Surface and subsurface oxygen on Pd(111)

F.P. Leisenberger a, G. Koller a, M. Sock a, S. Surnev a, *, M.G. Ramsey a, F.P. Netzer a, B. Klötzer b, K. Hayek b

a Institut für Experimentalphysik, Karl-Franzens-Universität Graz, Universitätsplatz 5, A-8010 Graz, Austria
b Institut für Physikalische Chemie, Universität Innsbruck, A-6020 Innsbruck, Austria

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Abstract

The interaction of O2 with Pd(111) in the temperature range from 300 K to 1000 K was studied by molecular beam adsorption, thermal desorption (TDS), low energy electron diffraction (LEED), high-resolution X-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). Using a capillary array doser and high effective oxygen pressures, evidence was found for the formation of a densely packed chemisorbed oxygen adlayer saturating at θO close to 1 and separately for subsurface migration of oxygen at elevated temperatures, but not at room temperature and below. Up to completion of a p(2 × 2) oxygen adlayer at 0.25 ML surface coverage, the dissociative sticking probability of oxygen into the chemisorbed state is high and masks the much slower diffusion into the bulk. Beyond 0.25 ML surface coverage, the adsorption rate into the chemisorbed state becomes small and the influence of bulk migration detectable. Exposure of the sample to high oxygen dosages at 1000 K fills up the subsurface reservoir and subsequent sticking measurements are no longer influenced by oxygen loss to the bulk. The subsurface oxygen could be distinguished in both XPS and off-specular HREELS. These latter techniques revealed that considerable concentrations of oxygen in the near-surface region can build up, even at lower temperatures (523 K) and oxygen exposures (40 L). In contrast to chemisorbed oxygen atoms on Pd(111), the subsurface species cannot be removed by reaction with CO. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last decades, numerous studies of the Pd(111)–oxygen system have been performed in wide temperature and pressure ranges [1–14]. Oxygen was found to adsorb dissociatively on Pd(111) above 200 K [8]. At room temperature, oxygen adsorption gives rise to a p(2 × 2) LEED pattern, which corresponds to an oxygen coverage of 0.25 ML [1], with O atoms occupying threefold hollow sites [14]. The oxygen surface coverage can be extended further up to 1.4 ML at high ‘effective’ O2 pressures, using the dissociative adsorption of NO2 on Pd(111) [10]. In most of the previous work, indications were found that oxygen atoms migrate into the palladium bulk [1,3,5,6,10], but detailed information about their true nature is rather scarce. Conrad et al. [1] have ascribed the high-temperature thermal desorption peak above 1100 K to the desorption of oxygen dissolved in
the subsurface region. According to Weissman- Wenocur et al. [5], the interaction between oxygen and Pd involves the following stages: (i) formation of surface chemisorbed oxygen; (ii) oxygen incorporation into steps or defect sites of the surface; (iii) oxygen migration into the bulk (subsurface oxygen); and (iv) bulk PdO formation. Oxygen migration into the subsurface region has been invoked even at substrate temperatures just slightly above 300 K [14]. However, others have excluded the oxygen diffusion into the bulk in their experiments and instead suggest the formation of a surface oxide [11]. These discrepancies in the published results have been attributed to the strong influence of the defect surface density on the rate of bulk migration [5,6].

Understanding the nature of the subsurface oxygen species is of practical importance for heterogeneous catalysis. Recent studies on Pd(110) surfaces [15,16] have indicated that subsurface oxygen can influence the catalytic oxidation of CO, causing kinetic oscillations in the CO₂ production rate. This interpretation has been disputed by Bondzic et al. [17], who have found evidence that the oscillatory behavior in this system is due to an oxidation-reduction mechanism, rather than the slow filling and depletion of subsurface oxygen as previously postulated [15,16]. Only a few studies so far have been concerned with the reaction of CO and oxygen on Pd(111), none of them referring to the chemical reactivity of bulk-located or subsurface oxygen. As a general result, however, high reactivity of dissociatively chemisorbed oxygen already at room temperature or below has been reported [18,19].

In this work the interaction of oxygen with Pd(111) has been investigated in a wide temperature range. By means of a high-intensity molecular beam, comparably high oxygen coverages up to 1 ML were produced by simple O₂ adsorption. Here, evidence for the formation of subsurface oxygen on Pd(111) and its characterization with several surface analytical techniques were obtained. In addition, the reactivities of the chemisorbed and subsurface oxygen species towards CO have been investigated and the results are reported herein.

2. Experimental

The experiments were carried out in three different UHV systems. One system, used for molecular beam and thermal desorption spectroscopy (TDS) experiments, was equipped with LEED/AES, a beam-forming gas doser and a shielded, differentially pumped quadrupole mass spectrometer for line-of-sight detection of thermally or reactively desorbing molecules. A multi-channel array doser (Galileo Optics), in a design similar to that proposed in [20], was used as a molecular beam source for controlled gas adsorption with small flux gradient across the sample surface, providing high fluxes at low background pressures in the system. Accurate calibration of absolute beam fluxes was achieved by measurement of the absolute pressure decrease in a separate differentially pumped gas dosing and mixing system by means of a MKS Baratron pressure transducer [21]. A second quadrupole mass spectrometer monitoring the ambient pressure changes in the main chamber was used to perform King and Wells type measurements [22] of net adsorption rates and sticking probabilities. Since only about 50% of the effusing gas from the doser hits the sample surface at the chosen dosing geometry, the accurate value for this fraction was determined from the ratio of the initial sticking probability for CO and O₂ measured in our system with data of absolute initial sticking probabilities from supersonic beam experiments [2,12,13]. On this basis, a calibration of the total oxygen uptake, due to both chemisorbed and subsurface oxygen, was possible by integrating the measured net adsorption rates dθ/dt = flux x s(t) over time. On the other hand, the oxygen coverage evaluated from the TDS areas is related exclusively to the chemisorbed (surface) oxygen, since the oxygen migration in the bulk was found to be largely irreversible in the TDS. Total beam fluxes, rates of adsorption and desorption and coverages given in this work refer to 1 ML as 1:1-ratio of oxygen atoms to Pd surface atoms. By comparison with the surface impingement rate of O₂ molecules at 10⁻⁶ mbar ambient oxygen pressure, an exposure of 1 ML (1 O atom/site) corresponds to 2.8 L (Langmuirs) of O₂(g). The Pd(111) single crystal surface (12 mm
diameter × 3 mm thick) was oriented within 0.2° of the bulk (111) plane and cleaned by flashing to 1250 K, sputtering with 700 eV Ar⁺, flashing to 1200 K, exposure to 5 × 10⁻⁷ mbar oxygen during cooling (1200 K to 600 K) and final annealing to 1200 K. This procedure yielded a clean surface as checked by AES and flash desorption of adsorbed oxygen which showed only O₂ desorption but no increase of the CO and CO₂ signal.

High-resolution X-ray photoelectron spectroscopy (HR-XPS) measurements were performed in a second UHV chamber at beamline 22 at the MAX I synchrotron radiation source in Lund, Sweden. This beamline is equipped with a modified SX-700 monochromator and a Scienta-200 hemispherical electron analyser. In the photoelectron spectroscopy measurements, photon energies of 400 eV and 600 eV were used for exciting electrons from the C 1s, Pd 3d₅/₂ and O 1s core levels, respectively. The corresponding experimental resolution was better than 250 meV (hν = 400 eV) and 400 meV (hν = 600 eV). The photoelectron spectra were recorded at normal-emission geometry, and the binding energy scale of the spectra were calibrated with respect to the Fermi edge. All spectra presented were normalised to the background at a few eV higher kinetic energy than the respective core level maxima. Here and in the third UHV chamber, described below, a second Pd(111) crystal was used. Clean Pd(111) crystal surfaces were prepared by Ar⁺ ion bombardment at 1 keV followed by annealing up to 1000 K. The Pd(111) crystal was heated by electron bombardment from the back side, and the temperature was measured with a chromel–alumel thermocouple spotwelded to the edge of the Pd crystal. The cleanliness of the Pd surface was checked by XPS and LEED. Oxygen was dosed in amounts of 40 L at a pressure of 2 × 10⁻⁷ mbar, while the Pd(111) sample was kept at two sample temperatures, 300 K or 523 K. CO exposures were done on clean and oxygen precovered Pd(111) surfaces at room temperature (300 K).

The third UHV chamber was equipped for high-resolution electron energy loss spectroscopy (HREELS), AES and LEED, as described elsewhere [23]. HREELS measurements were taken at a specular angle of 60° from the surface normal, an incident beam energy of 5.5 eV and the crystal at room temperature. The energy resolution was set to ~4.5 meV.

3. Results

In view of the different techniques employed in the present work, two different types of oxygen exposure experiments were performed, which will be presented in three separate subsections. In the first (Section 3.1), the kinetic measurements are described: the Pd(111) surface was exposed to large amounts of oxygen, expressed in ML units (1 ML = 2.8 L), while the surface was kept at temperatures ranging from 300 K to 900 K. In Sections 3.2 and 3.3, the electron spectroscopy results obtained for low oxygen exposures of 40 L on Pd(111) at 300 K and 523 K are presented.

3.1. Kinetic and TDS data

Fig. 1 displays the dissociative O₂ sticking probability at different sample temperatures as a function of the oxygen coverage. The oxygen sticking probability has been determined by the King and Wells technique in the low coverage range (0 < Θ₀ < 0.25) from the TDS peak areas in the high coverage-low sticking regime (0.25 < Θ₀ < 1). At Θ₀ below 0.25, the sticking is dominated by precursor kinetics, in agreement with recent supersonic beams data [12,13]. Consequently, increasing the sample temperature leads to a decrease in sticking at a given Θ₀. Beyond 0.25 ML the sticking probability becomes very low and the trend is reversed, i.e. the sticking increases with increasing sample temperature, indicating that the chemisorption process involves an activated step. The saturation concentration of the chemisorbed surface Ochem was found to be close to 1 ML. The mesoscopic and microscopic structural aspects of the high-coverage chemisorbed adlayers in the stages of nucleation and growth are out of the scope of this work and will be presented elsewhere [24].

At elevated temperatures additional complications arise, since oxygen migration in the bulk, which becomes more favourable, is expected to
occur in parallel with the activated chemisorption process step. This situation complicates the experimental approach both towards chemisorption and subsurface migration. In order to study these two effects separately, specific experimental conditions need to be met. Two approaches were found useful to focus experiments exclusively on strongly bound oxygen below the surface layer and to distinguish it from chemisorbed oxygen: (i) 'absorption' and 'desorption' at temperatures above the maximum desorption temperature of chemisorbed oxygen, and/or (ii) removal of the chemisorbed oxygen by means of a surface-specific reaction, e.g. with CO from the gas phase. In this section the first route will be mainly followed.

According to Weissman et al. [3], high oxygen exposures at sample temperatures of around 1000 K are the most effective way to populate the subsurface oxygen. Fig. 2 displays TDS spectra starting from a saturated chemisorbed oxygen adlayer after an exposure of 4000 ML at 623 K (beam flux 7.4 ML/s). Prior to this experiment, the sample was heated to 1273 K. The desorption maximum of chemisorbed O occurs at 750 K and desorption is complete for the chemisorbed O adlayer at 900 K; no additional TDS feature at higher temperatures is observed (trace a). Trace b was obtained after an oxygen pre-dose of up to 8000 ML at 973 K (at beam flux 11.5 ML/s), followed by 4000 ML of oxygen at 623 K. This pretreatment produces an additional desorption peak at 1142 K, similar to that observed in previous studies [1,3] and which has been attributed to the subsurface oxygen. Compared to Ref. [3], a five times higher exposure was necessary to produce this small TDS feature, probably because of the very low defect density of our sample surface. The desorption of the chemisorbed oxygen from this surface yields practically the same TDS peak at 750 K, as from the bulk-clean sample (cf. trace a). The chemisorbed oxygen could be removed thermally by heating up to 923 K (trace c) or by reaction with CO at 523 K (trace d) without markedly affecting the desorption feature at 1142 K.

Exposing the Pd(111) surface to a low intensity chopped molecular beam (0.05 ML/s) at a temperature slightly above the desorption limit for chemisorbed oxygen (900 K) should lead to an equilibrium situation with respect to adsorption and desorption within a few seconds, since the desorption rate is already high enough at low coverages to counterbalance the adsorption rate. Fig. 3 displays the temporal evolution of the
oxygen mass spectrometer signal at 900 K. This modified molecular beam relaxation technique has been described in details by Ali et al. [22] and used for measuring adsorption isotherms on single crystal surfaces. The areas of the oxygen adsorption and desorption peaks following chopping of the beam are equal, if merely the build-up and decay of the surface chemisorption equilibrium is monitored [22]. Surprisingly, the very first adsorption peak in Fig. 3 is significantly larger than the following ones. Only if the beam chopping was continued for several minutes, the adsorption and desorption peak areas become equal. The fast adsorption/desorption process appears to be therefore superimposed by a slow process (as indicated by the straight solid line in Fig. 3). At this temperature, irreversible uptake of oxygen takes place, which is associated with the filling up of a reservoir of more strongly bound oxygen as compared to chemisorbed $O_{chem}$. This is clearly due to subsurface migration at temperatures above the maximum desorption temperature for chemisorbed oxygen.

Fig. 4 demonstrates that oxygen chemisorption and subsurface migration compete also at lower temperatures on the Pd(111) surface. Fig. 4 shows sticking versus coverage curves for: (a) a presatu-

![Fig. 2. Thermal desorption spectra of oxygen from Pd(111): (a) after heating to 1273 K and 4000 ML oxygen at 623 K, (b) after exposure to 8000 ML at 973 K and 4000 ML of oxygen at 623 K, (c) after preparation (b), but desorption to 923 K and cooling to 300 K, (d) after preparation (b) followed by reaction with 300 ML CO at 523 K.](image)

![Fig. 3. Adsorption–desorption cycles at 900 K surface temperature, after heating to 1300 K prior to $O_2$ exposure. The dashed line corresponds to the base pressure level without adsorption or desorption; the solid line indicates the trend ascribed to the slow irreversible bulk migration of oxygen atoms.](image)
Fig. 4. Oxygen sticking versus coverage curves for 523 K sample temperature, gas temperature at 300 K. Curve (a) after pretreatment by 8000 ML oxygen at 973 K, before exposing to O$_2$ at 523 K; curve (b) after sample heating to 1273 K prior to O$_2$ exposure. Inset: TDS spectra obtained after the respective sticking experiments (a) and (b). The total oxygen exposure was 120 s at a flux of 0.045 ML/s (5.5 ML) in both cases.

rated sample (8000 ML at 973 K) and (b) a subsurface oxygen depleted sample (heated to 1273 K in vacuo). The sticking due to the slow formation of densely packed surface chemisorbed oxygen is about 0.01 at 0.25 ML and 523 K as derived from Fig. 1 and it can be assumed to be equal for both experiments since all parameters except the subsurface reservoir state are identical. The sticking curves (a) and (b) in Fig. 4 exhibit slightly different traces at coverages above 0.20 ML. The TDS spectra, taken subsequently to the adsorption experiments, are displayed in the inset to Fig. 4. They confirm that at 523 K part of the chemisorbed oxygen is lost to the oxygen deficient reservoir. The TDS area obtained after sticking experiment (a) corresponds to 0.24 ML oxygen, meaning that the mass balance of adsorbed and desorbed oxygen agrees very well. On the other hand, the TDS peak obtained after sticking experiment (b) on the oxygen-deficient sample is smaller than peak (a), although the sticking curve ends up at a higher final total coverage (0.35 ML). Therefore, adsorbed oxygen is partly converted into subsurface oxygen, which is not desorbed in the temperature range displayed in Fig. 4. Surface oxygen may diffuse to the oxygen-deficient subsurface reservoir not only during the 523 K sticking experiment itself, but also during the heating ramp up to the onset of thermal desorption at 673 K.

3.2. LEED and XPS

In order to distinguish further between chemisorbed and subsurface O species on the Pd surface, LEED, XPS and HREELS experiments are described where oxygen was dosed in amounts of 40 L at 300 K and 523 K. For the sake of convenience, we will refer to these two surfaces in the following as Pd(111)–O$_x$ and Pd(111)–O$_p$, respectively.

The LEED patterns from these two surfaces are presented in Fig. 5. It can be seen that dosing 40 L oxygen at 300 K results in a p(2×2) diffraction pattern (Fig. 5a) with sharp and intense half-order spots, in agreement with previous LEED results [1]. This suggests that this dose is sufficient for
Fig. 5. LEED patterns of the Pd(111)–O phases formed after dosing of 40 L O\textsubscript{2} at: (a) 300 K [Pd(111)–O\textsubscript{I}] and (b) 523 K [Pd(111)–O\textsubscript{II}]. The electron energy was 61 eV.

The formation of a chemisorbed oxygen layer with $\theta_0 = 0.25$ ML. Dosing the Pd(111) surface with oxygen at 523 K results in a LEED pattern (Fig. 5b) where the half-order reflections are significa
cantly weaker and more diffuse. This may be attributed to reduced long-range order in the che
misorbed adlayer and/or the decrease of the oxygen surface concentration as a result of subsur-
face penetration.

Fig. 6 shows the O 1\textsubscript{s} and Pd 3d\textsubscript{5/2} core level spectra obtained after dosing the clean Pd(111) surface to 40 L O\textsubscript{2} at 300 K and 523 K. The adsorbed atomic oxygen at 300 K can be detected as an O 1\textsubscript{s} structure at a binding energy of 529.2 eV, which is, however, overlapping with
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emission spectra. This was possible since no sig
ificant changes in the relatively broad Pd 3p\textsubscript{3/2} peak structure were found after O or CO expo-
sures. The corrected O 1\textsubscript{s} core level spectra are
After dosing 40 L O, O atoms occupy three-fold hollow sites, which is in good agreement with previous HREELS results [14]. The O 1s spectrum before CO exposure, because the oxidation reaction between oxygen and CO [18] yields CO₂, which desorbs. Instead, a new O 1s derived peak (marked as O_{ads}) appears at a BE of 531.2 eV, which is due to adsorbed CO. The corresponding Pd 3d₅/₂ spectrum shows the decomposed bulk (B) and CO-induced (C) components. The binding energy (335.3 eV), as well as the relative intensity of the C component, are very similar to that observed in the O 1s core level region now displays two well-resolved structures, with the larger part of the intensity coming from the CO-related peak. For comparison, the O 1s spectrum before CO exposure is also displayed here with a dashed line. As evident from the figure, the CO adsorption
Fig. 7. O 1\text{s} (left) and Pd 3d\text{5/2} (right) core level spectra after 5 L CO exposure on the Pd(111) surface predosed with O\text{2} at 300 K (bottom) and 523 K (middle). The top spectra are obtained after desorbing the CO by heating to 423 K, starting from the middle spectra. The Pd 3d\text{5/2} spectra have been decomposed into bulk (B), surface (S) and CO-induced (C) components. The O 1\text{s} components due to the chemisorbed O, subsurface O and chemisorbed CO are indicated as O\text{chem}, O\text{sub}, and O\text{CO}, respectively.

Fig. 8 shows the C 1\text{s} peak areas (a) and binding energy (BE) (b) versus CO exposure for CO adsorption on clean and Pd(111) oxygen precovered surfaces at 300 K and 523 K.

Fig. 8 shows the C 1\text{s} peak areas (a) and binding energy (b) as a function of the CO exposure on the clean Pd(111) and the two Pd(111)–O surfaces, on which 40 L of O\text{2} were predosed at 300 K and 523 K. The areas under the C 1\text{s} peaks were evaluated from sets of C 1\text{s} spectra as a function of CO exposure on the Pd(111)–O surfaces. As can be seen in Fig 8a, the initial slopes and the saturation levels of all uptake curves are similar within the measurement accuracy. This implies that the preadsorbed oxygen does not substantially change the initial sticking coefficient of CO or the CO saturation coverage on Pd(111). Also, the evolution of the C 1\text{s} BE (considered here as a single component) with the CO exposure (Fig. 5b) does not show significant differences between the clean and oxygen preadsorbed Pd surfaces. However, the C 1\text{s} peak position on the Pd(111)–O\text{2} surface exhibits some deviations at
low CO exposures, as compared to the clean and Pd(111)−O₃ surfaces. After a CO exposure of 5 L the C 1s BE for all three surfaces is almost identical.

3.3. HREELS

Fig. 9 shows two sets of HREELS spectra, obtained in specular geometry, for the oxygen predosed Pd(111) surfaces at 300 K and 523 K and after their exposure to different amounts of CO at 300 K. Prior to the CO dose, both Pd(111)−O surfaces showed single loss peaks at 58.6 meV with similar intensities, characteristic of the perpendicular vibrations of oxygen atoms, adsorbed in the threefold hollow adsorption sites on Pd(111)[14]. Dosing CO in increasing amounts on the Pd(111)−O surfaces results in a rapid decrease of the Pd−O stretch intensity, due to the progressive removal of the chemisorbed oxygen by the reaction with the adsorbed CO molecules. The CO adsorption is detected already at low exposures by the appearance of a loss peak at 225.5 meV, characteristic of the C−O stretching vibration. This peak exhibits a shift to higher energies with increasing the CO exposure, in correspondence with the IR data of Bradshaw and Hoffmann [27]. After a CO dose of ~1 L the Pd−O stretching intensity vanishes completely in the HREELS spectra for both Pd(111)−O phases; the whole chemisorbed oxygen has been reacted away. At CO saturation (5 L) both sets of vibrational spectra show the same loss features of adsorbed CO. It appears, therefore, that the HREELS in the specular mode is not capable of distinguishing between chemisorbed and subsurface oxygen on the Pd(111) surface. In view of the strong screening of the dynamic dipole moment by the metal conduction electrons, the lack of sensitivity of HREELS in the specular geometry to detect embedded species is not surprising: Johnson et al. [28] have, however, demonstrated in the case of H dissolved in a Ni(111) crystal that such species can be successfully detected and studied by HREELS in off-specular scattering geometry. They attributed an additional loss feature observed at 800 cm⁻¹ to vibrations of hydrogen atoms occupying sites beneath the Ni surface [28].

Fig. 10 shows HREELS spectra taken in 5° off-specular geometry from the Pd(111)−O₃ (a) and

![Fig. 9. HREELS spectra in specular geometry for different CO exposures on the (a) Pd(111)−O₃ and (b) Pd(111)−O₂ surfaces.](image-url)
Fig. 10. HREELS spectra in 5° off-specular geometry before and after removal of the chemisorbed oxygen by dosing (a) Pd(111)−O₀ and (b) Pd(111)−O₈ surfaces with 5 L of CO followed by a heating to 423 K.

Pd(111)−O₀ surfaces (b) before and after a 5 L CO dose at room temperature, followed by a heating to 423 K. Remember that similar treatment was performed (Section 3.1) (Fig. 7) in order to react the chemisorbed oxygen away and subsequently remove the adsorbed CO. As in the specular mode, the vibrational spectrum obtained from the oxygen predosed Pd(111) surface at 300 K (bottom spectrum in Fig. 10a) contains a loss peak at 58.9 meV (marked as O₈chem) characteristic for the chemisorbed oxygen on Pd(111). This peak is also present in the HREELS spectrum recorded from the 523 K oxygen dosed Pd surface (lower curve in Fig. 10b). Here, however, an additional weaker, but clearly observable, loss structure at 40 meV is detected. We believe the latter originates from vibrations of oxygen species located in the subsurface region (therefore marked as O₈sub). There are several reasons to support this hypothesis. Dosing the Pd(111)−O₀ surface with 5 L CO and subsequently heating to 423 K removes the O₈chem peak completely, but leaves the O₈sub loss peak virtually unaffected (Fig. 10, upper curves). Similar behaviour was also observed in the XPS data (Fig. 7). The O₈sub loss peak clearly differs from the ν₉₋₀ metal-molecule stretch, which appears at approximately the same energy upon CO adsorption (see Fig. 9). This was verified by the absence of the much more intense ν₉₋₀ vibrational peak at around 225 meV (not shown). Further, the O₈sub structure could be removed from the HREEL spectra only after prolonged (about 1 h) sputtering and annealing treatments (up to 1000 K), again suggesting its subsurface nature. Hence, the loss feature at 40 meV is assigned to vibrations of O located in the subsurface region of the Pd(111) surface.

4. Discussion

On the Pd(111) surface, slow oxygen uptake into chemisorbed states above 0.25 ML surface coverage occurs in parallel with slow migration into subsurface states. At 900 K and the low flux of 0.05 ML/s applied in the experiment of Fig. 3, the rate of absorption into the reservoir below the surface becomes low already after about 200 s, indicating that the mass transport of oxygen into the metal becomes small after an exposure of 10 ML. Considering the bulk migration of oxygen as an activated diffusion process, the supply of oxygen to the near-surface region is much faster than the migration deeper into the bulk, and the near-surface region can be filled up quite quickly. Once oxygen atoms are trapped in these regions, they can both migrate back to the surface or diffuse to deeper bulk regions. The latter case is more likely if the bulk is initially oxygen-free. This picture could explain the missing TDS feature at 1142 K after the slow additional uptake in Fig. 2 (curve a). Much higher exposures, up to 8000 ML at 973 K, are required to fill up the deeper bulk regions and eventually to enhance the diffusion back to the surface until the amount of diffusing and desorbing oxygen exceeds the detection limit (Fig. 2, curve b). At temperatures sufficient to remove thermally (923 K, curve c) or reactively (523 K, curve d) the chemisorbed O₈chem, the segregation velocity is not sufficient to induce measur-
able desorption or reaction rates. Therefore subsurface oxygen was found to be extremely unreactive towards CO on the surface. The experiments performed at 523 K (Fig. 4) clearly show that also at this temperature the loss of chemisorbed oxygen in the bulk plays a significant role in the adsorption experiments. At 300 K, the bulk migration of chemisorbed oxygen, however, is very slow, and chemisorption experiments can be performed without loss of O into the bulk.

The LEED, XPS and HREELS results (Sections 3.2 and 3.3) provide further evidence for subsurface oxygen migration into the near-surface regions on Pd(111) even at much lower O2 exposures (40 L) at 523 K. On the Pd(111) surface dosed with oxygen at 523 K a more intense O 1s peak, compared to that on the 300 K oxygen-covered Pd, has been observed (Fig. 6). On the other hand, only a small part of this oxygen is chemisorbed at the surface, as estimated from the areas under S and O Pd 3d5/2 peak components in Fig. 6 (θO = 0.12 ML) or from the TDS peak area in Fig. 4 (θO = 0.14 ML). This is also supported by the LEED observations (Fig. 5b), which indicated a reduced amount of the chemisorbed p(2 × 2) oxygen phase on the Pd(111) dosed at 523 K with oxygen. For comparison, a sharp p(2 × 2) LEED pattern was observed following the oxygen adsorption at 300 K, suggesting a surface oxygen coverage of 0.25 ML (Fig. 5a). The higher intensity of the O 1s peak in the Pd(111)–O2 phase may thus be related to an additional uptake of oxygen at 523 K in subsurface states, which is suppressed at 300 K. This agrees very well with the total oxygen uptake of 0.35 ML observed after an exposure of 5.5 ML (15 L) at 523 K in Fig. 4 (curve a). We therefore conclude that on the Pd(111) surface dosed at 523 K the major part of the O 1s core level intensity originates from oxygen atoms, which are located in the near-surface region. An estimate based on the escape depth of the O 1s photoelectrons yields a value of about 10 Å [29], suggesting that the information obtained with XPS about the location of the subsurface species is limited to the first three to four atomic layers below the surface.

Further support for the formation of subsurface oxygen species on the 523 K oxygen dosed Pd(111) surface comes from the HREELS spectra taken in the 5° off-specular geometry (Fig. 10b). The appearance of the loss structure at 40 meV in addition to the chemisorbed O loss peak at ~60 meV, can be associated with oxygen diffused into the near-surface region. For comparison, the loss spectrum taken after room-temperature oxygen exposure (Fig. 10a) displays only the O_{chem} peak. The inelastic mean free path of the 5.5 eV electrons used in the HREELS experiment is ~30 Å, i.e. about three times larger than that of the photoelectrons. This may explain the slow removal of the O_{chem} loss peak by Ar+ ion sputtering and annealing treatments. The CO adsorption experiments on the oxygen predosed Pd(111) revealed substantial differences in the reactivity of the chemisorbed (surface) and subsurface oxygen towards CO. The chemisorbed oxygen is quite effectively removed from the Pd, has been observed (Fig. 6). On the other hand, only a small part of this oxygen is chemisorbed at the surface, as estimated from the areas under S and O Pd 3d5/2 peak components in Fig. 6 (θO = 0.12 ML) or from the TDS peak area in Fig. 4 (θO = 0.14 ML). This is also supported by the LEED observations (Fig. 5b), which indicated a reduced amount of the chemisorbed p(2 × 2) oxygen phase on the Pd(111) dosed at 523 K with oxygen. For comparison, a sharp p(2 × 2) LEED pattern was observed following the oxygen adsorption at 300 K, suggesting a surface oxygen coverage of 0.25 ML (Fig. 5a). The higher intensity of the O 1s peak in the Pd(111)–O2 phase may thus be related to an additional uptake of oxygen at 523 K in subsurface states, which is suppressed at 300 K. This agrees very well with the total oxygen uptake of 0.35 ML observed after an exposure of 5.5 ML (15 L) at 523 K in Fig. 4 (curve a). We therefore conclude that on the Pd(111) surface dosed at 523 K the major part of the O 1s core level intensity originates from oxygen atoms, which are located in the near-surface region. An estimate based on the escape depth of the O 1s photoelectrons yields a value of about 10 Å [29], suggesting that the information obtained with XPS about the location of the subsurface species is limited to the first three to four atomic layers below the surface.

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523 K oxygen precovered Pd(111), may be attributed to a possible modification of the electronic properties of the surface by the subsurface oxygen atoms. A similar effect was observed recently for subsurface oxygen on Rh(111) by Wider et al. [30]. Using X-ray photoelectron diffraction, they found that the presence of oxygen in subsurface sites changes the surface potential energy for chemisorbed oxygen atoms in their vicinity. Another possibility would be the segregation of O atoms from the near-surface region to react with the adsorbed CO molecules. At higher CO exposures the effect of the near-surface O species on the C 1s binding energy becomes negligible, probably because of a reactive depletion of the underlying subsurface layer of dissolved oxygen.

The removal of the chemisorbed CO by thermal desorption offers the possibility of characterising the subsurface oxygen exclusively. The O 1s core level (Fig. 7) and HREELS spectra (Fig. 10b) recorded after desorbing CO may be considered as fingerprints of the subsurface oxygen species. The O_{sub} 1s peak appears at a BE of 529.7 eV; from the area under this peak the amount of the subsurface oxygen may be estimated to be ~0.45 ML under the present adsorption conditions (40 L, 523 K). This is based on the assumption that the area of the O_{sub} peak, detected after the room temperature O_{2} adsorption, corresponds to a surface oxygen coverage of 0.25 ML. In view of the relatively small sampling depth of the XPS (~10 Å), this result indicates a significant O concentration in the near-surface region. However, the presence of subsurface oxygen species does not substantially affect the Pd 3d_{5/2} core level line-shape, which after the CO desorption is identical to the clean Pd spectrum.

Finally, the possible formation of surface or bulk PdO under the present experimental conditions deserves some comment. Such oxides have been reported in the literature to form on Pd(111) after high temperature (~900 K) and high virtual O_{2} pressure (>10^{-7} mbar) treatments [1,4,6,10,11]. For the oxygen dosing conditions of the low-pressure experiments (40 L O_{2} at 2 × 10^{-7} mbar, T ≤ 523 K) this is quite unlikely to occur. The XPS and HREELS spectra do not show any specific features, characteristic of the oxide formation. For example, a substantial broadening of the Pd–O stretching loss, due to the appearance of additional oxide-related loss peaks, was observed by Banse and Koel, following the oxidation of Pd(111) using NO_{2} [10]. After O_{2} exposures at 4 × 10^{-7} mbar on Pd(110) at 400 K, Bondzie et al. [17] observed in the Pd 3d_{5/2} XPS spectra a component with a BE of 336.3 eV, corresponding to the binding energy of PdO. This component is clearly missing in our Pd 3d_{5/2} XPS data (Figs. 6 and 7). In the kinetic experiments, higher temperatures and higher effective oxygen pressures were employed, but again substantial surface or bulk PdO formation appears to be unlikely. Banse et al. have shown evidence from AES, HREELS and XPS that PdO formation is accompanied by an additional TDS feature at ~720 K, and explained this result with the low thermal stability of PdO [10]. This feature was not observed in our TDS spectra and it is very unlikely that the TDS feature at 1142 K in Fig. 2 is due to decomposition of surface PdO or three-dimensional islands of bulk PdO on top of the sample surface. These PdO species should as well be reducible by CO, but the 1142 K peak in Fig. 2 is by no means affected by CO adsorption. The saturation value for the chemisorbed oxygen adlayer of 1 ML was reached at an exposure of 4000 ML in Fig. 2. This was further tested by exposing the sample at the same temperature and flux to a 10 times higher amount of oxygen (40 000 ML), but neither the shape nor the area of the subsequent TPD differed from trace a in Fig. 2. This result rather implies formation of a densely packed, possibly reconstructed chemisorbed adlayer blocking further oxygen uptake, similar to Pd(100) [31]. Selective thermal or reactive desorption of this adlayer which exhibits a 7.5 Å × 7.5 Å square superstructure, described in [11], without affecting the 1142 K oxygen (traces c and d in Fig. 2) resulted in a good (1 × 1) LEED pattern, suggesting that the residual oxygen in the 1142 K state is not associated with structural alterations of the top Pd layer.

5. Summary
We have shown, through molecular beam adsorption, thermal desorption, XPS and
HREELS measurements, that upon oxygen adsorption at temperatures $\geq 523$ K, significant penetration of oxygen in the near-surface region of Pd(111) takes place. Evidence for the formation of a densely packed chemisorbed oxygen adlayer up to $\theta_0 \approx 1$ and for subsurface migration of oxygen at elevated temperatures was found using high effective oxygen pressures. The rate of oxygen diffusion to the bulk is slower than the adsorption rate when $\theta_0$ is up to 0.25. It strongly depends on the previous history of the sample and can be deliberately enhanced by depletion of the subsurface oxygen by high temperature treatment or sputtering. Distinct features in the photoemission and vibrational spectra have been observed, which correspond to the subsurface oxygen. XPS and HREELS measurements have shown that considerable concentrations of oxygen in the near-surface region can be reached even at relatively low temperatures (523 K) and oxygen exposures (40 L), but not at room temperature. In contrast to the chemisorbed oxygen atoms on Pd(111), the subsurface species could not be removed by reaction with CO.

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