Growth and decay of the Pd(111)–Pd$_5$O$_4$ surface oxide: Pressure-dependent kinetics and structural aspects

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Abstract

Growth and decomposition of the Pd$_5$O$_4$ surface oxide on Pd(111) were studied at sample temperatures between 573 and 683 K and O$_2$ gas pressures between $10^{-7}$ and $6 \times 10^{-5}$ mbar, by means of an effusive O$_2$ beam from a capillary array doser, scanning tunnelling microscopy (STM) and thermal desorption spectrometry (TDS). Exposures beyond the p(2×2)O adlayer (saturation coverage 0.25) at 683 K (near thermodynamic equilibrium with respect to Pd$_5$O$_4$ surface oxide formation) lead to incorporation of additional oxygen into the surface. To initiate the incorporation, a critical pressure beyond the thermodynamic stability limit of the surface oxide is required. This thermodynamic stability limit is near $8.9 \times 10^{-6}$ mbar at 683 K, in good agreement with calculations by density functional theory. A controlled kinetic study was feasible by generating nuclei by only a short O$_2$ pressure pulse and then following further growth kinetics in the lower ($10^{-6}$ mbar) pressure range.

Growth of the surface oxide layer at a lower temperature (573 K) studied by STM is characterized by a high degree of heterogeneity. Among various metastable local structures, a seam of disordered oxide formed at the step edges is a common structural feature characteristic of initial oxide growth. Further oxide nucleation appears to be favoured along the interface between the p(2×2)O structure and these disordered seams. Among the intermediate phases one specifically stable phase was detected both during growth and decomposition of the Pd$_5$O$_4$ layer. It is hexagonal with a distance of about 0.62 nm between the protrusions. Its well-ordered form is a $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ superstructure.

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Isothermal decay of the PdO4 oxide layer at 693 K involves at first a rearrangement into the $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ structure, indicating its high-temperature stability. This structure can break up into small clusters of uniform size and leaves a free metal surface area covered by a $p(2 \times 2)$O adlayer. The rate of desorption increases autocatalytically with increasing phase boundary metal-oxide. We propose that at close-to-equilibrium conditions (693 K) surface oxide growth and decay occur via this intermediate structure.

Keywords: Palladium; Oxidation; Surface oxide; Thermal desorption spectroscopy; Scanning tunnelling microscopy; Nucleation; Phase growth; Autocatalytic decomposition

1. Introduction

Catalytic combustion of hydrocarbons on Pd catalysts has received extensive attention due to the growing interest in power generation with gas turbines [1,2] and due to the need for removing small amounts of methane from emissions of fuel engines [3]. Because of the lower operating temperature catalytic combustion lowers NOx emissions, but a number of problems remain associated with the activity, stability and durability of the supported Pd catalysts. The complex kinetic behaviour of oxidation and reaction is connected with a pronounced kinetic hysteresis between formation and decay of the PdO bulk oxide phase. This redox hysteresis, playing a crucial role in all attempts to sustain and control catalytic activity, has been an important topic in the literature [4–6]. It is known that the surface and bulk properties of the O/Pd system are quite variable and that both morphology and catalytic activity are a function of oxygen pressure and temperature [7–9]. The bulk PdO phase is stable at low temperature and decomposes into metallic Pd and oxygen upon heating. On the other hand, palladium oxide is known for its high overall catalytic activity in the low-temperature regime and is expected to show a better catalytic performance than the metal in low-temperature combustion [7,10].

The two-dimensional Pd3O4 surface oxide phase on Pd(111) can be regarded as a well-defined intermediate state between chemisorbed oxygen on Pd metal and PdO bulk oxide. In a recent study [11] its structure was resolved by scanning tunneling microscopy (STM), surface X-ray diffraction (SXRD), high resolution core level spectroscopy (HRCLS), and density functional calculations (DFT). A combination of these methods revealed a purely two-dimensional incommensurate structure without resemblance to bulk oxides of Pd. In [11] it is also demonstrated how the atomic arrangement of a non-trivial incommensurate surface can be determined by molecular dynamics in a case where experimental techniques alone do not give a solution. In this computational work, the structure was resolved by an extensive search of the configuration space by first melting and then crystallizing Pd$_x$O$_y$ overlayers of different composition on a Pd(111) substrate, the only experimental input being the periodicity of the overlayer, as determined by LEED and STM. SXRD and HRCLS measurements and the perfect agreement of the simulated STM image with experiment confirmed the structure. In particular, the presence of differently coordinated coplanar O and Pd atoms within the 2D structure were clearly resolved in the HRCLS experiments and allowed for a safe distinction of Pd$_3$O$_4$ from any crystallographic plane of bulk PdO that would exhibit a chemically uniform environment of all Pd and O atoms. Moreover, the oxygen coverage calculated from the Pd$_3$O$_4$ structure in [11] could be verified in the present work by TPD calibration (section 2.1). The stoichiometry corresponds to a mean oxygen coverage of $1/\sqrt{3} = 0.58$ monolayers oxygen, referenced to bulk terminated Pd(111). The catalytic properties of Pd$_3$O$_4$ are still unknown, but may be very important for approaching microscopic understanding of the kinetic hysteresis between oxidation and reduction. In the present work we report new kinetic and structural aspects of the formation and decay of this surface oxide phase. Surface phase growth and decay are important factors in kinetic rate oscilla-
tions on Pd surfaces during oxidation of CO [12,13] and methane [14–16]. King [17] have convincingly shown that non-linear pressure-dependent phase growth must be considered a general reason for non-linear coupling of reaction steps in oscillating surface reactions. Hence, a detailed knowledge of the kinetics of formation and decay of oxygen-containing surface phases is needed to understand this hysteresis and the corresponding reaction regimes during catalytic oxidation.

From previous work it is known that a palladium surface is oxidized in several steps: dissociative chemisorption of oxygen, incorporation of oxygen atoms at step edges and defects, oxygen migration into the bulk, and, eventually, bulk oxide formation. Conrad et al. [18] were the first to report dissociative adsorption of oxygen on the Pd(111) surface under UHV conditions at room temperature, resulting in a p(2×2)/O structure with a saturation coverage of 0.25 monolayers (ML). Later it was shown that increasing oxygen exposure at higher pressure and temperature results in a higher oxygen coverage connected with restructuring of the metal surface. Different oxygen binding states were observed and assigned to subsurface oxygen and/or to two-dimensional oxide phases [19–26]. From ellipsometry and LEED measurements Voogt et al. [23] concluded that a surface oxide forms at a mean coverage of about 0.5 ML, which could not be simply assigned to a single bulk PdO plane on top of Pd(111). Higher oxygen coverages could be achieved by replacing molecular oxygen by nitrogen dioxide due to its higher oxidation potential [22,24]. In a combined STM, LEED and TPD study, Zheng and Altman [24] exposed the Pd(111) surface to NO₂ between 298 and 575 K and observed the consecutive formation of several intermediate states between metallic Pd and PdO, among them a “rectangular” structure formed on the Pd(111) terraces and a “square” structure prevailing on islands and peninsulas. It has not been studied, however, whether comparable structures are formed on Pd surfaces exposed to O₂. The kinetics of oxygen adsorption and desorption in the high-coverage range, measured upon exposure to effective pressures above 10⁻⁵ mbar, were unambiguously connected with formation and decay of a particular “high-density” phase [27]. As mentioned in detail above, the structure of this “square” phase, originally reported in [23,24], was finally resolved as the two-dimensional Pd₅O₄ oxide on top of the close-packed Pd(111) substrate [11]. DFT calculations [11,28,29] reveal its thermodynamic stability at intermediate oxygen pressures, between the stability ranges of the p(2×2) adlayer and of the bulk oxide PdO.

2. Experiments and computational methods

2.1. Kinetic measurements

The UHV chamber for kinetic measurements was equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), an effusive beam doser based on a capillary array for directional adsorption experiments (Galileo Optics, setup similar to that reported in [30]), and a differentially pumped quadrupole mass spectrometer (QMS) for line-of-sight detection of molecules desorbing from the central part (a 3 mm diameter spot) of the Pd(111) face. Calibration of beam fluxes was achieved by measurement of the pressure decrease in a differentially pumped gas dosing system by means of a MKS Baratron absolute pressure transducer [26]. A second QMS monitoring the pressure changes in the main chamber was used for King and Wells sticking measurements [31]. In the given geometry only about 80% of the gas effusing from the doser hits the sample, and the accurate value of this fraction had to be determined by comparison of the initial sticking probabilities of CO and O₂ with data from supersonic beam experiments [32,33]. Temperature programmed desorption (TPD) spectra were obtained with a heating rate of 10 K s⁻¹. Oxygen uptake was quantified by TPD peak integration. We define a gas dose of 1 MLE (monolayer equivalent), as a 1:1-ratio of oxygen atoms to 1.53×10¹⁹ Pd surface atoms/m² in the (111) bulk-terminated monolayer (ML). Exposures to molecular oxygen are given in Langmuir (1 L = 10⁻⁶ Torr s), or in monolayer equivalents (MLE) of O atoms, i.e. the twofold kinetic impingement rate of molecular O₂. At a gas temperature of
2.2. STM experiments

Scanning tunnelling microscopy (STM) was performed in a UHV chamber with a base pressure below $10^{-10}$ mbar, equipped with a customized Omicron micro-STM with electrochemically etched tungsten tips, a cylindrical mirror analyser for Auger electron spectroscopy, and LEED optics. The usual means for surface preparation were available in a separate preparation chamber containing an ion sputter gun for sample cleaning and an electron beam heater. A clean surface was routinely obtained by cycles of argon ion bombardment (2 keV, typically 1.5–1.8 µA for 30 min) and consecutive annealing at 1073 K. After a few preparation cycles all impurities were below the detection limit of AES. In the STM experiments oxygen gas dosing was performed in the preparation chamber. Oxygen pressures up to $6 \times 10^{-5}$ mbar were attained either by background dosing of O₂ in the preparation chamber or by means of a capillary array doser similar to the setup described in [30], but without additional pumping stage. Thus it was not possible to apply short pressure pulses in the STM experiments. The STM images were recorded in constant current mode with negative sample bias.

2.3. Theoretical calculations

The calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [34], using the projector augmented-wave (PAW) method in the implementation of Kresse and Joubert [35]. In this method the exact valence wave functions instead of pseudowave functions, as in conventional pseudopotential calculations, are used [36]. The PAW potentials applied in the present study were already described and tested before [11,37,38]. All calculations presented here were performed with the generalized gradient approximation (GGA) of Perdew et al. [39]. The calculation of the oxygen-on-Pd(111) phase diagram (oxygen gas phase chemical potential, equilibrium pressures and temperatures) is based on tabulated values for the chemical potential of oxygen in the gas phase, conveniently compiled in [28].

3. Results

3.1. Surface oxide phase growth

3.1.1. LEED and TPD experiments

The bulk of the clean Pd crystal was saturated with oxygen as described before, and surface oxygen was desorbed by flashing the crystal to 873 K. The adsorbate-free Pd(1×1) surface was exposed to the effusive oxygen beam at varying effective pressure at a constant sample temperature of 683 K. In the first experiments the total exposure was kept constant at 10,000 L O₂. Fig. 1(a) shows the TPD traces after exposure at effective oxygen pressures between $2.5 \times 10^{-7}$ and $6.6 \times 10^{-5}$ mbar. Exposure below about $3 \times 10^{-5}$ mbar results in a
reproducible coverage near 0.25 ML oxygen, equivalent to a completed p(2×2)O surface. However, increasing the pressure above this critical value immediately leads to a total coverage beyond 0.5 ML and the corresponding O₂ desorption spectra display a sharp maximum near 750 K. Peak size and shape are characteristic for desorption from an almost completed Pd₅O₄ surface oxide layer (the saturation coverage is 0.58 ML O). The total oxygen coverage measured after exposure to 10,000 L O₂ at 683 K (determined by TPD) is plotted vs. the effective oxygen pressure in Fig. 1(b). It is seen that the final coverage rises sharply at a critical pressure of 3.2×10⁻⁵ mbar and that under these conditions no intermediate coverage between about 0.25 [p(2×2) layer] and 0.5 ML is obtained. A maximum coverage of 0.58 is reached after exposure to 3.4×10⁻⁵ mbar, whereas the lower coverage values measured after exposure to increasingly higher pressures are most likely due to kinetic limitations, i.e. insufficient exposure times to complete the transition (note that increasing oxygen pressure corresponds to decreasing exposure time, see upper axis of Fig. 1(b)).

The sharp pressure threshold indicates the formation of a new phase beyond a critical coverage of chemisorbed oxygen on the (111) metal substrate. The critical pressure is a sensitive function of the sample temperature; upon a temperature rise of only 10 K (from 683 to 693 K) it is almost doubled, indicating that in the gas phase a critical chemical potential of oxygen is required in order to attain a sufficient coverage of chemisorbed O atoms. From the calculated phase diagram (section 3.3) we can indeed derive a doubling of the critical pressure upon a 10 K temperature increase. As shown below, the threshold observed experimentally at ~683 K is higher than the true thermodynamic limit, i.e., for driving the phase transformation a certain supersaturation is required for kinetic reasons. The critical pressure depends only to a certain extent on the preparation of the crystal surface and decreases somewhat with increasing surface roughness, indicating faster oxygen dissociation or nucleation of the surface oxide at steps or defects.

Growth of the oxygen-rich phase at 683 K could be studied in a controlled (i.e. time-resolved) manner by providing a small and reproducible amount of oxide as a starting point. We have applied a short high-pressure pulse (6×10⁻⁵ mbar oxygen for about two seconds, well beyond the exposure required for p(2×2) formation) using the effusive beam doser. Fig. 2 shows the TPD trace after this treatment (middle trace). A comparison with the TPD spectra typical for the Pd(111)-(2×2)O surface (lower trace) and for the Pd₅O₄ surface oxide (largest peak) indicates

![Fig. 1. (a) TPD spectra obtained after exposure to 10,000 L O₂ with increasing pressure at 683 K and (b) total coverage as a function of oxygen pressure obtained from the integrated TPD spectra in (a).](image)
the presence of a phase with higher oxygen concentration than the \((2 \times 2)\)O and weaker oxygen binding.

Thereafter, further growth of the oxide phase was studied by exposing the surface to additional \(\text{O}_2\) at the same temperature, but at a lower pressure. If the pressure was set constant at \(6.3 \times 10^{-6}\) mbar, the maximum oxygen coverage never exceeded 0.4 ML, even after very large exposures up to 20,000 L (Fig. 3(a)). At this pressure the complete oxidation of the surface to \(\text{Pd}_5\text{O}_4\) (0.58 ML coverage) was not observed. A LEED analysis in this state of oxidation showed only integer order spots and enhanced background intensity. Neither a \(p(2 \times 2)\) structure nor any other ordered pattern were observed.

Full oxidation to \(\text{Pd}_5\text{O}_4\) was only possible at a somewhat higher pressure of \(8.9 \times 10^{-6}\) mbar \(\text{O}_2\) (Fig. 3(b)). At this pressure oxidation towards the 0.4 ML state proceeded again at exposures between 2200 and 8400 L, just as in Fig. 3(a). Exposure between 5600 and 8400 L led to coverage...
values close to 0.4 ML, a preferred coverage regime also observed in the experiments of Zheng and Altman [24]. However, at exposures of more than 14,000 L a nearly complete Pd$_5$O$_4$ layer (>0.5 ML, Fig. 3(b)) developed. Hence, depending on oxygen pressure and total exposure, two separate categories of desorption traces corresponding to surface coverages of approximately 0.4 and 0.58 ML are obtained (Fig. 3(b)).

Taken together, these experiments suggest growth of at least two different oxide phases at 683 K, depending on the pressure. The formation of a complete and well-ordered Pd$_5$O$_4$ surface layer is only possible at the higher pressure of $8.9 \times 10^{-6}$ mbar O$_2$. Comparison of this limit to that measured without nucleation pulse ($\sim 3 \times 10^{-5}$ mbar, Fig. 1) indicates kinetic limitation of Pd$_5$O$_4$ formation in the experiment shown in Fig. 1; i.e. the pressure limit observed there does not correspond to the thermodynamic stability limit of the surface oxide. Obviously, the pressure limit observed after the “nucleation pulse” (between 6.3 and $8.9 \times 10^{-6}$ mbar) is closer to the thermodynamic stability limit of the Pd$_5$O$_4$ phase, and in a first approximation we may consider it an approximate value of the thermodynamic stability limit.

### 3.1.2. STM experiments

The experimental setup of the STM system did not allow us to follow nucleation and growth at identical temperature and O$_2$ pressure as in the experiments described above, but the conditions for phase growth resulting in a perfect Pd$_5$O$_4$ surface are well known from previous work in the same STM setup [27,11]. In the present study we retained the surface temperature during oxidation at 573 K, as in the experiments of Zheng and Altman [24]. The Pd(111) surface was exposed to a constant oxygen pressure (between $10^{-6}$ and $3 \times 10^{-5}$ mbar) for increasing periods of time (starting with about 1 min), and thereafter cooled to room temperature in oxygen environment in order to avoid reduction during the cooling stage (cooling time about 30 min). From series of STM images taken at room temperature one can conclude that under the chosen conditions surface oxide formation does not nucleate in the bulk-terminated metal structure on the flat Pd(111) terraces. Instead, various surface oxide structures start to grow as irregular “seams” formed along the step edges while island formation within the terraces is not observed. Fig. 4 shows different regions on the Pd(111) surface after exposure to $5 \times 10^{-6}$ mbar O$_2$ at 573 K for 10 min, followed by cooling in oxygen. Fig. 4(a) exhibits broad seams along the original steps, attributed to regions of a disordered oxidic phase, but also reveals onset of growth of a partly ordered oxide phase at the boundary between the p(2×2) structure and the irregular oxidic phase (wavelike pattern, arrow). Fig. 4(b) shows locally more advanced growth stages. The oxidic regions close to the original step edge are still irregularly structured whereas other regions display signs of a two-fold periodicity in one direction (peninsula), and also a well-ordered Pd$_5$O$_4$ structure (lower and right parts). Furthermore, we observe at this stage many bright clusters of unknown chemical state, most below 1 nm in size. They appear predominantly along the border between the p(2×2)O region and the seams dividing the individual terraces. The chosen preparation conditions did even lead to terraces completely oxidized to Pd$_5$O$_4$ (Fig. 4(c)). The second terrace from the right consists of peninsulas of ordered oxide; all three orientations rotated by 120° with respect to each other are present. Similar to Ref. [24], the formation of peninsulas can be easily explained as resulting from Pd atoms expelled when forming the Pd$_5$O$_4$ surface oxide with its lower Pd density than a Pd(111) terrace (the inverse process, formation of holes, has been observed in Ref. [27] during decay of the surface oxide). The coexistence of a Pd$_5$O$_4$ peninsula and the disordered seam indicates that this seam is not easily rearranged into the ordered surface oxide.

Fig. 4(d) shows one particular oxide phase appearing after a very similar preparation ($5 \times 10^{-6}$ mbar O$_2$ at 573 K for 10 min, followed by cooling in vacuum to room temperature), which is of particular interest because it was observed in more extended patches also after isothermal desorption at 693 K (see section 3.2). Its STM image shows that the mostly irregular seams may become locally arranged to a poorly ordered
variety of the $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ phase discussed below (distance between protrusions 0.62 nm). This phase was identified as an intermediate structure during desorption.

In summary, growth of the surface oxide layer observed at low temperature (573 K) by STM exhibits a high degree of heterogeneity. Since background oxygen dosing was applied, the different structures in Fig. 4 cannot be explained by different local exposures and must therefore be attributed to different oxidation states reached after the same local exposures. Among various metastable local structures the formation of a seam of disordered oxide at the step edges is a common structural feature characteristic of the initial stages of oxide growth. Further ordered growth appears to be particularly favoured along the interface between these disordered seams and the $p(2 \times 2)$O structure.

3.2. Thermal decay of the surface oxides

In view of the fact that intermediate oxidation states (Fig. 4) exhibit a broad structural heterogeneity, at least at 573 K, while full Pd$_3$O$_4$ coverages (0.58 ML) are structurally uniform, the thermal decomposition of different oxide phases was also studied. A 0.4 ML and a 0.58 ML oxygen adlayer were prepared by exposing the Pd surface, which was initially exposed to the nucleation pulse, to

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Fig. 4. STM images illustrating increasing oxidation stages obtained under the same preparation conditions (exposure to $5 \times 10^{-6}$ mbar O$_2$ at 573 K for 10 min): (a) $-0.12$ V, 0.48 nA, 50 nm; (b) $-0.47$ V, 0.21 nA, 50 nm; (c) $-0.24$ V, 0.42 nA, 100 nm and (d) terraces on the left: regions with disordered $(\sqrt{67} \times \sqrt{67})R12.2^\circ$-like structure; $-0.13$ V, 0.77 nA, 17 nm. The contrast of the individual terraces has been enhanced.
1000 L oxygen at a pressure of $5.8 \times 10^{-6}$ mbar and to 7000 L oxygen at $1.5 \times 10^{-5}$ mbar, respectively, at 683 K. Both surfaces were subjected to isothermal desorption at 693 K. The results—desorption rate vs. time—are shown in Fig. 5. Desorption from the 0.4 ML phase starts immediately at a high rate, and is followed by an almost linear rate decrease. After this process a $p(2 \times 2)$O layer with a negligible desorption rate remains, as confirmed by subsequent LEED and TPD measurements. On the contrary, desorption from the completed Pd$_5$O$_4$ layer (0.58 ML film) starts with a lower and almost coverage-independent desorption rate, followed by a significant rate increase at constant temperature, pointing to an autocatalytic decay. At the end, the rate decreases again as the coverage decreases and the system returns to the less reactive $p(2 \times 2)$ structure. We note that in temperature programmed desorption the rate maximum is shifted to higher temperature by about 10 K if the initially present surface oxide is a complete Pd$_5$O$_4$ layer (Fig. 3(b)). As pointed out previously [27], this is another indication of an autocatalytic step during oxide decay.

The STM image in Fig. 6 was obtained after partial desorption of oxygen from an almost complete Pd$_5$O$_4$ surface oxide at approximately 693 K, followed by cooling to room temperature. The surface consists of terraces containing individual small clusters and of an ordered superstructure. The apparent height of the clusters is about 140 pm, the width of the clusters measured at half height approx. 0.5 nm. A two-dimensional Fourier transform of the cluster positions shows six sharp maxima corresponding to the Pd(111) $(1 \times 1)$ lattice. Thus, the clusters form a 2D lattice gas on the Pd substrate. In other words, all clusters reside in equivalent sites, as expected from their monodisperse size distribution revealed in Fig. 6. The surface structure between the clusters is not resolved in this figure, but other images of the same sample indicate that it is the Pd(111) lattice with a $p(2 \times 2)$ oxygen overlayer. The small clusters represent building blocks for larger units also visible in the lower left part of Fig. 6. Their similar apparent height also suggests that the ordered superstructure (seen as an upper level in Fig. 6) consists of the same entities.

With a distance between the maxima of approx. 0.62 nm this ordered structure seems to be incommensurate at a first glance. An analysis of the Fourier transformed STM images reveals that it is actually a commensurate $(\sqrt{67} \times \sqrt{67})R12.2^\circ$ superstructure which exhibits many defects, however. This unit cell is indicated by a large rhomb in Fig. 6 (inset). The superstructure cell contains 13 maxima in an almost perfect hexagonal lattice; in a loose notation this lattice could be described

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Fig. 5. Isothermal desorption of oxygen (monolayers O/s) at 693 K: (a) from a 0.4 ML adlayer, (b) from a 0.58 ML adlayer (completed Pd$_5$O$_4$ structure) and (c) temperature profile.
as \(\left(\sqrt{67/13} \times \sqrt{67/13}\right)R1.7\)”, resulting in an average distance between the maxima of 0.62 nm (small rhomb in Fig. 6). As pointed out above, the same type of structure, but less perfectly ordered, was also observed as an intermediate stage of oxide growth at 573 K.

### 3.3. Calculated phase diagram

The computed phase diagram presented in Fig. 7 displays the regions of thermodynamic stability of the relevant oxygen-containing phases on Pd(111) by plotting the surface free energy \(\gamma\) of each phase as a function of the gas phase chemical potential of oxygen \(\Delta \mu_O\). The conversion from \(\Delta \mu_O\) to experimental conditions (\(O_2\) pressure and temperature) is based on the ideal gas equation and the approach extensively described in [28,29]:

\[
\begin{align*}
\mu_O(T, P_{O_2}) - \frac{1}{2} E_{O_2}^{\text{total}} &= \Delta \mu_O(T, P_{O_2}) \\
&= \frac{1}{2} \mu_O(T, P^0) + \frac{1}{2} k_B T \cdot \ln \frac{P_{O_2}}{P^0}
\end{align*}
\]

As reference energy for \(\Delta \mu_O\), half the energy of an oxygen molecular, as calculated by DFT \(\left(\frac{1}{2} E_{O_2}\right)\), has been chosen. This implies that \(\Delta \mu_O = 0\) corresponds to the highest possible oxygen potential attainable using molecular oxygen \((T = 0\) and/or large \(O_2\) pressures). The temperature scale on the top axis of Fig. 7 is calculated on the basis of an oxygen gas phase pressure of 10\(^{-5}\) mbar, close to that chosen in our experiments. The Gibbs free surface energy was evaluated for a variety of possible states of the system, i.e., different surface phases and the bulk oxide. The Gibbs free surface energy can be written as a function of the oxygen chemical potential

\[
\gamma(\Delta \mu_O) = \frac{N_O}{A} \left(E_{O/\text{slab}}^{\text{bind}} + \Delta \mu_O\right),
\]

where \(E_{O/\text{slab}}^{\text{bind}}\) is the average binding energy of oxygen with respect to \(\frac{1}{2} E_{O_2}\). Obviously, the higher the oxygen content of a considered surface structure, the steeper its surface energy will decrease with increasing chemical potential. In the limiting case of an infinitely thick bulk oxide, this gives rise to...
a vertical line that crosses the zero axis at the stability condition for the bulk oxide, at $E_{\text{ads}} = \mu_O = 0.98$ eV per oxygen atom (DFT values). For any higher $\mu_O$ the bulk oxide will be the stable phase, but the crucial issue is whether a regime $\mu_O$ exists, for which lines of a surface oxide structure are lower than for on-surface adsorption and the clean surface.

The informations required therefore are the oxygen adsorption energies and the oxygen coverage per surface area. The adsorption energies were calculated by first-principles calculations combined with extensive simulated annealing molecular dynamics. For details we refer to Ref. [11]. In the present case we have considered the Pd$_5$O$_4$, Pd$_3$O$_5$, and Pd$_3$O$_6$ layers as determined in Ref [11], as well as the stable p(2×2) 0.25 ML oxygen adlayer and a hypothetical p(2×1) oxygen overlayer with 0.5 ML coverage. As already emphasised in Ref. [11], the Pd$_3$O$_4$ structure turned out to be the only stable surface oxide phase. This structure has neither the stoichiometry nor a structural similarity to any plane of the only comparable bulk oxide, PdO. Concerning the energetics, the surface oxide is found to have an oxygen binding energy of $E_{\text{ads}} = 1.24$ eV (see Ref. [11]), between the p(2×2) overlayer ($E_{\text{ads}} = 1.36$ eV) and the fictitious p(2×1) overlayer ($E_{\text{ads}} = 0.95$ eV).

Important for the present experimental work is the transition between the p(2×2)O adlayer and the Pd$_5$O$_4$ surface oxide, calculated to occur at a chemical potential of $-1.17$ eV (intersection of p(2×2) and Pd$_3$O$_4$ surface energy lines), corresponding to a critical temperature of 640 K at 10$^{-5}$ mbar oxygen pressure. As mentioned previously, the true thermodynamic stability limit is difficult to determine experimentally. We recall that, if a small amount of oxide has been provided as starting point, the transition to the surface oxide is observed at 683 K and 8.9×10$^{-6}$ mbar, very close to the calculated values. Due to the small angle between the lines of the p(2×2) and Pd$_3$O$_4$ structures in Fig. 7, this corresponds to an error of only about 30 meV in the calculated energy difference between these two structures.

4. Discussion

From adsorption and TDS experiments we conclude that in the temperature range around 683 K growth of the ordered Pd$_3$O$_4$ layer still involves
kinetic barriers, which can be partly overcome by providing a small amount of an initial surface oxide. The effect of the “nucleation pulse” is most likely the formation of a large number of evenly distributed, disordered surface oxide patches which facilitate further oxygen activation, e.g. by an increased oxygen sticking probability at the phase boundary.

These experimental results must be correlated with the evidence obtained by STM, taking into account the different conditions of oxygen exposure (sample temperature of 573 K) and the fact that STM images could only be taken near room temperature. Summarizing the STM information we can conclude that oxide formation starts along the step edges, and that during the initial growth irregular seams containing a disordered oxidic phase are formed (Fig. 4). At this rather low temperature (573 K), growth of ordered phases, e.g. the “wavelike” structure, is noted at the boundary between the p(2×2)O phase and the irregular oxidic seam. More extended structures like the \((\sqrt{67} \times \sqrt{67})R12.2^\circ\) phase (Fig. 4(c)) can be assigned to more advanced stages of growth, eventually ending at a well-ordered Pd\(_5\)O\(_4\) layer (Fig. 4).

Preparation conditions far off thermodynamic equilibrium lead to a variety of metastable states. In the work of Zheng and Altman [24], which was also performed at non-equilibrium conditions, a comparable variety of structures is documented, e.g. the square Pd\(_5\)O\(_4\) structure and a rectangular one as well as a structure similar to our “wavelike” pattern. Since we are far from equilibrium at 573 K, the whole structural bandwidth observed in Fig. 4 must be largely determined by kinetic effects inducing local heterogeneity, e.g. different orientations of the step edges. The seams near the step edges are rather stable and not readily converted into periodic structures. Again it is worthwhile to discuss the connection to the work of Zheng and Altman [24] who studied the phase growth of oxygen on Pd(111) upon adsorption of NO\(_2\). The high oxidation potential of NO\(_2\), in combination with the low temperature of 575 K, is sufficient to oxidize Pd atoms directly from the terraces, and nucleation at the steps is not predominant. Hildebrandt et al. [40] investigated the initial oxidation of a Ni(111) surface in the temperature range between 400 and 470 K and observed a gradual transformation of the terraces into a thin epitaxial oxide after initial nucleation at the step edges. Their results are in agreement with our arguments if we consider that nickel–oxygen species are in general thermodynamically more stable than Pd–O species and that the above-mentioned temperatures are comparatively low.

As the reverse reaction is concerned, isothermal desorption at 693 K tells that the decomposition of the initially complete Pd\(_5\)O\(_4\) layer occurs by an autocatalytic reaction. In both formation and decay of the Pd\(_5\)O\(_4\) phase we find evidence of an intermediate phase between the p(2×2) structure and Pd\(_5\)O\(_4\) at a coverage of about 0.4 ML. We can think of two possible scenarios describing our experimental findings for both adsorption and desorption, and for both scenarios we have to assume that the intermediate phase is stable in a narrow range between p(2×2) and Pd\(_5\)O\(_4\).

In scenario (1), the rate-limiting steps do not involve the adsorption/desorption process itself but rather occur on or in the surface. In this scenario, nucleation of the surface oxide(s) occurs only at a sufficient supersaturation, which is surpassed in the “nucleation pulse” experiments. As our experiments after the pulse show, transition of the intermediate phase to Pd\(_5\)O\(_4\) does not require high supersaturation but occurs at low supersaturation and 683 K, though not very fast (in several hundred seconds). Assuming that the desorption process is not rate-limiting, the explanation of the isothermal desorption experiments must be as follows: Decay of Pd\(_5\)O\(_4\) is slow in the beginning, but accelerates when the length of the borderline between the well-ordered Pd\(_5\)O\(_4\) phase and the intermediate phase increases.

In scenario (2), adsorption (during growth), and vice versa desorption, is the rate-limiting process. If the sticking probability of oxygen on the intermediate phase is higher than on the well-ordered p(2×2) structure, the effect of the pulse can be explained as the formation of small patches of mainly the intermediate phase. Oxygen can adsorb and dissociate on these areas, facilitating conversion of the whole surface into Pd\(_5\)O\(_4\). As the rates of dissociative adsorption and desorption at near-equilibrium conditions are linked by the require-
ment of detailed balance, also the process of recombinative desorption is more efficient on the intermediate phase. This mechanism therefore explains the increase of desorption in the isothermal decay experiment by an increasing area of the intermediate phase.

For both mechanisms, it is helpful to identify and characterize the intermediate phase. We have indeed observed an intermediate structure occurring during both formation and decay of the Pd$_5$O$_4$ surface oxide, characterized as a hexagonal more or less well-ordered ($\sqrt{67} \times \sqrt{67}$)R12.2° superstructure. During adsorption at 573 K it is formed only locally, but the decay of the Pd$_5$O$_4$ oxide layer at 693 K involves large-scale rearrangement into this particular structure, also indicating its high-temperature stability. Although the structure was experimentally observed after cooldown, we consider it likely to exist also near thermodynamic equilibrium at 693 K. Hence, we may speculate that it is the main intermediate not only in desorption, but in some very close modification also during adsorption under near-equilibrium conditions at 683 K.

In view of the fact that the ($\sqrt{67} \times \sqrt{67}$)R12.2° phase seems to consist of densely packed clusters, we may further speculate that building and decay of Pd$_5$O$_4$ occur via an inverted mechanism, with the clusters constituting the same building blocks in either direction. Since the direct formation of Pd$_5$O$_4$ from the p(2×2)O phase would involve a considerable local fluctuation of a rather large number of atoms to form large nuclei, it is reasonable to assume that at first a structure consisting of smaller building blocks containing less oxygen is formed. In this model, it is difficult to imagine that decay of Pd$_5$O$_4$ into the cluster phase should be a rate-limiting step, we therefore consider scenario (2) more likely, i.e. a higher probability of dissociative sticking on a more or less well-ordered ($\sqrt{67} \times \sqrt{67}$)R12.2° phase as compared to the well-ordered p(2×2) and Pd$_5$O$_4$ surfaces. In other words, we propose that the ($\sqrt{67} \times \sqrt{67}$)R12.2° phase and the associated cluster phase are a “reactive” intermediate phase between the less reactive p(2×2) and Pd$_5$O$_4$ phases.

The information about the complex kinetics of phase transitions obtained in the present experiments may help to rationalize kinetic hysteresis effects. The Pd(1 1 1) surface oxide is a good example to show that the fundamental processes underlying hysteresis effects are (i) strongly non-linear pressure-dependent phase growth kinetics near gas phase equilibrium with respect to temperature and pressure and (ii) autocatalytic phase decay with the growing reduced surface area, catalyzing the conversion of oxidic into gaseous oxygen. Analogous effects may influence the reaction kinetics and phase stability in oscillating oxidation reactions involving molecular oxygen.

5. Summary

The experimental results and our interpretation can be summarized as follows:

At 683 K the formation of the Pd$_5$O$_4$ structure can be divided into two steps: formation of an intermediate phase with an oxygen coverage of approx. 0.4 ML followed by growth of the Pd$_5$O$_4$ phase. Dissociation of oxygen on the intermediate phase seems to be easier than on the p(2×2)O phase, since oxidation on the intermediate phase proceeds at lower pressure (8.9 × 10$^{-6}$ mbar, 683 K) than on the (2×2)O phase (3.5 × 10$^{-5}$ mbar, 683 K). At 573 K, growth of the oxide proceeds via several intermediate states, among these a ($\sqrt{67} \times \sqrt{67}$)R12.2°-like phase. The thermodynamic limit for the transition between the p(2×2) adatom structure and the Pd$_5$O$_4$ surface oxide could be substantiated by DFT calculations.

Decay of the Pd$_5$O$_4$ oxide layer at 693 K involves rearrangement into the same intermediate ($\sqrt{67} \times \sqrt{67}$)R12.2° structure, which finally breaks up into its building blocks, small clusters of uniform size with the unreconstructed metal surface area covered by a p(2×2)O adlayer in between. The desorption rate increases autocatalytically with increasing area of the intermediate phase.

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