On the oxidation–reduction kinetics of palladium

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The oxidation–reduction kinetics of Pd was investigated on polycrystalline Pd foils using XPS and sputter-depth profiling over a wide range of temperatures. The observed behavior can be explained in terms of a desorption-controlled process at lower temperatures ($T < 230\,^\circ$C) and a diffusion-controlled process at higher temperatures ($T > 450\,^\circ$C). In the intermediate range ($230 < T < 450\,^\circ$C) a transition between the two processes is observed which gives rise to a pronounced shoulder in the reduction time trace. The interpretation is qualitatively confirmed using a simple mathematical model for a coupled bulk diffusion/surface reaction system.

Keywords: palladium, oxidation–reduction, XPS, sputter-depth profiling, reaction–diffusion model

1. Introduction

Palladium is a widely used oxidation catalyst, not only as a major component in the automotive exhaust catalyst, but also as a combustion catalyst in the total oxidation of hydrocarbons in catalytically stabilized burners and in catalytic abatement of volatile organic compounds. This is due to the fact that Pd shows a high oxidation activity even under very fuel lean conditions unlike most other noble metal catalysts [1,2]. This unusually high activity has been attributed to the fact that not only metallic Pd but also palladium oxide are active oxidation catalysts. This “double” activity also seems to give rise to a very complex behavior of Pd/PdO catalysts which is still poorly understood. Among the many complex phenomena that have been observed in this system are temporal and spatial oscillations in the reaction rate over Pd catalysts, a hysteresis in the oxygen uptake and release, formation of several different subsurface and bulk oxides, and an unusually high activity for methane oxidation. Due to this wealth of interesting phenomena, the Pd/PdO system has been studied in great detail for many years, and a brief overview over the literature will be given in the following.

The first studies on the interaction between oxygen and Pd single crystals date as far back as the late 60s from the group of Ertl [3–5]. In UHV investigations of Pd(110) and Pd(111) single crystals the authors find a rather complex behavior particularly on Pd(111), where they postulate at least three different adsorption states of oxygen atoms: chemisorbed oxygen, subsurface oxygen and a strongly bound surface oxide. These three states can be transformed into each other depending on the catalyst temperature, suggesting a rather high mobility of oxygen in the Pd bulk. High temperatures (∼1000 K) and high “virtual” oxygen pressures (achieved by dosing NO instead of O_2 under UHV conditions) were seen to be necessary to achieve the formation of a strongly bound surface oxide, which the authors interpreted as a transition state between chemisorbed oxygen and bulk PdO.

Following these investigations, many studies on the Pd–O system have been published and a complete overview will not be attempted here. Despite this large number of investigations, the picture emerging from these studies is still far from clear. While all studies seem to agree on the fact that there are several different oxygen bonding states, the specific assignment of these states to the different oxygen species is still disputed [6–12]. The system has been shown to be sensitive to imperfections of the single-crystal surface [7]. The importance of high oxygen partial pressure for the formation of deep bulk oxides has been stressed in several studies [5,6,10]. However, with the exception of the study by Voogt et al. [12], all authors seem to find some evidence for subsurface and/or bulk oxide formation, although the evidence given is typically indirectly inferred from surface studies.

Repeated oxidation/reduction cycles are also responsible for the occurrence of temporal oscillations in CO oxidation over Pd catalysts [13,14]. These oscillations occur over a wide range of $p_{\mathrm{CO}}/p_{\mathrm{O}_2}$ ratios of 0.05–2.0, and a temperature range of 230–350 °C [13]. Imbihl and coworkers modified the original model by Sales et al. [13,14] and set up a mathematical model, which involves the formation of a subsurface species and a periodic emptying and re-filling of this subsurface oxygen reservoir [15,16]. This model was recently further modified by Hartmann et al. to include repulsive interactions between adsorbed oxygen atoms, changing the activation energy for subsurface oxygen formation [17]. While this model gave a good qualitative agreement with the experimental findings for the temporal oscillations in this system, a quantitative description has not yet been at-

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tempted. Further studies of this system by Christmann, Block and coworkers yielded interesting results about the spatial and temporal dynamics of CO oxidation on Pd, however, no further insights into the mechanism or the kinetics of Pd oxidation and reduction resulted from these studies [18–20].

More recently, several studies have reported an unusual activity of Pd catalysts for methane combustion. This opened up again the question whether PdO or metallic Pd is the active phase for hydrocarbon oxidation. The earliest study of Pd-catalyzed hydrocarbon oxidation seems to be the 1968 article by Firth and Holland, who reported a break in the activation energy for methane oxidation with increasing reaction temperature, which they interpreted as a competitive vs. non-competitive adsorption of methane and oxygen on different catalyst sites [21]. About ten years later, Schwartz et al. report a decreased combustion activity on oxidized Pd catalysts, suggesting that metallic Pd is the active phase of the catalyst [22]. Recently, more detailed investigations of this system have been conducted. In contrast to the results of Schwartz et al., these investigations found an increased combustion activity on PdO as compared to Pd [23–27]. Farrauto et al. were the first to report a pronounced hysteresis in the reaction rate in thermogravimetric studies of methane oxidation on γ-Al_2O_3-supported PdO [23]. A few years later, this hysteresis was studied in detail independently by McCarty [24] and by Salomonsson et al. [25]. Both studied methane oxidation on supported Pd catalysts at ambient pressures in a strongly He-diluted CH_4/O_2 atmosphere. They both confirmed the existence of the strong hysteresis between roughly 450 and 750 °C, however, they came to different conclusions about the origin of this phenomenon: while McCarty attributed the hysteresis to the nucleation and growth dynamics of PdO crystallites [24], Salomonsson et al. interpreted their findings in terms of a non-ideal three-phase system, containing oxygen in solid solution in the catalyst [25]. Both found PdO to be more active for methane combustion than the metallic phase. This is also confirmed in other studies by Ziauddin et al. [1,2], Haak and Otto [26] and Sekizawa et al. [27]. Ziauddin et al. also showed that Pd has exceptional activity for hydrocarbon oxidation far into the fuel lean regime supporting palladium oxide's unusually high catalytic activity.

In contrast to all these studies, Lyubovsky et al. reported higher methane combustion activities for metallic Pd supported on low surface area α-Al_2O_3 than for the oxidized phase [28], in agreement with the early study by Schwartz et al. [22]. This was confirmed in a study by Deng and Nevell in which temporal oscillations were observed for methane oxidation over supported Pd catalysts in the temperature range between 350 and 550 °C [29]. As in previous studies on CO oxidation [13–15], they again correlate the oscillations with an oxidation/reduction cycle of the Pd catalyst, and infer that PdO is the less active catalyst phase. This is further supported by a study on methanol oxidation over Pd thin film catalysts by Chan et al., in which PdO was found to be entirely unreactive for both methanol combustion and decomposition [30].

Contrasting their own results on methane combustion on low surface area supported Pd catalysts, however, Lyubovsky et al. [28] found that for high surface area supports the oxide phase is more active than the metallic phase, suggesting that the morphology of the Pd phase and/or metal–support interactions might be an important factor for the catalytic activity of Pd catalysts. The picture is even further complicated by particle size effects, as shown, for example, in studies by Chen and Ruckenstein [31,32], Sekizawa et al. [27] and Voogt et al. [33].

Due to the overwhelming complexity of the system and the inconsistency of previous studies which were pointed out in this brief overview, we decided to take a rather pragmatic approach in the present study. Instead of adding yet another study in the attempt to elucidate the detailed elementary mechanisms and energetics in this system, we measured the kinetics of the oxidation and reduction of Pd foil catalysts. A high purity Pd foil was used in order to minimize complications by particle size and influence by catalyst support. High partial pressures of oxygen (40 mbars) were used to oxidize the foil. This study should therefore be seen as a base case for the study of oxidation kinetics of Pd catalysts.

2. Experimental

All experiments were conducted in a stainless steel UHV chamber (base pressure $<10^{-9}$ mbar) which was equipped with XPS, mass spectrometry, and a sputter gun. Oxidation of the foils was carried out in an attached pre-chamber after which introduction into the main vacuum chamber could be done without exposing the sample to atmosphere. The samples were polycrystalline Pd foils of highest available purity (dimensions $5 \times 20 \times 0.25$ mm, 99.9975% purity and were spotwelded onto a sample holder on the end of a transfer rod. The sample was heated resistively, and the sample temperature was determined using a chromel/alumel thermocouple spotwelded to the back of the foil. The XPS system used in these investigations was a modified Physical Electronics PHI-555 with a Mg X-ray source. The area analyzed on the sample had a diameter of 4 mm.

Before each experiment, the sample was cleaned by heating to 990 °C at 10^{-9} mbar for 10 min thereby removing any impurities on the catalyst surface. A full-range XPS scan of the sample was taken to ensure sample cleanliness within the detection limits of our XPS system (see figure 1(a)). The sample was then transferred into the pre-chamber and oxidized in a dry air atmosphere at a pressure of 400 mbar ($p_{O_2} = 80$ mbar) at 450 °C for 3 min. These conditions were found in a first set of experiments to be the mildest conditions under which the sample could be deeply oxidized. The oxidized sample was then cooled down to room temperature and transferred back into the

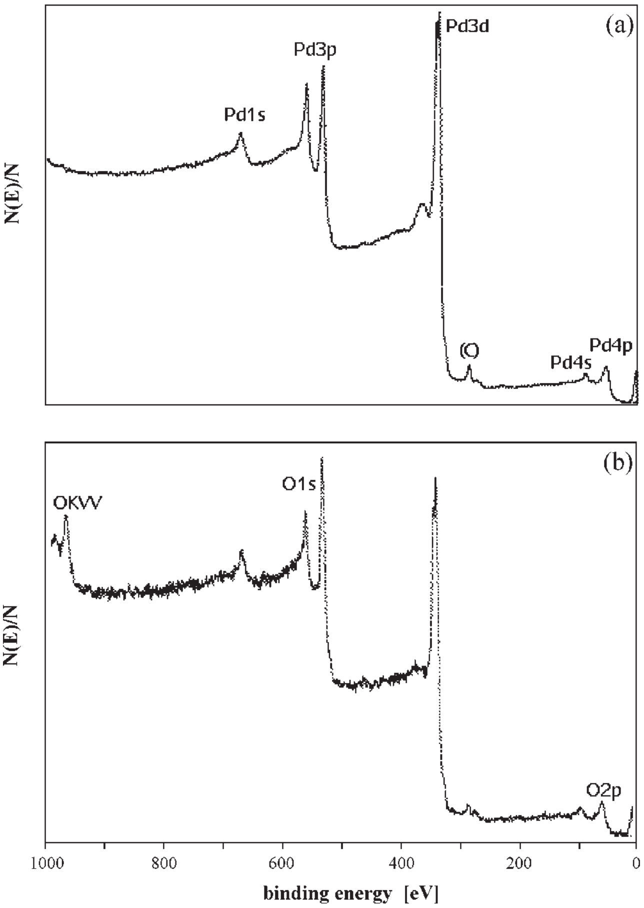

Figure 1. Typical full-range scan of a Pd sample before (a) and after oxidation (b). The main palladium and oxygen peaks are indicated. Only the Pd 3d peaks were used for further quantitative analysis. Trace amounts of carbon which are still detectable in the reduced sample are removed by oxidation.

UHV chamber. An XPS scan was taken to ensure again the cleanliness and the degree of oxidation of the sample (figure 1(b)). The sample was then quickly heated to the temperature of the respective run and the reduction of the sample in vacuum (i.e., the thermal decomposition of the oxide) was monitored at this (fixed) temperature by high-resolution XPS scans of the Pd $3d_{5/2}$ peaks which were taken in 30 s intervals with proceeding time. Due to the initial heating to the respective reduction temperature an uncertainty of about 20 s existed with respect to the start of the reduction process. The fraction of oxide on the sample surface was determined by deconvoluting the Pd $3d_{5/2}$ peak for the metal from that of the oxide, these being separated by about 1 eV.

For the sputter-depth profiling experiments, the oxidation step was carried out for different durations under otherwise unchanged conditions, and the thickness of the oxide layer was measured by again taking XPS scans of the Pd $3d_{5/2}$ range. The sputtering was done with argon gas at an accelerating voltage of 5 kV and the sputtered area was 8×8 mm^2. The sputter rate, calibrated with Ta_2O_5, was 10 A/min and the samples were sputtered for 15 s between each analysis step. In this comparative studies, the sputter rate for PdO was estimated as 35 A/min using sputtering yields published by Czanderna [34].

All experiments were repeated several times and a very good reproducibility was obtained for all runs.

3. Results and discussion

3.1. Kinetic studies

Figure 2, left two panels, shows the temporal development of an XPS scan in the Pd 3d region for a sample at reduction temperatures of 180 and 450 °C, respectively. The curves shown are representative for the behavior at the lower and upper boundaries of the temperature range studied. For temperatures below 150 °C the reduction process becomes too slow to be detectable (no measurable reduction was observed at 130 °C over the course of several hours), and above 500 °C too fast to be monitored (at 550 °C the reduction is virtually complete within a minute so that our data acquisition is too slow to gather enough data points for evaluation). As expected, a decreasing PdO signal is observed along with increasing Pd metal peaks. Except for the different time scales, the data looks very similar at the two different temperatures shown.

The two right-hand panels in figure 2 show the development of the oxide fraction of the Pd sample with time, as calculated from the scans. For the fitting of kinetic rate laws to these time traces, different apparent reaction orders were tested, and for all data series the best fit was found to be a first-order rate law. While at higher temperatures a perfect fit could be attained with this first-order kinetics, the kinetics at lower temperatures deviate somewhat from an ideal first-order behavior. This could be due to repulsive interactions between the adsorbed oxygen atoms. Such repulsive interactions have been shown previously by Hartmann et al. [17] to be essential to attain a good model description of the rate oscillations in CO oxidation over Pd. They would also change the kinetic behavior to deviate from an ideal first-order behavior in the way observed in the low-T scans: in the early stages of the reduction (i.e., at high coverages) the desorption would be strongly accelerated due to the repulsion energy, while this influence would get less and less pronounced as the coverage drops, giving rise to an apparent reaction order of less than 1. However, since the first-order fit is still very satisfactory within experimental error, and since repulsive interactions would require an additional fit parameter, no attempt at fitting a repulsion energy was made here.

Apparent activation energies were obtained from a plot of the fitted reaction rate constants with varying temperatures, as shown in figure 3. Clearly, the data does not follow a unique rate law over the whole temperature range, but rather falls into two distinct regions at low ($T < 230$ °C) and high temperatures ($T > 400$ °C). (The data for the intermediate range is not shown in the figure for reasons that will be discussed below.) For the low-temperature regime

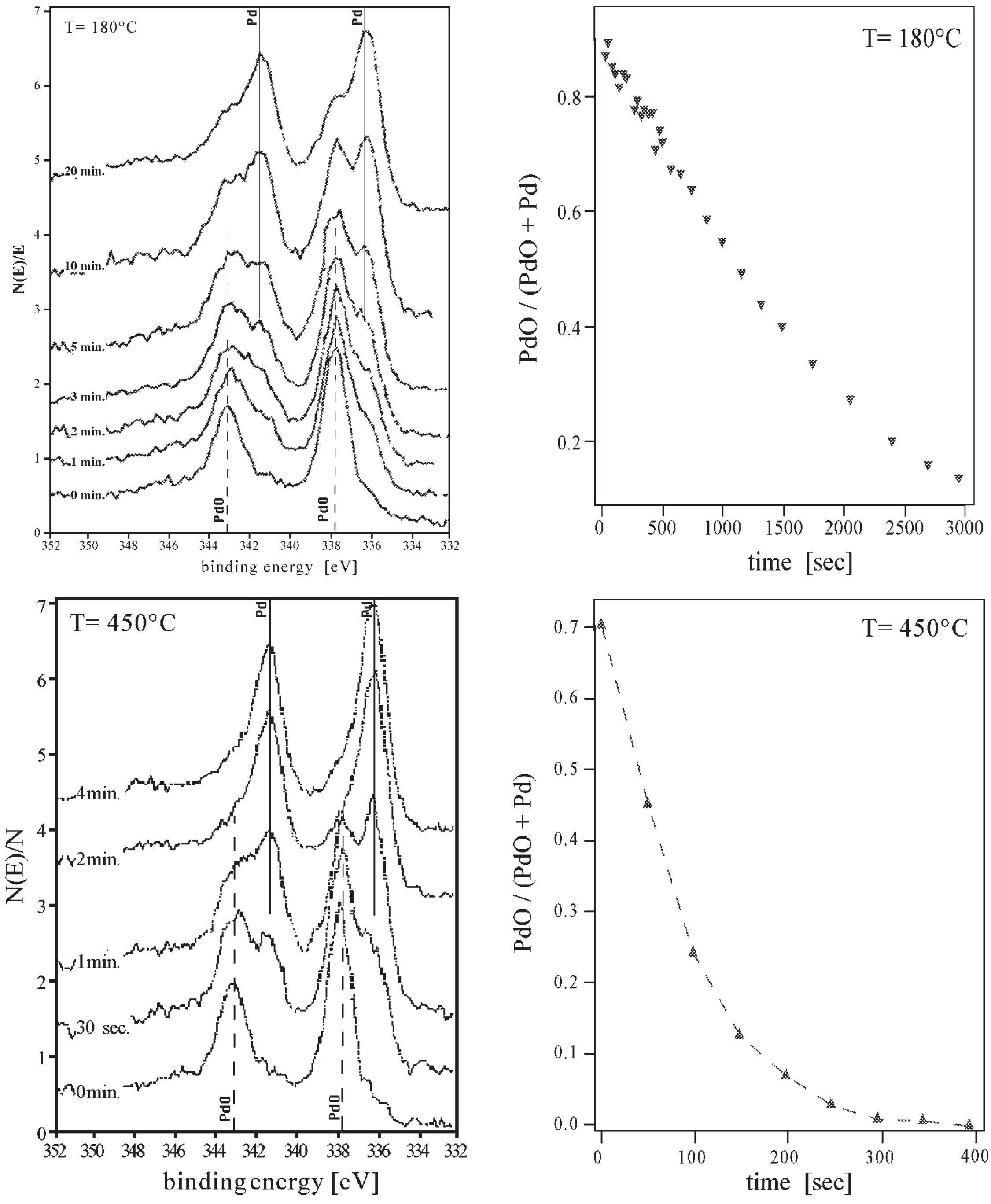

Figure 2. Temporal development of the Pd 3d range in XPS (left graphs) and corresponding time traces of the calculated sample oxide fraction (right graphs) during reduction of an oxidized Pd sample at two sample temperatures, $T = 180\,^\circ\mathrm{C}$ (top row) and $T = 450\,^\circ\mathrm{C}$ (bottom row). The sample was oxidized for 3 min at $p_{\mathrm{O}_2} = 80$ mbar and $T = 450\,^\circ\mathrm{C}$ prior to reduction.

an activation energy of about 106 kJ/mol (±12 kJ/mol) is obtained and for the high-temperature regime an activation energy of about 180 kJ/mol (±6 kJ/mol).

Surprisingly the apparent first-order rate constant seems to drop at intermediate temperatures as the sample temperature is raised from 230 to 400 °C, indicating a negative apparent activation energy in this intermediate temperature range. A closer inspection of the time dependent XPS signal in this intermediate temperature range reveals a pronounced shoulder in the reduction time trace of the sample (figure 4, curve (a)). This behavior cannot be fitted with a unique, simple rate law and suggests a transition between distinct processes with different kinetic rate constants taking place. The second curve in figure 4 shows the change in the oxide fraction as a function of time for a different oxide loading, i.e., the sample was oxidized for 6 min instead of 3 min under the same temperature and pressure conditions. Clearly, the shoulder gets much more pronounced as the oxidation time is increased. This suggests that some oxygen reservoir is being filled during the oxidation process

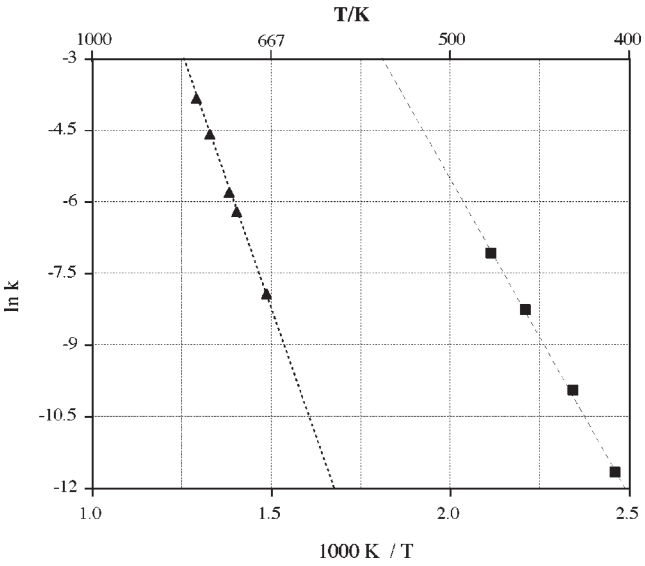

Figure 3. Reduction rates (calculated from the time traces in figure 2) versus reciprocal temperature for the investigated temperature range between 150 and 500 °C. Data from the intermediate temperature range (230–400 °C) is omitted for the sake of clarity. Two separate activation energies can be derived for the low-temperature regime ($T < 230\,^\circ$C, $E = 106 \pm 12$ kJ/mol) and the high-temperature regime ($T > 400\,^\circ$C, $E = 180 \pm 6$ kJ/mol).

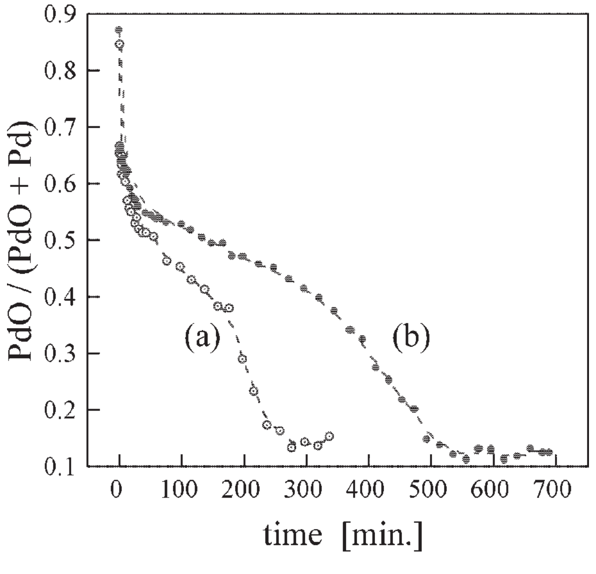

Figure 4. Example of reduction time traces in the intermediate temperature regime ($T = 300\,^\circ$C) for two different durations of the sample oxidation, (a) 3 min oxidation and (b) 6 min oxidation. Except for the different durations, the sample treatments were identical in the two depicted cases. A strong shoulder is visible in the time trace which, therefore, cannot be described by a simple kinetic rate law. The shoulder gets more pronounced for longer oxidation times and is indicative of a transition between two different kinetic mechanisms.

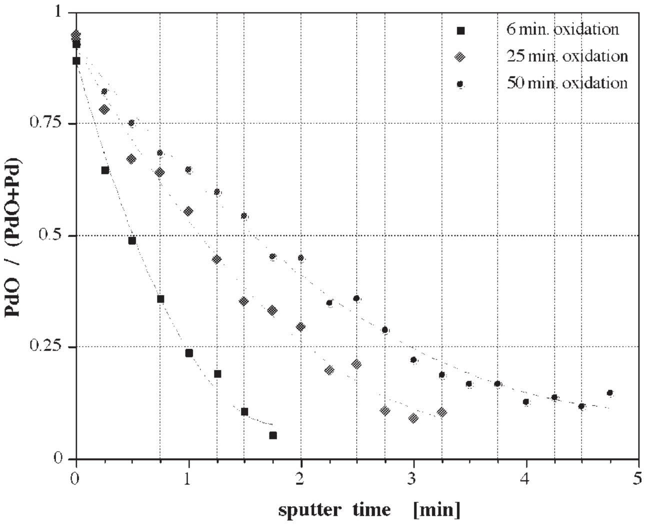

Figure 5. Oxide fraction as calculated from XPS measurements versus sputter time during sputter-depth profiling of several samples that had been oxidized for different durations ($t = 6$, 25, and 50 min) at $p_{O_2} = 80$ mbar and $T = 450\,^\circ$C.

and subsequently emptied during reduction of the sample. Since formation of subsurface oxygen as well as bulk oxides are well established in the Pd/PdO system, it seems reasonable to assume that one or both of those "deep" oxide phases might form this reservoir. (The subsurface oxide has been suggested to be a pre-cursor or a nucleation phase for the bulk oxide in UHV investigations [5,11], so that a further distinction between the two phases might become meaningless at higher (ambient) pressures.)

This interpretation can also explain, why at lower reduction temperatures ($T < 230\,^\circ$C) the (integrated) PdO signal in the XPS scan never drops below about 10% (see figure 2): at low T the diffusion process is obviously too slow to lead to an efficient depletion of the bulk reservoir. As consistent with this picture, this "residual" 10% PdO signal could be reduced to below the detection limit when samples that had previously been reduced at low T were subsequently heated up to temperatures above 400 °C. Heating these samples stepwise to higher temperatures within the transition region yielded with every step a transient increase in the PdO signal due to this stepwise "tapping" into the bulk oxygen reservoir. In contrast to that, heating a sample that had been reduced in the high-temperature range to even higher temperatures or holding it at temperatures in the transition range did not yield any further signal in XPS, nor could we detect any further oxygen release in mass spectrometry.

3.2. Depth profiling

The depth of the oxide layer was investigated by sputter profiling surfaces that has been oxidized for different periods of time under the same experimental conditions ($p_{O_2} = 80$ mbar, $T = 450\,^\circ$C). Figure 5 shows the changes in oxide fraction as a function of time (depth) for three different periods of oxidation with a spread of one order of magnitude. Clearly the oxide depth is not directly proportional to the length of the oxidation process. In contrast, a plot of the square root of the sputter time versus the time of oxidation shows a very good linear relationship (figure 6). Since the sputter time is directly proportional to the probing depth, this indicates that the high-temperature ox-

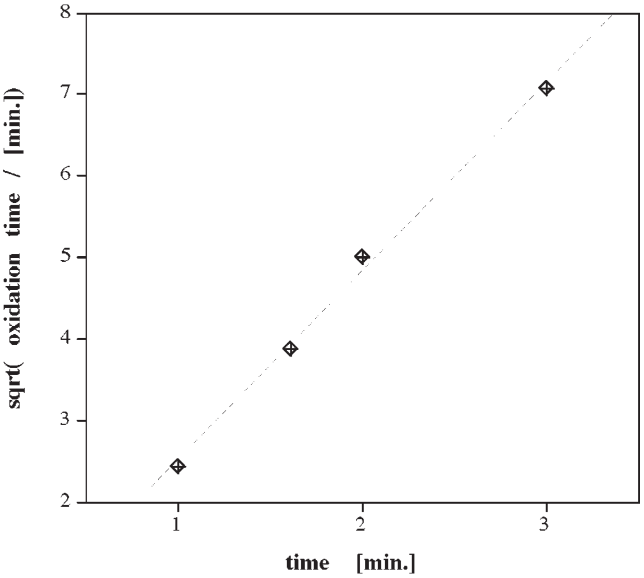

Figure 6. Plot of the square root of the oxidation time versus sputter time (which is proportional to the probing depth). The very good linear fit agrees with the Einstein–Smoluchowski relation for diffusion-limited processes, indicating that oxygen diffusion into the Pd bulk is the rate-limiting step at high temperatures ($T > 400\,^{\circ}\mathrm{C}$).

idation/reduction process is diffusion controlled following the Einstein–Smoluchowski relation,

$$x^2 = 2Dt,$$

where x is the diffusion length, D the diffusion coefficient and t the diffusion time.

A diffusion rate constant of 4×10^{-15} cm^2/s at 450 °C is obtained from the graph using the estimated sputtering rate of 35 A/min. Using the above measured activation energy of $E_{\mathrm{act}} = 180$ (± 6) kJ/mol, a pre-exponential of 10^{-1}–10^{-2} cm^2/s can be obtained. Both the values of the pre-exponential and of the activation energy are within the range of typical values for solid-state diffusion processes.

3.3. Reaction/diffusion model

To further test the interpretation of our XPS data as the result of a transition between a bulk diffusion controlled and a surface reaction (desorption) controlled regime, a qualitative mathematical model for this reaction–diffusion process was constructed. The model includes diffusion of oxygen from the bulk to the surface as well as loss of oxygen from the surface by a first-order desorption/decomposition process. A distinction between the oxide decomposition and the oxygen desorption process is not possible based on the experimental data and was therefore not attempted in the model. For the sake of simplicity, we assume a uniform oxide layer of thickness L on the surface of palladium metal as the starting configuration. Zero-flux (gradient-free) boundary conditions were assumed at distance L from the surface, which implies that the sample is oxidized considerably deeper than $z = L$, and limits the validity of the model to initial reduction times where the reduction wave front has not yet reached this boundary. These assumptions, however, do not limit the applicability of the model for all our purposes.

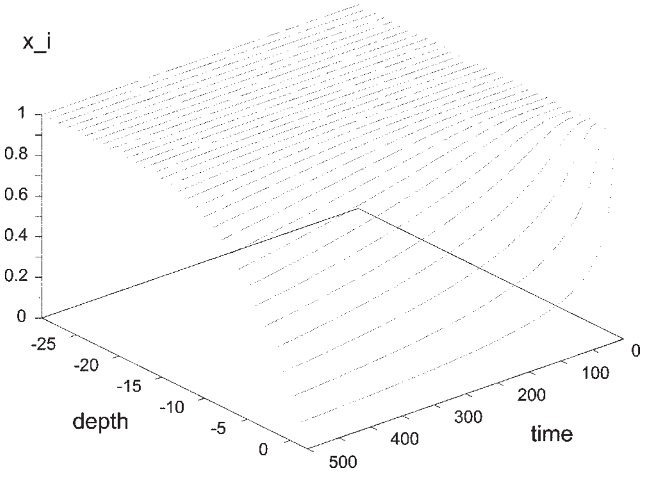

Figure 7. Simulation results for the simple reaction–diffusion model. Shown are profiles of the oxide concentration over sample depth and reduction time. No indication of the experimentally observed shoulder in the time traces can be seen.

Mathematically, the differential equations governing the model in one dimension are therefore:

bulk diffusion:

$$\partial c/\partial t = -D\,\partial^2 c/\partial z^2, \quad 0 < z < L,$$

reaction (decomposition) at the surface:

$$\partial c/\partial t = kc, \quad z = 0,$$

zero-flux boundary condition at L:

$$\partial c/\partial z = 0, \quad z = L,$$

and the initial condition:

$$c(z) = c_0, \quad t = 0,$$

where c is the oxide concentration, D is the diffusion constant, k is a first-order reaction rate constant, c_0 the initial oxygen concentration in the bulk, and z denotes distance from the sample surface.

This set of equations is analogous to well known systems of equations from heat conduction problems. It can be solved to yield a semi-analytical series solution for $c(z,t)$, the derivation of which can be found in standard text books on heat conduction [35]:

$$c(z,t) = 2c_0 \sum_{m=1}^{\infty} \mathrm{e}^{-D\beta_m^2 t} \left[-\frac{k}{2(\beta_m^2 + k^2) - k} \right] \left[\frac{\cos\beta x}{\cos\beta L} \right],$$

where β_m are the eigenvalues of the equation

$$\beta_m \tan\beta_m L = k.$$

The resulting profiles of the oxide concentration over sample depth and reduction time are shown in figure 7. Obviously, the time development of the oxide concentration in the local time trace of the surface layer (or any of the deeper layers alone) does not show the expected shoulder. Therefore, the near-surface concentration of oxygen was summed

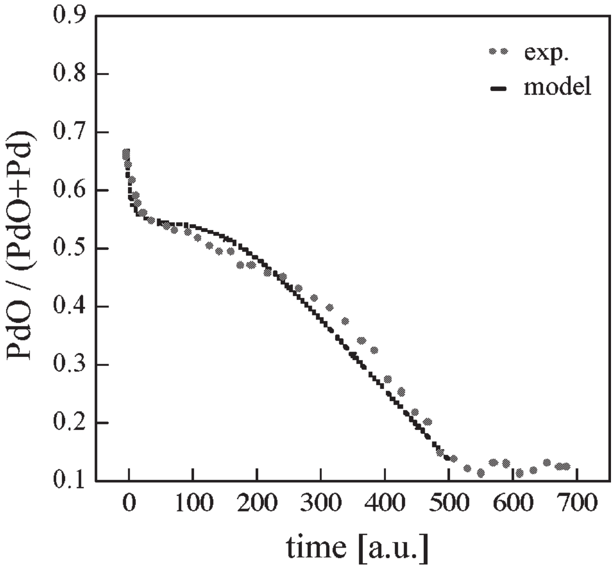

Figure 8. Time traces of experimentally measured oxide fractions (symbols, $T_{\mathrm{exp}} = 300\,^{\circ}\mathrm{C}$) along with simulation results (lines). The near-surface concentration of oxygen in the simulation results was summed with an exponential weighting factor to mimic the finite probing depth of the XPS measurement. A very good (qualitative) agreement is obtained between model and experiment.

with an exponential weighting factor that served to mimic the finite probing depth of the XPS measurement. Figure 8 shows the results of the model (line) superimposed on the experimental data (symbols) for a reduction temperature of 300 °C. The very good qualitative fit supports the interpretation that the intermediate temperature results are caused by a transition from a reaction-controlled to a diffusion-controlled process. A quantitative fit for the whole transition region would require a more elaborate model and was not attempted in this work.

It should finally be noted here, that the observed complexity of the system in the transition region ($230 < T < 400\,^{\circ}\mathrm{C}$) is due to a convolution of the intrinsic complexity of the dynamics of the Pd/PdO system (i.e., the transition between the kinetically and the diffusionally controlled process) with the fact that the experimentally observed XPS signal is not a strictly surface sensitive signal but rather averages between surface and near-surface regions. Only the superposition of the temporal and the spatial dynamics of the reduction process in the XPS data gives rise to the apparent complex behaviour and, therefore, hints at the importance of both the spatial (diffusion) and the temporal (surface reaction) processes.

3.4. Comparison with previous work

Most of the investigations on the unusual behavior of the Pd/PdO system have previously focussed on the energetics of the different binding states of oxygen in this metal/oxide system. While a large amount of information has been gathered in the course of these investigations, no unambiguous picture of the mechanism of oxygen uptake and release by Pd has resulted so far. One of the key problems seems to be that most studies were conducted under high and ultra-high vacuum conditions, although several reports clearly point out the difficulties of studying this system under low-pressure conditions, since rather high oxygen partial pressures are required for the formation of a true oxide. While some studies tried to achieve higher “virtual” oxygen pressure by using NO or NO_2 as an oxidant [5,10], a quantification of these pressures is virtually impossible. Therefore, the applicability of those low-pressure studies to near-ambient or even elevated pressure conditions, under which typical oxidation reactions are conducted, seems doubtful.

This study therefore did not attempt to solve any open questions regarding the different binding states of oxygen in the Pd/PdO system, but rather aimed at a purely phenomenological description of the macroscopic oxidation/reduction kinetics in this system. Our observations allow for a surprisingly straightforward explanation of the oxidation/reduction process of palladium in terms of a transition from a kinetically controlled process at lower temperatures to (bulk) diffusion control at higher temperatures as shown above. While thus giving a simple and consistent explanation of our experimental data, this picture of the Pd reduction kinetics is in contradiction to many of the previously published reports: most previous studies attributed the high-temperature TDS signals to strongly bound surface oxygen, while suggesting that bulk oxides are less stable and, therefore, decompose at lower temperatures. However, this does not seem to hold for our higher pressure experimental conditions, in agreement with reports that found that higher oxygen partial pressures – even far below the ambient pressure range – tend to stabilize PdO [6].

Of the few studies that were conducted under similar conditions to the current investigation, the study by Peuckert appears to be the most relevant to our findings [9]. That study focussed on the thermal stability of the Pd/PdO system, i.e., it attempted to measure thermodynamic equilibrium states rather than decomposition kinetics. In a comparison of those results with ours we come to an interesting conclusion: the report describes a hysteresis during oxidation and reduction of the Pd samples in the temperature range between about 500 and 750 K, i.e., roughly the same temperature range in which we find the transient behavior. Also, the reported values of the detected PdO signal in the hysteresis plateau coincide quite exactly with the plateau values that we measure in our study (40–60%). It seems, therefore, very likely that in fact no true steady state (i.e., thermodynamic equilibrium) had been attained in the (apparent) hysteresis regime, but that rather the transient plateau in the decomposition kinetics (the “shoulder” in figure 5) was erroneously taken to be stationary. This is also supported by the fact that constant signal intensities were reported to have been obtained after 5–20 min, which is exactly when the plateau in the decomposition time trace was reached in our studies. Due to the deep oxidation of the samples under higher oxygen partial pressure conditions –

which were comparable in the two studies – the second decomposition step sets in only after about another hour, thus giving rise to an apparently stationary signal. Re-evaluating Peuckert's data in this light resolves any contradiction between our findings and his, and yields (even quantitatively) very consistent results.

These findings suggest that a re-evaluation of previous investigations on the oxidation/reduction of palladium catalysts in the light of a diffusion/reaction system that is governed not only by the (temporal) dynamics of a surface reaction process but also by the (spatial) dynamics of a bulk diffusion process might help to resolve at least some of the apparent complexities and inconsistencies in previous reports on this catalytic system.

4. Summary

The oxidation–reduction kinetics of a polycrystalline Pd foil was investigated under well-controlled conditions in a high-pressure reaction chamber connected to an UHV chamber equipped with XPS and a sputter gun. The observed behavior can be explained in terms of a kinetically controlled process at lower temperatures ($T < 230\,^\circ\mathrm{C}$), characterized by a low activation energy of about 106 kJ/mol and a diffusion-controlled process at higher temperatures ($T > 450\,^\circ\mathrm{C}$), characterized by a high activation energy of about 180 kJ/mol, which could be confirmed in sputtering depth profile experiments.

In the intermediate temperature range ($230 < T < 450\,^\circ\mathrm{C}$) the system displays a complex kinetic behavior with an apparent negative activation energy. This behavior could be shown to be caused by a transition between the reaction- and the diffusion-controlled processes giving rise to a pronounced shoulder in the reduction time trace. The interpretation was qualitatively confirmed using a simple mathematical model.

This work shed some new light on previously reported results and forms a basis for further investigations of the behavior of Pd catalysts under reactive conditions.

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References

[1] M. Ziauddin, G. Veser and L.D. Schmidt, Catal. Lett. 46 (1997) 159.
[2] G. Veser, M. Ziauddin and L.D. Schmidt, Catal. Today 47 (1999) 219.
[3] G. Ertl and P. Rau, Surf. Sci. 15 (1969) 443.
[4] G. Ertl and J. Koch, in: *Adsorption–Desorption Phenomena*, ed. F. Ricca (Academic Press, London, 1972) p. 345.
[5] H. Conrad, G. Ertl, J. Küppers and E.E. Latta, Surf. Sci. 65 (1977) 245.
[6] C.T. Campbell, D.C. Foyt and J.M. White, J. Phys. Chem. 81 (1977) 491.
[7] D.L. Weisman, M.L. Shek and W.E. Spicer, Surf. Sci. 92 (1980) L59.
[8] E.M. Stuve, R.J. Madix and C.R. Brundle, Surf. Sci. 146 (1984) 155.
[9] M. Peuckert, J. Phys. Chem. 89 (1985) 2481.
[10] B.A. Banse and B.E. Koel, Surf. Sci. 232 (1990) 275.
[11] V.A. Bondzie, P. Kleban and D.J. Dwyer, Surf. Sci. 347 (1996) 319.
[12] E.H. Voogt, A.J.M. Mens, O.L.J. Gijzeman and J.W. Geus, Surf. Sci. 373 (1997) 210.
[13] J.E. Turner, B.C. Sales and M.B. Maple, Surf. Sci. 109 (1981) 591.
[14] B.C. Sales, J.E. Turner and M.B. Maple, Surf. Sci. 114 (1982) 381.
[15] S. Ladas, R. Imbihl and G. Ertl, Surf. Sci. 219 (1989) 88.
[16] M.R. Bassett and R. Imbihl, J. Chem. Phys. 93 (1990) 811.
[17] N. Hartmann, K. Krischer and R. Imbihl, J. Chem. Phys. 101 (1994) 6717.
[18] M. Ehsasi, M. Berdau, T. Rebitzki, K.P. Charle, K. Christmann and J.H. Block, J. Chem. Phys. 98 (1993) 9177.
[19] M. Ehsasi, O. Frank, J.H. Block and K. Christmann, Chem. Phys. Lett. 165 (1990) 115.
[20] M. Berdau, M. Ehsasi, A. Karpowicz, W. Engel, K. Christmann and J.H. Block, Vacuum 45 (1994) 271.
[21] J.G. Firth and H.B. Holland, J. Chem. Soc. Faraday Trans. 65 (1969) 1121.
[22] A. Schwartz, L.L. Holbrook and H. Wise, J. Catal. 21 (1971) 191.
[23] R.J. Farrauto, M.C. Hobson, T. Kennelly and E.A. Waterman, Appl. Catal. A 81 (1992) 227.
[24] J.G. McCarty, Catal. Today 26 (1995) 283.
[25] P. Salomonsson, S. Johansson and B. Kasemo, Catal. Lett. 33 (1995) 1.
[26] L.P. Haak and K. Otto, Catal. Lett. 34 (1995) 31.
[27] K. Sekizawa, K. Eguchi, H. Widjaja, M. Machida and H. Arai, Catal. Today 28 (1996) 245.
[28] M. Lyubovsky, R. Weber and L. Pfefferle, in: *Symposium (International) on Combustion* (Combustion Inst., Pittsburgh, 1996) p. 1779.
[29] Y. Deng and T.G. Nevell, Faraday Discuss. Chem. Soc. 105 (1996) 33.
[30] H.Y.H. Chan, C.T. Williams, M.J. Weaver and C.G. Takoudis, J. Catal. 174 (1998) 191.
[31] J. Chen and E. Ruckenstein, J. Catal. 69 (1981) 254.
[32] J. Chen and E. Ruckenstein, J. Phys. Chem. 85 (1981) 1606.
[33] E.H. Voogt, A.J.M. Mens, O.L.J. Gijzeman and J.W. Geus, Surf. Sci. 350 (1996) 21.
[34] A.W. Czanderna, *Methods of Surface Analysis* (Elsevier, Amsterdam, 1984).
[35] M.N. Ozisik, *Heat Conduction* (Wiley, New York, 1980).