surface orientations [35]. This process has been studied intensively on Pt(110) [36-38]. By exposing the surface under appropriate conditions to a constant CO+O₂ flow, structural transformations of the surface have been observed. The experimental data (diffraction patterns) revealed that the structure of the facets consists of steps with a (100) orientation and (110) terraces [37]. The faceting of Pt(110) is associated with an increase in catalytic activity, which is connected with the formation of (100) steps in the faceting process, since these exhibit a higher sticking coefficient for oxygen compared to the flat (110) surface [28,39]. There is a high temperature limit for faceting, at about 530 K above which no faceting can take place (depending on partial pressures). A CO covered (1x1) surface constitutes the starting point of an oscillation cycle. On this surface the reaction rate is low and the facets grow slowly. These facets have a high sticking coefficient for O₂, and at a certain point the surface becomes oxygen-covered. This destabilizes the facets and they are removed by surface diffusion of Pt atoms. The surface becomes CO-covered again and the cycle starts all over [28, 40].

Carbon model

A different mechanism for the oscillations was first suggested by Burrows *et al.* [41] and further developed by Collins, Sundaresan, and Chabal in 1985 [42]. In short, in this model the adsorption sites on the catalyst surface are blocked by carbon impurities. Two sources for carbon impurities have been suggested. The first one refers to the diffusion of atomic carbon from the bulk metal, while the presence of hydrocarbons in the gas stream constitutes the second source. According to the carbon model the oscillations result from the cyclic activation and deactivation of adsorption sites, by atomic carbon impurities.

Subsurface oxygen model

Some authors have proposed that the origin of the oscillations in a catalytic system is the formation of a different oxygen species, called “subsurface oxygen”. The subsurface oxygen model was first put forward to explain the oscillatory behaviour of Pd(110) [43]. At low P_{co} some fraction of the oxygen atoms of an oxygen-covered surface are thought to penetrate below

the outermost atomic layer of the Pd catalyst. The subsurface oxygen species is thus in thermodynamic equilibrium with the chemisorbed oxygen on top. Experimental evidence for the existence of subsurface oxygen has been acquired by TDS, XPS, ion scattering, and titration techniques [44]. The oscillation mechanism can be rationalized as follows: starting with an active oxygen-covered surface (high reaction rate branch) oxygen starts to penetrate into the subsurface region. This leads to a deactivation of the surface as the surface becomes CO-covered (low reaction rate branch). But as soon as subsurface oxygen begins to diffuse back to the surface and reacts with CO, the decreasing subsurface oxygen concentration leads to a reactivation of the surface and the initial situation is established again.

Oxidation-reduction model

In 1981, Sales, Turner and Maple have explained their experimental observation of kinetic oscillations in CO oxidation on polycrystalline Pt, Pd and Ir at atmospheric pressure by a model in which they have included the formation of a surface oxide [7, 45]. The basic idea of their model is that the slow oxidation and reduction of the metal surface layer can induce transitions between the two branches of a Langmuir-Hinshelwood reaction. The model is based on the following assumption: the oxide formation blocks the site with respect to CO and O₂ chemisorptions; the rate of the oxide formation is proportional to the concentration of adsorbed oxygen and the fraction of free sites for oxide formation in the subsurface layer; the oxide reduction is assumed to proceed via the interaction with adsorbed CO [28, 45].

4.3 Comparison with experimental observations

Most of the models reviewed above, with exception of the oxidation-reduction model of Sales, Turner and Maple, are based on experimental results obtained under UHV conditions. The importance of investigating these phenomena under more realistic conditions has been emphasized before in this thesis. The high-pressure STM experiments in Chapter 3 have revealed that during CO oxidation over Pd(100) and Pd(1.1.17) the reaction rate spontaneously oscillates between two states, one with high reactivity and the other with low reactivity. In the next chapter we show similar behaviour for CO oxidation over Pt(111). In this section we confront the models discussed above with these experimental results. We will see that none of these models apply. In order to substantiate this point, we recall the main conclusions of our observations in Chapter 3. At atmospheric pressures and elevated temperatures CO oxidation on Pd(100), Pd(1.1.17) and Pd(553) can occur in two different modes. On the metal surface the reaction follows the classic Langmuir-Hinshelwood mechanism, with CO molecules and O

atoms competing for adsorption sites and with the reaction rate going through a distinct maximum as a function of the partial pressure of either CO or O₂. At sufficiently high oxygen partial pressure and/or sufficiently low CO partial pressure the surface undergoes a first-order phase transition to a surface oxide. Evidence for the oxidation was seen in the STM images and confirmed by SXRD. The simultaneously performed kinetic measurements show that the oxide exhibits a higher reactivity to CO oxidation than the original metal surface. On the oxide the reaction follows the Mars van Krevelen mechanism, according to which a CO molecule reacts with an oxygen atom from the oxide lattice. The resulting oxygen vacancies are refilled with oxygen from the gas phase. During the reaction the temporarily uncoordinated Pd atoms sometimes diffuse out of the surface layer forming pits and protrusions. As a consequence the roughness of the oxide surface gradually increases. The metallic surface observed immediately after the oxide has been removed shows a high step density due to the formation of adatom and vacancy islands. Surface diffusion is seen to smoothen the metallic surface, making it evolve towards the initial, flat metallic surface that formed the starting configuration, before the oxidation process. Another important outcome of the experiment is the observation of spontaneous oscillations in the reaction rate, which were shown to go back and forth between the metal (with LH kinetics) and the oxide with (MvK kinetics). We have observed such oscillations for Pd(100) and its vicinal surface Pd (1.1.17). No oscillations have been observed during CO oxidation on Pd(553). Figure 4.2 illustrates the oscillation of the CO oxidation reaction on Pd(100) in a constant reactant flow at ambient pressures. We clearly see how the reaction rate spontaneously switches periodically between two levels, labelled R_{oxide} and R_{metal} . The oscillations in CO₂ production are in anti-phase with the variations in CO pressure, as a result of the difference in the CO consumption at the two reaction rates. The accompanying STM images that were acquired simultaneously show that during the periods with the low reaction rate the height variations of the surface are all multiples of the Pd(100) step height and a square symmetry is visible in the step orientations, which is the geometry that we have recognized before (Chapter 2) as the metallic state. All images during the high rate show the disordered, rough character of the surface oxide. Even during the few minutes of a reaction oscillation period we observe that the surface roughness increases in the oxide phase and decays in the metal phase. As already explained in the previous chapter the oscillations are periodic switches between the low-activity metal phase and the high-activity oxide. The terrace and step configurations of the metallic phase are reflecting the geometry (square symmetry) and the step height of Pd(100), while the oxide phase has a disordered, rough appearance. Despite the fact that metal-oxide and oxide-metal transitions take only a fraction of a second, the period of an oscillation can be several minutes.

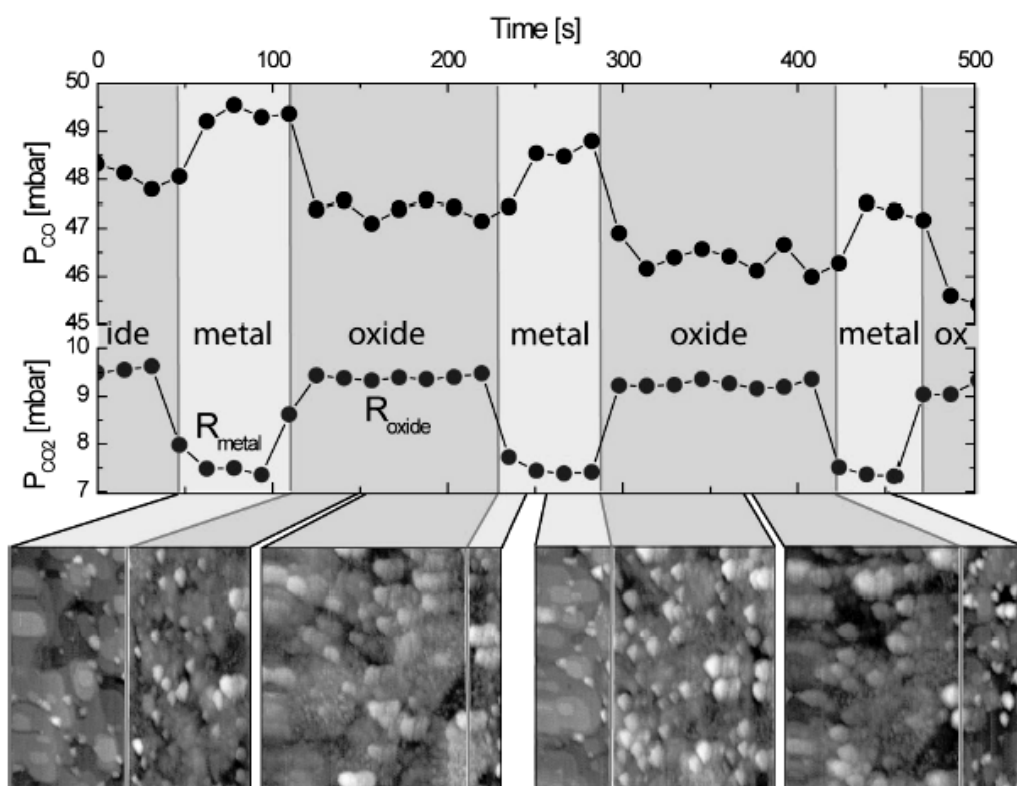


Figure 4.2: Spontaneous oscillations in the CO oxidation rate on Pd (100) at a constant oxygen pressure of 1.25 bar and temperature of 408 K. The combination of the reaction rate and simultaneously recorded STM images (100 nm × 100 nm) shows that the oscillations are the periodic oxidation and reduction of the surface. $V_i=100$ mV, $I_i=0.2$ nA.

As will be discussed below, we attribute the long oscillation period to the slow variation of the surface roughness. Indeed, even during the short times in Fig.3.2 that the surface stays in the metal phase, we observe a decrease in surface roughness, while the roughness can be seen to increase somewhat in the oxide phase.

Since clean Pd surfaces and Pt(111) do not reconstruct, kinetic oscillations attributed to adsorbate-driven transformations of the surface structure, such as (de)-reconstruction, are unlikely. Contrary to Pt(110) [36-38], the Pd(110) surface does not undergo faceting during CO oxidation, so also the faceting scenario can be ruled out as the cause for reaction oscillations on the palladium surfaces. Although it would be difficult to exclude the possibility of sub-surface oxides, based on the STM observations alone, our SXRD measurements provide additional, strong evidence for the formation of a surface oxide, rather than a mere sub-surface

layer of oxygen [46]. So, we are forced to also disqualify the sub-surface oxygen model. The SXRD observation of surface oxides on Pt and Pd surfaces makes the oxidation-reduction model of Sales, Turner and Maple (STM) a very interesting, potential explanation for the oscillations observed during high-pressure CO oxidation over palladium model catalysts. However, there is one striking difference between this model and our measurements. STM model assumes that the surface oxide formed at ambient pressures shows no reactivity at all. By contrast, our combined “in situ” STM and SXRD measurements clearly prove that the formation of the surface palladium (platinum) oxides are associated with higher catalytic activity than that on the metal.

We have arrived at the conclusion that none of the existing models for reaction oscillations apply to our observations on Pd(100) and Pd(1.1.17). In the next we introduce a new mechanism that is fully consistent with all our observations for reaction oscillations during CO oxidation.

4.4 The role of roughness

On the basis of the experimental results that have been discussed in the previous chapter plus additional results obtained with SXRD [46], Hendriksen *et al.* have proposed a new model for the origin of oscillations on palladium surfaces [47]. There are two new elements in this new scenario that combine to cause the oscillatory behaviour of CO oxidation on Pd surfaces. The first essential ingredient is the continuous roughening of the oxide surface and the smoothening of the metal surface observed under reaction conditions. The other key element is a one-to-one relation between the roughness (step density) of the surface and the conditions, e.g. the partial pressure of CO, at which the transition metal-oxide takes place.

The idea that the roughness of a catalyst plays an important role in the dynamic behaviour of a chemical reaction is not new. There is a lot of literature containing experimental observations about oscillatory phenomena associated with oxidation reactions on unsupported catalytic surfaces as wires and gauzes on a variety of materials, such as Pt, Pd, Ni and their alloys. Summarizing the experimental results reported in the literature, we identify three aspects that stand out [48]:

- i) Completely smooth wires do not readily ignite, but must “activated” by heat treatment, which roughens the surface [49-52]
- ii) Smooth wires do not exhibit reaction oscillations and analysis of the simple models confirms that such oscillations should not be possible [53]
- iii) Roughened wires oscillate for a rather wide range of catalysts and reactant gases, and these oscillations tend to be very complex (a complete overview of these observations has been given in reference [48]).

We now show how surface roughness can play an important role also in the oscillations of oxidation reactions on single crystals. Figure 4.3 summarizes the four stages of our oscillations model.

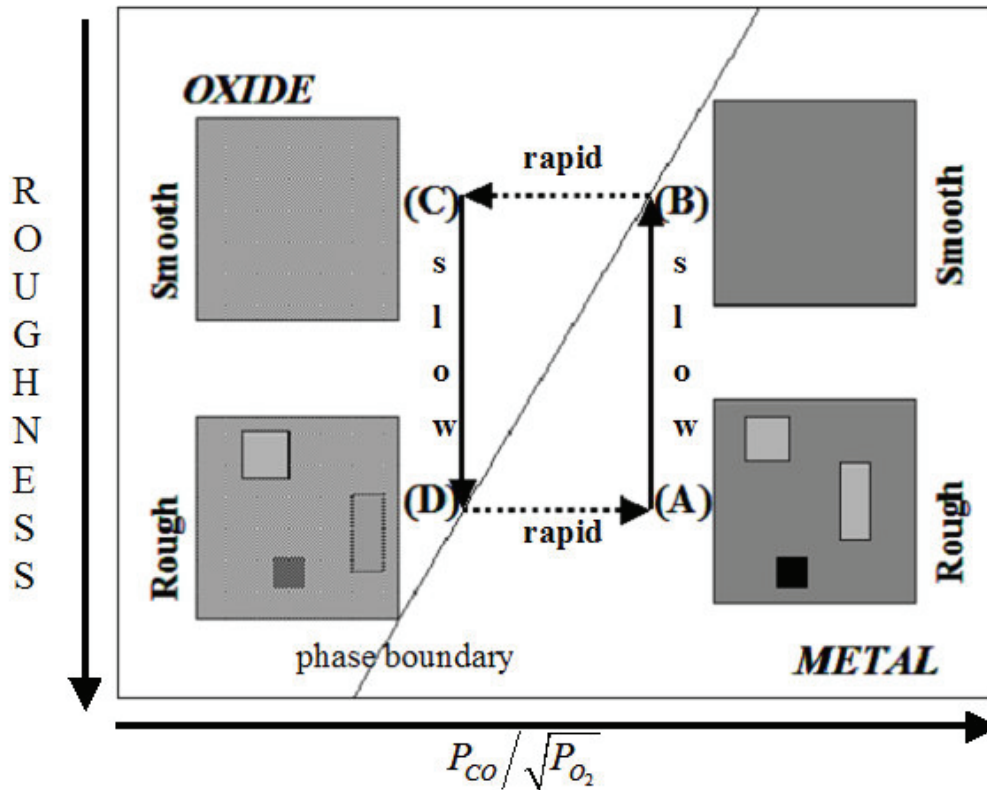


Figure 4.3: Schematic representation of an oscillation cycle. The starting point is a rough metallic surface. In the metallic phase, the surface smoothens. When the step density has reduced sufficiently, the surface suddenly oxidizes. The reaction on the oxide makes the surface increasingly rough. When the roughness is strong enough the oxide is suddenly removed and the surface is back to metallic and rough. The difference in reaction rate on the metal and the oxide leads to a noticeable difference in P_{CO} in the reactor.

We start our description of an oscillation cycle with a rough metal surface (situation A in Fig. 4.3). As explained previously the reaction on the metallic surface follows the Langmuir-Hinshelwood mechanism (gas adsorption and reaction, followed by desorption of the product) and results in a low reaction rate R_{metal} . The first part of the cycle (A)→(B) is the observed *smoothening* of the rough metal surface (cf. Fig. 4.2). The second part of the cycle (B)→(C) is the sudden *metal-oxide transition*. It takes place when the step density has become low enough. While the surface is in the oxidized state, the reaction follows the Mars-van-Krevelen mechanism with a high reaction rate R_{oxide} . In the third stage (C)→(D) the oxide becomes progressively *rough*. We have explained previously that this is due to the

Mars-van-Krevelen mechanism, which leads to temporarily undercoordinated metal atoms that become mobile for a brief period of time. Finally, the fourth part of the cycle (D)→(A) is the *oxide-metal transition*. When the oxide has become sufficiently rough the system switches back to a (rough) metal surface with lower reactivity R_{metal} .

The self-sustained cycle proposed in Fig. 4.3 is possible by virtue of a dependence of the critical CO pressure – or, more accurately, the ratio $P_{Co}/\sqrt{P_{O_2}}$ – at which the surface switches between metal and oxide or vice versa and the roughness (step density) of the surface. Indeed, such a one-to-one correspondence has been measured in high-pressure SXRD experiments [46]. There are several ways in which such dependence can be introduced. For example, when the difference in adsorption energy between CO molecules and O atoms is stronger at the steps than on the terraces of a Pd surface, the free energy of a surface with steps will reduce more quickly as a function of the CO partial pressure than that of a step-free surface. If this effect is stronger on the metal surface than on the oxide, this shifts the critical CO pressure down for rougher surfaces.

There are several qualitative features to our roughness model that can be checked immediately. For example, the timing of the oscillations should exhibit strong temperature dependence. In particular, we may expect that the time required for the metal surface to smoothen is reduced at higher temperatures due to the faster diffusion. This trend seems to be consistent with the data in Fig. 3.9, but more measurements will be necessary over a wider range of temperatures in order to really prove this point. Also, the steps introduced deliberately by turning to vicinal surfaces in Chapter 3 should have a significant effect. First of all, they should shift the critical P_{Co} to lower values than that on the low-index (100) surface, which appears to be consistent with our observations in Chapter 3. Secondly, the steps of the vicinal surfaces very much reduce the typical distance over which metal atoms need to diffuse in order to smoothen the surface, thus noticeably shortening the time that the surface spends in the metallic phase. The shape of the oscillations should therefore change for vicinal surfaces to relatively long periods of oxide phase with relatively brief interruptions by a short-lived metallic phase. Also this change in character can be recognized in the experimental data in Chapter 3 for the Pd(1.1.17) surface. Finally, when the step density is very high, the variation in roughness introduced by the oxide and metal phases becomes very small, which should make the oscillation period rather short and it should make the window of conditions over which the reaction oscillates very narrow. This seems to be the case for the Pd(553) surface, which we have not been able to bring into oscillation.

A complete description of the roughness scenario, including full mathematical details of the rate equations behind the model, will be provided in a future publication [46-47].

4.5 Conclusions

Regarding the oscillatory behaviour of catalytic systems we have briefly reviewed the most well-known models in the literature. We have also indicated where they fail to explain the experimental data introduced in Chapter 3. A new model has been proposed that provides a natural explanation of our data. The model involves two key quantities and a phase boundary between the two states of the catalyst (metal with low activity and oxide with higher activity). One of the key quantities is the partial pressure of CO. During oscillations, changes in this quantity always drive the system away from the phase boundary. The other quantity is the surface roughness. During the oscillations, the variations in roughness are such that they drive the system back to the phase boundary. Our model is fully rooted in experimental observations. The qualitative features predicted by the roughness model are consistent with the oscillations measured on Pd(100) and Pd(1.1.17).

The mechanism introduced in this chapter is not necessarily restricted to the oxidation of CO on Pt-group metals. We speculate that similar scenarios could be behind oscillations of other catalytic reaction systems.

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