INTERACTION OF OXYGEN WITH Pd(111):
HIGH EFFECTIVE O₂ PRESSURE CONDITIONS BY USING NITROGEN DIOXIDE

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High effective O₂ pressures can be simulated by using NO₂ as a source of atomic oxygen on Pd(111) at exposure temperatures at or above 530 K. Large oxygen concentrations (θ₂ = 0.0–3.1 ML) have been studied using TPD, AES, HREELS, and XPS. TPD results show four O₂ desorption peaks at 625, 715, 765, and 800 K. The low temperature desorption states have never been reported in previous work concerning oxygen adsorption on Pd(111). Upon heating an atomic oxygen adlayer, diffusion of oxygen into the near surface region is competitive with O₂ desorption for θ₂ = 0.76–1.4 ML. For θ₂ > 1.4 ML, spectroscopic evidence shows the presence of an oxide on or near the surface. Our results for the interaction of atomic oxygen with Pd(111) are compared with the behavior of atomic hydrogen on Pd(111). Finally, a model for the chemical state and desorption behavior of oxygen for these coverages is proposed.

1. Introduction

Many fundamental studies of CO and H₂ oxidation reactions have been reported on single crystal Pd surfaces [1–7] since palladium is an important oxidation catalyst. The need to understand the elementary steps in oxidation reactions on Pd has led to numerous studies of the chemical nature of surface oxygen formed from O₂ exposure on the low Miller index crystal planes of Pd, including the (111) [8–16], (100) [17–21], and (110) [22–28] surfaces. In most of this previous work, oxygen atoms have been found to migrate into the bulk of palladium. A "subsurface" oxide structure has been proposed in some studies [8,10]. Also, using high pressures of oxygen (1 atm O₂ at 900 K), bulk palladium oxide has been formed, which decomposes in vacuum at temperatures greater than or equal to about 450 K [29].

Previous studies have shown that NO₂ is a clean and very efficient source of oxygen adatoms on Pt(111) [30–32]. The observed oxygen coverages are three times greater than those generated by O₂ exposure in UHV (0.75 ML of oxygen from NO₂, compared to 0.25 ML oxygen from O₂ exposure) [32], and thus one can simulate the effects of high O₂ partial pressures to produce atomic oxygen on the surface. This ability is due to the higher dissociative sticking probability of NO₂ (1.0 [30]) when compared to O₂ (0.025 [33]) on clean Pt(111) and to the relative insensitivity of the dissociative sticking probability of NO₂ to surface oxygen. Recently, we have found that NO₂ is an efficient source of atomic oxygen on the Pd(111) surface as well [34]. NO₂ dissociates into NO(a) and O(a) above 180 K and desorbs between 230 and 300 K depending on the surface oxygen coverage. By carrying out the NO₂ exposure at 530 K (NO₂ desorption is complete below 500 K), the NO(a) product desorbs from the surface to cleanly leave atomically adsorbed oxygen on the Pd(111) surface.

In this paper, we report new information regarding the interaction of large concentrations of atomic oxygen with Pd(111) using exposures of NO₂ to the surface at or above 530 K. The chemistry of this system is characterized using temperature programmed desorption (TPD), Auger elec-
tron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The UHV chamber used in these experiments has been described in detail elsewhere [35]. The chamber is equipped with a quadrupole mass spectrometer for TPD, a double-pass CMA with a coaxial electron gun, sputter ion gun, LEED optics, a dual anode X-ray source, and an HREELS spectrometer which is made of single 127° cylindrical sectors in the monochromator and analyzer. Specular reflections in HREELS corresponds to \( \theta_{\text{in}} = \theta_{\text{out}} \approx 65° \) from the sample normal. The typical base pressure of the system was \( 2 \times 10^{-10} \) Torr. A computer was interfaced to the system for data acquisition in all TPD, AES, and HREELS studies.

High purity NO\(_2\) was prepared in our laboratory and the procedure has been described in detail previously [31]. Ultra-high purity O\(_2\) (Scientific Gas Products, 99.97%) was used for calibration of the oxygen coverage and surface cleaning. Oxygen coverages were determined by comparing the O\(_2\) TPD areas obtained from O\(_2\) exposures on Pd(111) at 110 K to those resulting from high temperature NO\(_2\) exposures. The atomic oxygen coverage at saturation from O\(_2\) exposure at 110 K has been determined in previous work to be 0.25 ML [8,13,15].

The Pd(111) crystal was heated resistively and cooled by direct contact with a liquid nitrogen reservoir. Care was taken to insure that the sample was clean and free of common contaminants such as sulfur and carbon. Cleaning in UHV consisted of argon ion sputtering (1 kV, 13 \( \mu \)A cm\(^{-2}\)) at 800–1000 K for 24 h. It was found that sulfur diffusion from the bulk was increased at temperatures between 900 and 1000 K and carbon diffusion from the bulk was maximized at temperatures around 800–900 K.

Since the Pd signal interferes with carbon detection by AES, the presence of carbon was determined by measuring either CO or CO\(_2\) production in TPD after exposure of the surface to oxygen. Initially, following O\(_2\) exposure at 110 K, the high temperature thermal desorption of O\(_2\) due to atomically adsorbed oxygen was not observed even though the low temperature molecular O\(_2\) desorption peaks agreed well with those reported by Matsushima [13]. The surface was then cleaned in NO\(_2\) for approximately two hours at 1000 K. Following this treatment, the area ratio of O\(_2\) TPD states for atomically adsorbed oxygen to molecularly adsorbed oxygen did agree with Matsushima’s spectra, however, an oxygen signal was detected with AES which was still present after the sample was heated to 1000 K. This was due to refractory oxide contaminants and could be removed by argon ion sputtering for 15 min at 110 K. Annealing the crystal to 1000 K for 5 min provided a good, clean Pd(111) LEED pattern. Additional AES analysis and reproducible TPD spectra during the course of experiments were used to confirm that the surface was always free from contamination.

Quantitative AES studies were performed using a 2 \( \mu \)A beam current and 8 eV p–p modulation voltage. A heating rate of 7.5 K s\(^{-1}\) was used for all TPD studies. The resolution in HREELS was \( \approx 70 \) cm\(^{-1}\) FWHM. XPS spectra were taken using Mg K\( \alpha \) (1253.6 eV) radiation. The CMA was operated in constant resolution mode at 25 eV pass energy for XPS, corresponding to a 25 eV pass energy for XPS, corresponding to an analyzer resolution of 0.4 eV. All binding energies reported in this paper are referenced to the clean Pd (3d\(_{3/2,5/2}\)) and Pd(3p\(_{3/2}\)) peaks at 340.6, 335.0, and 532.3 eV binding energy, respectively, as reported by Peuckert [29].

3. Results

3.1. Temperature programmed desorption

Figs. 1–3 show O\(_2\) TPD spectra following NO\(_2\) exposure on the Pd(111) surface at 530 K. By carrying out the NO\(_2\) exposure at 530 K (NO desorption is complete below 500 K), the NO(a) desorbs from the surface to cleanly leave atomically adsorbed oxygen on the Pd(111) surface. Fig. 1 shows O\(_2\) TPD from low oxygen coverages with \( \theta_{O_2} = 0.0–0.61 \) ML. Trace (a) shows no background
effects occur from a clean Pd surface. Curve (b) shows a small peak ($\beta_4$) with a peak temperature of 875 K. With increasing oxygen coverage, this peak shifts to lower temperatures until reaching about 800 K. This behavior is indicative of second-order $O_2$ desorption kinetics. Assuming this reaction order and a pre-exponential factor of 0.01 cm$^2$ s$^{-1}$, standard Redhead analysis [36] gives an activation energy for desorption of 48 kcal mol$^{-1}$. This compares well to 53 kcal mol$^{-1}$ in the limit of zero coverage calculated by Guo et al. [16] from $O_2$ exposure. Curve (d) corresponds to $\theta_O = 0.24$ ML, which is near the maximum coverage obtainable by $O_2$ exposure at 120 K under normal UHV conditions [8,13,15]. For comparison, the dashed TPD spectrum in fig. 1 shows the oxygen coverage (0.4 ML) at saturation resulting from NO$_2$ exposure at 110 K [34]. With $\theta_O = 0.6$ ML, curve (g), a new desorption state ($\beta_3$) is populated with a peak at 725 K. The Redhead method for determining activation energies probably cannot be used reliably here, since the reaction order and a pre-exponential factor must be assumed and the behavior of this peak with increasing oxygen coverage is quite irregular, as will be shown in fig. 2. Such a low temperature $O_2$ TPD peak has been seen previously on Pd(111) only in one very recent study by Guo et al. [16], who reported $O_2$ desorption results from the photolysis of molecularly adsorbed $O_2$. They observed a low temperature $O_2$ TPD peak ascribed to recombination of chemisorbed atomic oxygen that shifted from 660 to 725 K with increasing $\theta_O$. However, they did not study the more complicated $O_2$ desorption behavior at higher coverages reported in our work in fig. 2.

Fig. 2 shows $O_2$ desorption traces for $\theta_O = 0.6$–1.2 ML. For reference, curve (a) in fig. 2 is the same desorption trace as curve (g) in fig. 1. We interpret $O_2$ desorption at the higher oxygen coverages of curves of (b) through (d) as still due to the $\beta_3$ state, however, this desorption state shows complex kinetic behavior with increasing oxygen coverage. The leading edge of curve (b) is superimposable on that of curve (a) and the peak temperature shifts to higher values, characteristic of zero-order desorption kinetics. However, the high temperature side of curves (a) and (b) are not characteristic of zero-order kinetics, with the desorption rate decreasing much too slowly after the peak maximum. The leading edges of the higher
coverage desorption traces (c) and (d) cross through the curves (a) and (b). This complicated TPD behavior has never been seen before in previous oxygen studies on Pd(111), but must be due to dynamical effects in O₂ desorption or strong variation of the desorption activation energy with θₐ.

Fig. 3 shows O₂ desorption traces for θ₀ ranging from 1.2 to 2.3 ML. Spectrum (a) in fig. 3 is the same as spectrum (d) in fig. 2. Above θ₀ = 1.4 ML, curve (b), another desorption state (β₂) appears with a peak temperature of 715 K. This peak does not shift in temperature with higher oxygen coverages. For θ₀ > 2.1 ML, curve (e), another state (β₃) grows in with a peak temperature of 625 K. The β₁ and β₂ desorption states were not saturated for any of the oxygen coverages studied here. However, the β₃ state did saturate for θ₀ ≥ 2.2 ML. None of these low temperature O₂ desorption peaks have ever been reported in previous studies on Pd(111) resulting from O₂ exposures between 300 and 1273 K [10].

An experiment was carried out to study the effects of NO₂ exposure temperature on the subsequent O₂ desorption. Fig. 4 shows the O₂ TPD spectra resulting from constant NO₂ exposures (4 L), but two different exposure temperatures: (a) 530 K and (b) 580 K. Curve (a) in fig. 4 is the same NO₂ exposure that resulted in the O₂ TPD trace in fig. 3 curve (b). The peak position for the β₃ state is the same for both exposure temperatures, however, the intensity of this state is lower for the 580 K exposure in (b) than for the 530 K exposure in (a). Exposure at 580 K does not populate the β₂ O₂ desorption state for this NO₂ exposure, while exposure at 530 K does. Also, a larger O₂ TPD yield is generated by the 530 K exposure (1.4 ML compared to 1.2 ML from NO₂ exposure at 580 K), indicating a decreased sticking coefficient for NO₂ at this higher temperature.

3.2. Auger electron spectroscopy

Fig. 5 shows the results of AES measurements of the Pd(330 eV) and O(519 eV) signals and the O(519)/Pd(330) AES ratio versus atomic oxygen concentration determined independently by TPD. The oxygen concentration associated with the O₂ TPD area is shown on the top scale of fig. 5, using the calibration from atomically adsorbed oxygen formed by saturation O₂ exposure at 110 K de-
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Fig. 5. Plot of O(519 eV) (○), Pd(330 eV) (△), and the O(519 eV)/Pd(330 eV) ratio (□), AES signal as a function of O₂ TPD area. Oxygen coverage is shown on the top axis and is calibrated from TPD area.

Fig. 6. HREELS spectra obtained for several oxygen coverages and are shown in fig. 6. All of the vibrational spectra were taken at 110 K. The bottom curve was obtained from the clean Pd(111) surface. The energy loss peak at 475 cm⁻¹ at θ₀ = 0.4 ML is in good agreement with a value of 480 cm⁻¹ assigned by Imbihl and Demuth [14] to the νₚd-0 stretching mode of chemisorbed oxygen adatoms with θ₀ = 0.25 ML on Pd(111). Increasing the oxygen concentration to θ₀ = 0.5 ML causes little change, except for an increased νp₀d-0 loss peak intensity. Large changes occur at θ₀ = 1.4 ML (this oxygen concentration causes the 715 K β₂ state in TPD to appear with a similar TPD spectrum to that shown in fig. 3, curve (b)). A broad energy loss peak is still visible in the region of 475 cm⁻¹, however, it appears to be composed...
of two loss features, one at 425 cm\(^{-1}\) and an additional mode at 510 cm\(^{-1}\). Two more weak loss peaks are also visible near 675 and 750 cm\(^{-1}\). The vibrational spectrum for the highest oxygen coverage, \(\theta_O = 1.8\) ML, was taken after a 4 L NO\(_2\) exposure at 580 K, followed by a 60 L NO\(_2\) at 530 K. The peak structure is similar to that seen for \(\theta_O = 1.4\) ML, with a small peak at 275 cm\(^{-1}\) and increased intensity at 750 and 1225 cm\(^{-1}\). It should be noted that the O\(_2\)(a) peaks detected by Imbihl and Demuth [14] at 650, 850, and 1035 cm\(^{-1}\) are absent in all of the spectra of fig. 6. Thus, no stable formation of O\(_2\)(a) occurs upon cooling of these large concentrations of atomic oxygen on Pd(111).

Palladium oxide has been studied previously by both Raman and IR spectroscopy [37–39]. Weber et al. [37] report a strong PdO Raman mode at 650 cm\(^{-1}\) with smaller peaks in the regions of 280, 430, and 723 cm\(^{-1}\). Kliche [38] reports IR bands for PdO at 160, 612, and 668 cm\(^{-1}\), as well as a strong Raman mode at 652 cm\(^{-1}\). Tura et al. [39] also report IR absorption bands for PdO at 610 and 670 cm\(^{-1}\). Therefore, the vibrational loss peaks observed in fig. 6 are likely due to the initial formation of PdO modes, particularly the energy loss peaks at 275, 425, 675, and 750 cm\(^{-1}\). The energy loss peak at 510 cm\(^{-1}\) could be due to a "defective" PdO mode or the presence of a new chemisorbed state of atomic oxygen.

3.4. \textit{X-ray photoelectron spectroscopy}

The Pd(3d\(_{3/2}\)) and (3d\(_{5/2}\)) peaks are shown in fig. 7 for the range of \(\theta_O = 0.0-3.1\) ML. Peaks due to Pd metal at 340.6 and 335.0 eV BE are present in all of the spectra shown. However, a shoulder due to oxidized Pd is observed to grow in on the higher binding energy side of both of the Pd metal peaks for oxygen coverages of \(\theta_O \geq 2.2\) ML in spectra (d) through (f).

Fig. 8 shows the Pd(3p\(_{3/2}\)) and the O(1s) region for the same oxygen coverages shown in fig. 7. The Pd(3p\(_{3/2}\)) peak due to metallic Pd is at 532.3 eV BE in agreement with Peuckert's data [29] and is detected at all oxygen coverages studied. A shoulder in the O(1s) region is visible at the lowest oxygen coverage shown (0.4 ML) and continues to

![Fig. 6. HREELS spectra for various oxygen coverages on Pd(111) generated by exposure to NO\(_2\) at and above 530 K.](image)

![Fig. 7. XPS spectra of the Pd(3d\(_{3/2}\)) and Pd(3d\(_{5/2}\)) region for varying amounts of oxygen on Pd(111). The oxygen coverages are: (a) clean Pd, (b) 0.4 ML, (c) 1.1 ML, (d) 2.2 ML, (e) 3.1 ML, (f) > 3.1 ML.](image)
grow in for the higher oxygen coverages. The Pd(3p$_{3/2}$) peak interferes with the binding energy determination for the O(1s) peak and some deconvolution (vide infra) is helpful.

In order to obtain more information on the chemical state of Pd and oxygen at the high oxygen concentrations studied, we have deconvoluted the XPS spectra for oxygen concentrations greater than 3.1 ML shown in figs. 7, curve (f) and 8, curve (f). These results are shown in figs. 9a and 9b, respectively. Pd(3d$_{3/2}$) and (3d$_{5/2}$) peaks due to oxidized Pd occur at about 1.5 eV higher binding energy than metallic Pd and are centered at 341.9 and 336.6 eV, respectively. These peak positions are 0.4 eV lower in binding energy than those reported by Peuckert [29] (342.3 and 337.0 eV, respectively), but are 0.3 eV higher than that reported by Kim et al. [40] from a study of oxidized Pd electrodes (336.3 eV for the Pd(3d$_{5/2}$) peak). However, the chemical shift of the Pd(3d$_{5/2}$) level in our study (+1.6 eV) agrees well with that reported by Tura et al. [39] attributed to PdO, who also studied oxidized Pd electrodes. It should be noted that the chemical shift detected in this study (+1.6 eV) is not consistent with that reported for either PdO$_2$ (2.1–2.9 eV) or a higher oxide (3.5–3.6 eV) [39,40].

Fig. 9b shows the deconvolution of the O(1s) peak from the Pd(3p$_{3/2}$) peak for two different oxygen coverages. The smallest (dotted) curve shows the deconvolution of the O(1s) peak from the Pd peak of fig. 8, curve (c), which corresponds to $\theta_0 = 0.6$ ML. This is a coverage where only chemisorbed atomic oxygen is present, as indicated by TPD. This species has an O(1s) BE of 529.0 eV. The larger curve in the O(1s) region (dashed) in fig. 9b is the deconvoluted O(1s) peak from fig. 8, curve (f), which corresponds to $\theta_0 = 3.1$ ML. This peak is broader than the O(a) peak and is centered around 529.6 eV. This peak could contain contributions due to O(a) at 529.0 eV BE and an oxide at 530.3 eV BE. The value assigned by Peuckert [29] indicative of an oxide (530.3 eV) agrees well with our value, but is different from value reported by Kim et al. [40] (529.3 eV). Peuckert [29] also observed a separate Pd(3p$_{3/2}$) peak at 533.8 eV BE due to oxidized Pd. Although a separate peak is not visible in fig. 9b, it is obvious that the Pd(3p$_{3/2}$) peak is broader at high binding energy than seen for the clean Pd(111) spectra (the largest dashed curve in fig. 9b). Thus,
for $\theta_0 \geq 2.2$ ML, the XPS data clearly show that oxidized Pd is present.

4. Discussion

The discussion of our results is divided into two parts. In the first part, we compare our results for the oxygen-Pd(111) system with results for a similar system involving hydrogen-Pd(111), which has received much attention in the recent literature [41-44]. In the second part, we propose a physical model for the chemical state and desorption behavior of large concentrations of oxygen on Pd(111).

4.1. Comparison of $O_2$ desorption from Pd(111) with $H_2$ desorption from Pd(111)

The $O_2$ TPD results reported in this paper have not been observed before. Some insight into the origin of the $O_2$ TPD peaks may be gained by comparison of these results to another system: $H_2$ desorption from Pd(111) [41-44]. Hydrogen exhibits similar behavior to oxygen on Pd surfaces. In addition to molecular and dissociative chemisorption of $H_2$, hydrogen atoms have been found to diffuse into the bulk of Pd[41]. A near-surface hydride phase has also been observed by TPD [43]. Since both bulk diffusion and chemical reaction with the surface to form an oxide is proposed for oxygen on Pd, comparison between these two systems is valuable.

The diffusion of both atomic hydrogen [41-43] and atomic oxygen [8,10,11,20] into the bulk of Pd has been reported. $H_2$ desorption from a Pd(111) surface due to the recombination of chemisorbed hydrogen atoms occurs at about 320 K [41,42] for near saturation coverages. However, $H$ atoms which have diffused into the bulk cause a broad $H_2$ TPD peak between 400 and 1000 K [41,42]. Desorption from this latter state is dependent upon the $H_2$ exposure temperature as well.

An early study by Conrad et al. [8] reported $O_2$ desorption from a chemisorbed, atomic oxygen state at 900 K. A broad additional desorption peak occurring between 1000 and 1300 K was also reported. These $O_2$ TPD states were also observed in a later study by Weissman et al. [10]. Desorption from this high temperature peak was attributed to a “subsurface oxide” state because it correlated to an increase in work function and a new feature in the ultra-violet photoelectron (UPS) spectrum. By comparison to the $H_2$ TPD behavior on Pd(111), it is likely that this desorption peak is a result of oxygen diffusion from deep in the bulk of Pd.

The high temperature TPD state reported first by Conrad et al. [8] was seen as a shoulder on the chemisorbed state with a significant desorption rate at 1000 K. In our study, the initial and final baseline values of the $O_2$ pressure in the TPD curves were in quantitative agreement, indicating that $O_2$ desorption was complete during our TPD experiments (terminated at 1000 K). We found no evidence for the $O_2$ desorption state detected in earlier studies attributed to bulk diffusion in our results, however, a temperature ramp to 1300 K would be necessary to prove conclusively that desorption from this state was not characteristic of Pd(111).

Another hydrogen desorption state has been reported in recent studies [41,42] to occur at a lower temperature than the chemisorbed hydrogen state. This $\alpha$ state is populated following high $H_2$ exposures (greater than 20 L) at temperatures ranging from 90 to 140 K and does not saturate after exposures of 10 000 L. Initial $H_2$ desorption occurs with a peak at 170 K, but shifts to 210 K with increasing hydrogen coverages. Desorption from this state is very rapid, with a very narrow (30 K FWHM) peak shape. This desorption peak is attributed to the decomposition of a near-surface hydride phase [41,42].

Although the thermodynamics of the formation of a hydride is different, it can be compared to the formation of an oxide in a first approximation. In figs. 2 and 3, new $O_2$ desorption states were observed at lower temperatures than the peaks due to the chemisorbed state of atomic oxygen. The peak shape of the $\beta_2$-$O_2$ state is similar to that seen with the $\alpha$-$H_2$ state in that it is sharp and narrow (30 K FWHM) suggesting it could be a result of oxide decomposition. However, we believe that the $\beta_2$-$O_2$ desorption state results from the recombination of chemisorbed oxygen sup-
plied by oxygen that diffuses from the near-surface region. The reasoning behind this proposal will be presented in the next section. Instead, we attribute desorption from the \( \beta_2\)-O\(_2\) state to the decomposition of an oxide near or at the surface. Although the peak shape is different than that observed for the \( \alpha\)-H\(_2\) state, the spectroscopic evidence provided by AES, HREELS, and XPS is consistent with this conclusion. Like the behavior reported for the \( \alpha\)-H\(_2\) state, both the \( \beta_1\)- and \( \beta_2\)-O\(_2\) states did not saturate for the oxygen concentrations studied in this paper. Another similarity to the hydrogen–Pd system is that desorption from the \( \beta_2\)-O\(_2\) state attributed to oxide decomposition occurs at a lower temperature than desorption from the \( \beta_2\)-O\(_2\) due to O(a).

The assignment of the \( \beta_2\)-O\(_2\) state to oxide decomposition is also strengthened by comparison to results obtained previously by Peuckert [29]. In his study, bulk PdO was grown on Pd(110) and Pd powder surfaces at high O\(_2\) pressures. The bulk oxide samples were then transferred into a UHV chamber. XPS spectra of the Pd(3d) and O(1s) regions were taken after sequential heating of the samples at 50 K intervals between 300 and 1000 K. It was found that the oxide decomposed in two steps. The first step occurred at 420 K and was attributed to bulk PdO decomposition. The second step occurred between 720 and 820 K and was assigned to the decomposition of an “intermediate” structure of PdO. These results support our suggestion that desorption from the \( \beta_2\)-O\(_2\) state results from surface or subsurface oxide decomposition, since the \( \beta_2\) peak temperature of 715 K is near the temperature at which decomposition of an intermediate oxide phase observed by Peuckert [29].

4.2. Proposed model for the chemical state and desorption behavior of oxygen on Pd(111)

We have extended the range of oxygen concentrations studied previously on Pd(111) from \( \theta_0 = 0.25 \) ML (from O\(_2\) exposure in UHV [8,10,11,13,15]) to \( \theta_0 = 3.1 \) ML. We propose the following model for the chemical state and desorption behavior of oxygen on Pd(111). From \( \theta_0 = 0.0–0.25 \) ML, oxygen adatoms are stable at low temperatures, in agreement with previous work form O\(_2\) exposure [8,11,13,15]. In addition, we propose that the concentration of atomically chemisorbed oxygen can reach 1.4 ML. This conclusion is based on spectroscopic data from AES, HREELS, and XPS that show no change in the chemical state of oxygen for this coverage regime.

An oxygen adatom coverage of 1.4 ML does not exceed the density of a closest-packed O(a) layer. Calculation of the ratio of oxygen atom surface density to that of Pd (1.3 \( \times 10^{15} \) atoms cm\(^{-2}\)) gives a \( \theta_{O}(\text{sat.}) = 1.3 \) ML, using an ionic radius of 1.21 Å for O\(_2^-\) [45]. This is probably an upper limit to the oxygen radius, since the actual size of the oxygen adatom on the surface is likely to be smaller (but is probably larger that the covalent radius of 0.66 Å [46], which leads to \( \theta_{O}(\text{sat.}) = 4.4 \) ML). If our measured value of \( \theta_{O}(\text{sat.}) = 1.4 \) ML actually represents a closest-packed layer, the oxygen adatom radius is 1.16 Å. This value is intermediate between the covalent and the ionic radii, but is close to the value of the O\(_2^-\) ionic radius.

Therefore, according to our model, the \( \beta_3\) TPD state is due to chemisorbed oxygen desorbing from a dense chemisorbed oxygen overlayer. As noted in the discussion of fig. 2, the complex desorption behavior for the \( \beta_1\) state is observed for \( \theta_0 > 0.76 \) ML, with the leading edges for these TPD traces crossing through the leading edges of those for \( \theta_0 < 0.76 \). We believe that a competition exists near the desorption temperature between desorption and subsurface migration for \( \theta_0 > 0.76 \) ML, even though the spectroscopic evidence shows no change in chemical state of the oxygen for \( \theta_0 < 1.4 \) ML. One explanation is as follows. All of the spectroscopic data was taken following NO\(_2\) exposure at 530 K and subsequent cooling of the sample. The acquisition of TPD data, however, involves heating the sample to temperatures greater than 530 K. We propose that during the heating of the sample between 530 and 725 K in the TPD experiment, some of the oxygen in the chemisorbed layer migrates into the subsurface region and then desorbs from subsurface states via rate-limited diffusion to the surface with peaks between 750 and 800 K. Desorption from the \( \beta_3\) state for oxygen concentrations greater than 0.76 ML occurs at higher temperatures than seen for
\( \theta_0 < 0.76 \text{ ML} \) because this process is rate-limited by diffusion from the near surface region.

The above model for the interaction of oxygen with Pd(111) for \( 0.6 < \theta_0 < 1.4 \text{ ML} \) is consistent with the \( \text{O}_2 \) TPD behavior from large oxygen concentrations on Pd(110) [27,28]. Two \( \text{O}_2 \) TPD states, \( \beta_1 \) and \( \beta_2 \), are observed on Pd(110). The \( \beta_1 \) state desorbs between 720 and 730 K and has a similar shape to the \( \beta_3 \) state in our study with respect to the narrow desorption profile, however, the complex behavior of the leading edges of the \( \beta_3 \) state is not seen on Pd(110). He et al. [27,28] suggest that desorption from the \( \beta_1 \) state originates from oxygen located below the top surface layer by using work function, LEED, AES, and TPD data. They also conclude that the high oxygen coverages attained during TPD (up to 1.7 ML) also indicate either oxide formation or at least subsurface penetration of oxygen into the Pd lattice.

For \( \theta_0 \geq 1.4 \text{ ML} \), each of the techniques that we used to study the oxygen–Pd(111) system support the conclusion that oxygen penetration below the surface occurs and that an oxide is formed at or near the surface. A change in slope of the O AES signal versus \( \theta_0 \) occurs at this oxygen concentration. This “break” in the AES plot is correlated to the appearance of a new \( \beta_2 \text{-O}_2 \) TPD state with a desorption peak temperature of 715 K. Vibrations detected using HREELS that could be indicative of oxide modes are present for \( \theta_0 \geq 1.4 \text{ ML} \). Finally, XPS shows that oxidized Pd is clearly present for \( \theta_0 \geq 2.2 \text{ ML} \).

Therefore, we believe that O\((a)\) is present on the surface for oxygen coverages up to 1.4 ML. Between 0.76 and 1.4 ML, the concentration of O\((a)\) and subsurface oxygen depends on the surface temperature, since oxygen desorption can be rate limited by either diffusion of subsurface oxygen to the surface or surface oxygen recombination. Finally, at oxygen coverages greater than or equal to 1.4 ML, palladium oxide is present and its decomposition is observed with TPD.

5. Summary

Large concentrations of oxygen can be supplied to the Pd(111) surface from exposure to \( \text{NO}_2 \) at elevated temperatures. This study is concerned with \( \theta_0 \leq 3.1 \text{ ML} \), which compares with \( \theta_0 = 0.25 \text{ ML} \) obtained by \( \text{O}_2 \) exposure in UHV, and thus greatly extends our understanding of the interaction of oxygen with Pd(111). These large concentrations of oxygen on Pd(111) correspond to high “effective” pressures of \( \text{O}_2 \) and are made possible by the relatively low activation energy barrier for \( \text{NO}_2 \) decomposition kinetics on the Pd(111) surface compared to \( \text{O}_2 \), especially in the presence of surface oxygen.

We propose the following physical picture of the interaction of high concentrations of oxygen on Pd(111) from the results using TPD, AES, HREELS, and XPS. Chemisorbed oxygen adatoms are present for oxygen concentrations of \( \theta_0 \leq 1.4 \text{ ML} \). \( \text{O}_2 \) desorption from this adlayer displays complicated desorption kinetics and could be due to an equilibrium that is established between oxygen on the surface and in the subsurface region. For \( \theta_0 > 1.4 \text{ ML} \), spectroscopic evidence shows that an oxide is present on or near the surface. At these oxygen coverages, new HREELS vibrational modes are detected at 275, 675, and 750 cm\(^{-1}\) and are assigned to the initial formation of PdO. AES and XPS data also support the conclusion that an oxide is present at or near the surface for oxygen coverages greater than 1.4 ML.

\( \text{O}_2 \) TPD shows four \( \text{O}_2 \) desorption states, \( \beta_1 \) to \( \beta_4 \), occurring at 625, 715, 765, 800 K, respectively. The low temperature states, \( \beta_1 \) and \( \beta_2 \), detected in this study have never been reported before on a Pd(111) surface. The decomposition of an oxide phase is correlated to the \( \beta_2 \) desorption state occurring at 715 K. Thus, we have characterized the formation and thermal stability of the initial products of oxidation of the Pd(111) surface entirely under UHV conditions. These results suggest a tremendous potential for initial oxidation studies of Pd and other metals in UHV using powerful oxidants such as \( \text{NO}_2 \).

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