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Interaction between Oxygen and Polycrystalline Palladium at O₂ Pressures of 10⁻⁶–10 Pa

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Abstract—The interaction between oxygen and polycrystalline palladium (Pd(poly)) at $P_{O_2} = 2.6 \times 10^{-6}$ –10 Pa and $T = 300$ –1300 K was studied by the thermal desorption (TD) method. The interaction between O₂ and Pd(poly) is governed by the O₂ pressure and the sample temperature. At low pressures of P_{O_2} ($\leq 1.3 \times 10^{-5}$ Pa), O₂ is chemisorbed dissociatively on the Pd(poly) surface. During chemisorption, the O_{ads}–surface bond energy and the O₂ sticking coefficient gradually decrease as the surface coverage θ increases. At $P_{O_2} \geq 10^{-2}$ Pa and $T \leq 500$ K, after the saturation of the O_{ads} layer ($\theta \sim 0.5$), O_{ads} atoms penetrate under the surface layer of the metal to form surface palladium oxide. At $P_{O_2} \geq 1$ Pa and $T > 500$ K, after the saturation of the surface oxide film 2 ML in thickness ($n \sim 2$), O_{ads} atoms penetrate into the oxide film and then into the subsurface palladium layer and diffuse deep into the metal bulk. As a result, the oxygen uptake at 700 K is $n \sim 50$. Upon heating, the surface oxides decompose, desorbing O₂, which gives rise to a low-temperature TD peak with $T_{\max} = 715$ K. The release of oxygen inserted in the subsurface layers of palladium shows itself as a distinct high-temperature TD peak with $T_{\max} \geq 750$ K.

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Palladium is extensively used as the main component of catalysts for a wide variety of important catalytic processes, including the neutralization of automotive exhaust gases [1], ammonia oxidation [2], and methane combustion in gas turbines [3]. Palladium is employed in these processes owing to its high activity in hydrocarbon, CO, and H₂ oxidation and in NO reduction. In addition, PdO shows a high activity in oxidation reactions [3]. The wide use of palladium in industrial catalysis has stimulated extensive investigation of the mechanisms of adsorption of O₂, H₂, NO, CO, and CH₄ and the catalytic reactions of these molecules on palladium single crystals by modern methods. Particular attention is focused on the interaction between oxygen and palladium, because the resulting different PdO phases exert a considerable effect on the catalytic oxidation reactions on palladium [3].

The interaction between oxygen and a transition metal is known to include three basic steps, namely, (1) the dissociative chemisorption of O₂, (2) the insertion of oxygen atoms into the metal lattice, and (3) the formation of surface and bulk metal oxides. The most thoroughly studied step of the interaction in the Pd–O₂ system is the dissociative chemisorption of O₂ on various palladium crystal faces at low O₂ pressures ($\leq 10^{-5}$ Pa). For example, O₂ chemisorption at $P_{O_2} \leq 10^{-5}$ Pa and $T = 100$ –600 K on Pd(poly) [4, 5], Pd(111) [6–10], Pd(100) [11–15], and

Pd(110) [16–21] was studied in detail by thermal desorption (TD) [5–7, 9, 10, 12, 13, 15, 18, 21], low-energy electron diffraction (LEED) [6, 8, 10–17], scanning tunneling microscopy (STM) [10, 15, 19, 20], and high-resolution electron energy loss spectroscopy (HREELS) [8, 14]. It was demonstrated by LEED and STM that O₂ chemisorption on palladium single crystals yields various ordered adsorption structures [6, 8, 10, 11–15, 19, 22, 23]. For example, oxygen chemisorption on the Pd(111) surface successively yields a $p(2 \times 2)$ structure with a chemisorbed oxygen surface coverage of $\theta = 0.25$ and a $(\sqrt{3} \times \sqrt{3})R30$ structure with $\theta = 0.33$ [6, 8, 10]. Oxygen chemisorption on Pd(100) results in $p(2 \times 2)$ ($\theta = 0.25$) and $c(2 \times 2)$ ($\theta = 0.5$) [11–15]. Oxygen chemisorption on Pd(110) gives (2×3) –1D ($\theta = 0.2$) and $c(2 \times 4)$ ($\theta = 0.5$) [19, 22, 23]. The saturation of the Pd(111), Pd(100), and Pd(110) surfaces with adsorbed oxygen (O_{ads}) is followed by the formation of the $(\sqrt{3} \times \sqrt{3})R30$, $c(2 \times 2)$, and $c(2 \times 4)$ structures with O_{ads} coverages of $\theta = 0.33$, 0.50, and 0.50, respectively.

The insertion of chemisorbed oxygen atoms into palladium subsurface layers, resulting in surface reconstruction structures, was studied in [10, 11, 13–15, 19, 22–30]. It was found that O_{ads} insertion and surface reconstruction in various palladium samples take place

after the saturation of the chemisorbed oxygen layers ($\theta \sim 0.5$) at $T \geq 500$ K. For example, during NO_2 chemisorption on $\text{Pd}(111)$, a new metal layer with a rectangular cell (3.94×6.38 Å) and then with a square cell (6.79×6.79 Å) forms in the O_{ads} layer with a $p(2 \times 2)$ structure. As this takes place, O atoms penetrate into the subsurface palladium layer [10]. For $\text{Pd}(100)$, it was demonstrated by LEED [11, 13, 14] and STM [15] that a $p(5 \times 5)$ reconstruction structure ($\theta = 0.64$) similar to the $(110)\text{PdO}$ face initially forms in the $c(2 \times 2)$ adsorbed oxygen layer, and at $\theta \geq 0.64$ this is followed by the formation of the reconstruction structure ($\sqrt{5} \times \sqrt{5} \text{R}27$ ($\theta = 0.8$)), which is related to the $(001)\text{PdO}$ face. For the $\text{Pd}(110)$ surface, the formation of $-\text{Pd}-\text{O}-\text{Pd}-$ chains running in the $[110]$ direction is observed at the earliest stage of O_2 chemisorption at $T \geq 200$ K. These chains gradually form added row-type reconstruction structures. This is followed by the formation of a $(2 \times 3)-1D$ structure at $\theta \leq 0.2$ and a $c(2 \times 4)$ structure at $\theta = 0.2-0.5$ [19, 22, 23]. It was established that, after the saturation of the chemisorbed oxygen layers ($\theta \sim 0.5$) in various palladium samples, O_{ads} penetrate into the subsurface layers of the metal [24–29]. For example, at $T \geq 550$ K and $P_{\text{O}_2} \geq 10^{-3}$ Torr, O atoms penetrate into the $\text{Pd}(\text{poly})$ bulk; at $T = 1050$ K and $P_{\text{O}_2} = 3.5 \times 10^{-2}$ Torr, palladium absorbs ~ 350 ML of oxygen ($n \sim 350$) [24]. It is believed that a solid solution of oxygen in the metal lattice forms under these conditions because these P_{O_2} values are far below the dissociation pressure of the bulk oxide PdO . For $\text{Pd}(111)$, TD experiments revealed high-temperature O_2 desorption peaks at $T \sim 1100$ K. These peaks are attributed to the diffusion of oxygen inserted in the metal [25]. It was demonstrated by TD, LEED, XPS, and HREELS that, after the saturation of the O_{ads} layer on $\text{Pd}(111)$ at $T \geq 520-530$ K, oxygen atoms penetrate into the subsurface metal layers and n reaches ~ 2 [26, 27]. For $\text{Pd}(110)$, it was shown by TD and work function ($\Delta\phi$) measurements that, at $T \geq 270-300$ K and an O_2 exposure of $\geq 1-1.5$ L (L = Langmuir; 1 L = 10^{-6} Torr s), the saturation of the $c(2 \times 4)-\text{O}$ ($\theta = 0.5$) adsorbed layer is followed by the insertion of O_{ads} atoms into the subsurface palladium layers: $n \sim 1.8$ at $T = 475$ K and an exposure of 7228 L [28, 29]. DFT calculations [30] demonstrated that oxygen atoms from the O_{ads} layer chemisorbed on $\text{Pd}(111)$ at $\theta \geq 0.5$ can occupy tetrahedral holes between the first and second metal layers. At $\theta > 0.5$, the insertion of O_{ads} under the surface layer is energetically more favorable than oxygen chemisorption on the surface because of the $\text{O}_{\text{ads}}-\text{O}_{\text{ads}}$ bonding markedly weakened by the repulsive $\text{O}_{\text{ads}}-\text{O}_{\text{ads}}$ interactions.

Thus, by studying the interaction of O_2 with different palladium crystal faces by a variety of physical methods, it was demonstrated that the saturation of the chemisorbed oxygen layers ($\theta \sim 0.5$) is followed by the

insertion of O_{ads} into the subsurface palladium layers. This insertion of oxygen can cause surface reconstruction. However, O_{ads} insertion into the subsurface layers has not been studied in detail and it is unknown how this process depends on the O_2 pressure and the sample temperature. The purpose of this work was to gain insight into the insertion of O atoms into the subsurface zone of polycrystalline palladium by investigating the interaction between O_2 and $\text{Pd}(\text{poly})$ at O_2 pressures of $10^{-6}-10$ Pa and temperatures of 300–1300 K and to see how the insertion of O atoms depends on the O_2 pressure and sample temperature.

EXPERIMENTAL

Experiments were carried out in an LEED-240 ultrahigh-vacuum spectrometer (Varian) with an AES analyzer (HCVA-850, VG) and a quadrupole mass spectrometer (Q-7, VG). The spectrometer was pumped with an ion pump down to a residual pressure of $(1-2) \times 10^{-8}$ Pa. It was additionally equipped with a catalytic chamber vacuumizable with a diffusion pump. This chamber allowed the samples to be treated in wide ranges of O_2 pressure ($10^{-5}-10^3$ Pa) and temperature (300–1600 K). The sample was a $10 \times 5 \times 0.1$ mm piece of polycrystalline palladium ($\text{Pd}(\text{poly})$) foil. The sample temperature was measured with a W-Re thermocouple (W/Re 5%–W/Re 20%) welded to the lateral surface of the sample. Before oxygen adsorption, the impurity carbon was removed from the foil by treating it with O_2 at $T = 500-600$ K and $P_{\text{O}_2} = 1$ Pa followed by heating to $T = 1300$ K in a vacuum. As the sample was purified, it underwent gradual recrystallization. It was found by scanning electron microscopy (SEM) that the surface of recrystallized palladium consists of 10- to 100- μm crystallites [31]. According to X-ray crystallographic data, $\sim 32\%$ of the crystallites are (100)-oriented, $\sim 18\%$ of them are (111)-oriented, $\sim 34\%$ are (311)-oriented, and $\sim 15\%$ are (331)-oriented. The residual level of carbon on the palladium surface was determined by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The amount of oxygen sorbed by the sample was derived from TD spectra and XPS data. The saturated oxygen adsorption layer on the $\text{Pd}(\text{poly})$ surface was formed at 500 K by exposing the sample to O_2 (~ 200 L). Saturation of the palladium single crystal faces (111), (100), and (110) with chemisorbed oxygen is known to yield ($\sqrt{3} \times \sqrt{3} \text{R}30$), $c(2 \times 2)$, and $c(2 \times 4)$ structures with $\theta = 0.33$, 0.5, and 0.5, respectively [6, 8, 10, 11–15, 19, 22, 23]. The $\text{Pd}(\text{poly})$ sample used in this work consisted largely of (111)- and (100)-oriented crystallites, so it was accepted that the saturated oxygen adsorption layer on this sample at 500 K forms at an O_2 exposure of 180 L and is characterized by $\theta = 0.5$. A detailed description of our experimental setup and sample pre-

treatment and experimental procedures is presented elsewhere [31].

RESULTS AND DISCUSSION

Interaction between Oxygen and Pd(poly) at $P_{O_2} = 2.6 \times 10^{-6}$ –10 Pa

The interaction between oxygen and palladium on polycrystalline palladium foil was studied at $T = 500$ –600 K and $P_{O_2} = 2.6 \times 10^{-6}$ –10 Pa by the TD method. Figure 1 plots the number of oxygen monolayers (n) sorbed by Pd(poly) as a function of O_2 exposure. These data were obtained in the exposure range from 10^{-1} to 10^9 L at 500 and 600 K. Because of the wide O_2 exposure range, the sample had to be treated at different P_{O_2} values between 2.6×10^{-6} and 10 Pa. At the top of Fig. 1, we indicate the P_{O_2} intervals in which the O_2 exposures were performed. At $P_{O_2} > 10^{-5}$ Pa, the sample was exposed to oxygen at a certain P_{O_2} for 0.5–180 min until the preset exposure dose was reached. The oxygen uptake was determined from the ratio of the area of the TD spectrum of the sample exposed to a given oxygen pressure P_{O_2} for the corresponding time to the area of the TD spectrum recorded after the saturation of the adsorption layer at $T = 500$ K and an exposure of 180 L ($\theta = 0.5$). It is clear from Fig. 1 that, at low pressures of $P_{O_2} \leq 2.6 \times 10^{-5}$ Pa, the oxygen coverage of the surface increases rapidly to $\theta = 0.5$ as the O_2 exposure is raised to 200 L (region A). This is due to the dissociative chemisorption of O_2 and the gradual formation of saturated $c(2 \times 2)$, $c(2 \times 4)$, and $(\sqrt{3} \times \sqrt{3})R30$ adsorption layers on the (100), (110), and (111) crystallite faces, respectively, with a chemisorbed oxygen coverage of $\theta \sim 0.5$ [6, 8, 10, 11–15, 19, 22, 23]. Upon an increase in P_{O_2} from 10^{-2} to 10 Pa, the oxygen uptake gradually increases from $\theta = 0.5$ to $n \sim 2.0$ as the O_2 exposure is raised from 200 to $\sim 2 \times 10^7$ L (Fig. 1, region B). This may be due to the insertion of oxygen atoms into the subsurface layers of palladium followed by the formation of oxide-like reconstruction structures. The insertion of O_{ads} in the subsurface metal layers and the formation of reconstruction structures was observed earlier for Pd(111), Pd(100), and Pd(110) single crystals after the saturation of the oxygen adsorption layers at $\theta \sim 0.5$ [10, 11, 13–15, 19, 22–30]. In the O_2 exposure range 10^{-1} – 2×10^7 L, the oxygen uptakes at 500 K (curve 1) and 600 K (curve 2) are similar (Fig. 1). Therefore, neither the formation of the adsorption layer at $\theta \leq 0.5$ nor O_{ads} insertion into the subsurface Pd(poly) layer yielding reconstruction structures at $n = 0.5$ –2.0 depends significantly on the sample temperature between 500 and 600 K. At higher O_2 exposures of

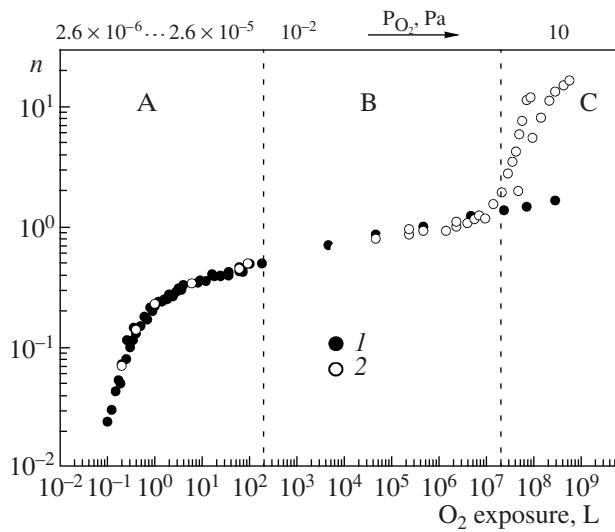


Fig. 1. The amount of oxygen sorbed by Pd(poly) (n) as a function of the O_2 exposure at $T = (1) 500$ and (2) 600 K. A, B, and C are the P_{O_2} intervals in which the corresponding exposures were performed. See text for details.

$\geq 2 \times 10^7$ L (Fig. 1, region C), the O_2 uptake at 600 K is much higher than the O_2 uptake at 500 K. For example, at an exposure of 2×10^8 L, the oxygen uptake is ~ 2.0 ML at 500 K and $n \sim 11.3$ at 600 K. The accelera-

Parameters of oxygen adsorption on Pd(poly) at 600 K (TD spectra are shown in Fig. 2)

Spectrum number	P_{O_2} , Pa	Exposure	O_2 uptake (n), ML
(a)			
1	2.6×10^{-6}	10 s	0.07
2	2.6×10^{-6}	20 s	0.14
3	2.6×10^{-6}	50 s	0.23
4	2.6×10^{-5}	30 s	0.35
5	2.6×10^{-5}	5 min	0.45
6	2.6×10^{-5}	15 min	0.50
7	10^{-2}	15 s	0.81
8	10^{-1}	10 min	0.92
9	10^{-1}	30 min	0.93
10	10^{-1}	50 min	1.01
11	10^{-1}	85 min	1.08
12	10^{-1}	120 min	1.17
(b)			
1	2.6×10^{-5}	15 min	0.5
2	5	"	0.84
3	7	"	1.52
4	8	"	1.93
5	10	"	3.03
6	15	"	4.19
7	20	"	5.38
8	30	"	6.13

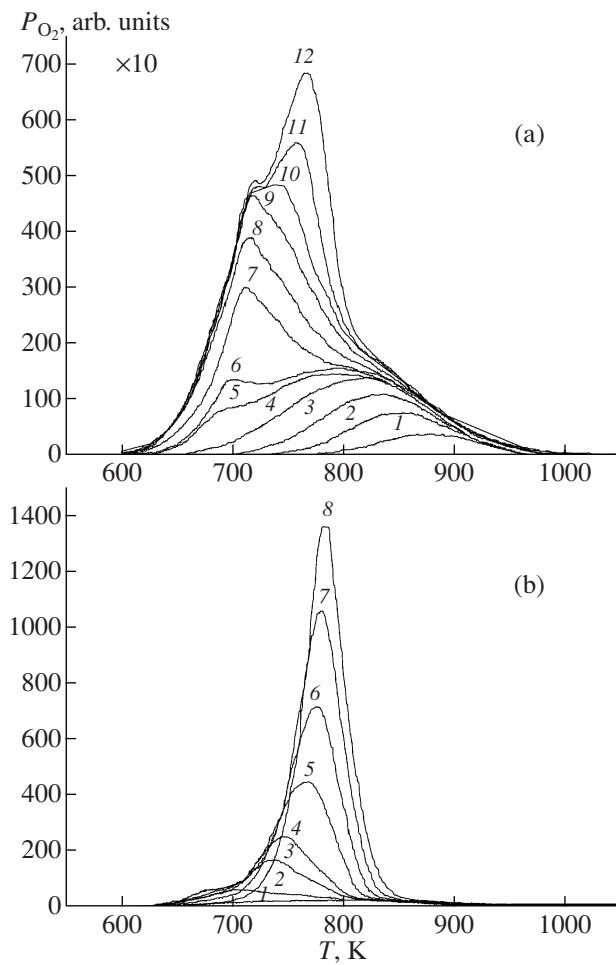


Fig. 2. Oxygen TD spectra recorded at $\beta = 10$ K/s after the treatment of Pd(poly) at 600 K. The adsorption conditions are specified in the table. The spectrum numbers are the same as in the table.

tion of oxygen sorption on Pd(poly) at 600 K relative to oxygen sorption at 500 K, observed at exposures of $\geq 2 \times 10^7$ L, may be due to the insertion of O atoms into deeper palladium layers. At $n \geq 1.0$, a high-temperature peak at $T \geq 750$ K appears in the TD spectrum, which shifts progressively to higher temperatures as n increases (Fig. 2, table). This indicates the release of oxygen dissolved in palladium, because PdO decomposition yielding O_2 takes place at $T \sim 600$ K [10].

Figure 2 shows the oxygen TD spectra recorded at a sample heating rate of $\beta = 10$ K/s after O_2 adsorption on Pd(poly) at 600 K and $P_{O_2} = 2.6 \times 10^{-6}$ –30 Pa. The shape and intensity of spectra 1–6 (Fig. 2a) and the way they vary as the O_2 exposure is increased from 0.2 to 180 L are similar to those observed earlier for the same sample after O_2 adsorption at $T = 500$ K [31]. Therefore, the formation of the adsorption layer on the Pd(poly) surface depends insignificantly on the sample temperature between 500 and 600 K. For example, the

change in the TD peak temperature (T_{\max}) from 875 K (spectrum 1) to 800 K (spectrum 4) in Fig. 2a indicates second-order O_2 desorption from the disordered chemisorption layer with $E_{\text{des}} = 230$ kJ/mol [31]. The low-temperature peak at $T \sim 700$ K in spectra 5 and 6 in Fig. 2a indicates O_2 desorption arising from the decomposition of the adsorption structure $c(2 \times 2)$ of the saturated O_{ads} layer on the (100) crystallite faces. In this structure, the O_{ads} –surface bond energy is substantially reduced by the repulsive lateral O_{ads} – O_{ads} interactions ($\epsilon_{\text{aa}} \sim 10$ kJ/mol); as a consequence, O_2 is desorbed at a lower temperature (700 K) with $E_{\text{des}} = 150$ kJ/mol [31].

Raising P_{O_2} ($\geq 10^{-2}$ Pa) causes an increase in the number of sorbed oxygen monolayers ($n > 0.5$) and marked changes in the O_2 TD spectrum. Figure 2a presents O_2 TD spectra recorded after oxygen adsorption at $P_{O_2} = 10^{-2}$ Pa (spectrum 7) and $P_{O_2} = 10^{-1}$ Pa (spectra 8–12). It is clear from spectra 7–10 that, as n changes from 0.81 to 1.01, the intensity of the low-temperature peak (~ 715 K) increases. It is possible that this peak is due to the decomposition of oxide-like surface reconstruction structures that form on Pd(111) [10] and Pd(100) [11, 13–15] as the oxygen uptake increases from $n = 0.5$ to $n \sim 2.0$. At $n \geq 1.0$, the TD spectrum exhibits a new high-temperature peak with $T_{\max} \geq 750$ K (Fig. 2a, spectra 11, 12). Raising P_{O_2} above 5 Pa causes a further increase in the oxygen uptake ($n > 1.0$) and in the intensity of the TD peak with $T_{\max} > 750$ K. Figure 2b shows the O_2 TD spectra recorded for the sample treated with O_2 at 600 K and $P_{O_2} = 5$ –30 Pa for 15 min (spectra 2–8). Spectrum 1 was obtained after a 180 L exposure of the sample to O_2 at $P_{O_2} = 2.6 \times 10^{-5}$ Pa. For spectra 1–8, the oxygen uptake changes from $n = 0.5$ to 6.13. Clearly, as P_{O_2} is raised from 5 to 30 Pa, n gradually increases from 0.84 to 6.13. As n increases, the intensity of the TD spectrum grows and T_{\max} shifts progressively to higher temperatures (Fig. 2b). For example, $T_{\max} = 700$ K at $n = 0.84$ and $T_{\max} = 785$ K at $n = 6.13$ (spectra 2, 8). An analysis of the spectra presented in Fig. 2 has made it possible to identify the phase resulting from the interaction between O_2 and Pd(poly) at O_2 pressures of 10^{-6} to 30 Pa. At low pressures of $P_{O_2} \leq 10^{-5}$ Pa, the TD spectra show a high-temperature peak indicating O_2 desorption from the disordered chemisorbed layer and a low-temperature peak indicating repulsive lateral interactions in the saturated chemisorbed O_{ads} layer. At higher pressures of $P_{O_2} \geq 10^{-2}$ Pa, the low-temperature TD peak with $T_{\max} \sim 715$ K gradually grows as n increases ($n > 0.5$). After the saturation of the adsorbed oxygen layer ($\theta \sim 0.5$) on various palladium samples, a further increase in θ can cause both the formation of oxide-like reconstruction phases [10, 11, 13–15] and

the insertion of O atoms into the metal bulk resulting in a solid solution of oxygen in the palladium lattice [24–29]. The reconstruction structures form on the (111) and (100) palladium surfaces at an oxygen uptake of $n = 0.5$ –2.0 and decompose with O_2 desorption at $T = 650$ –700 K [10, 15]. Therefore, the low-temperature O_2 TD peak with $T_{\max} \sim 715$ K in spectra 7–12 in Fig. 2a may be due to the decomposition of the oxide-like reconstruction structures that have formed on the Pd(poly) surface at $P_{O_2} \geq 10^{-2}$ Pa and $n > 0.5$. As the oxygen uptake increases at $n > 1.0$, a high-temperature peak with $T_{\max} > 750$ K appears in the O_2 TD spectrum. At $n \geq 2.2$, the formation of clusters on the Pd(111) surface was revealed by STM [10], and it was hypothesized that these clusters are PdO particles. Note, however, that the thermal decomposition of PdO particles with O_2 desorption occurs at $T \sim 600$ K [10]. Therefore, it can be assumed that the high-temperature peak observed in the O_2 TD spectra for Pd(poly) at $n \geq 1.0$ and $T > 750$ K (Fig. 2a, spectra 10–12; Fig. 2b, spectra 2–8) is due to the release of oxygen from the subsurface palladium layers, because T_{\max} of this peak shifts to higher temperatures as n increases, occurring at 750 K for $n \sim 1.0$ and at 785 K for $n \sim 6$ (Fig. 2b). Thus, O_2 desorption takes place at much higher temperatures (>750 K) than would be observed for the decomposition of PdO particles (~ 600 K).

*Chemisorption and Desorption of O_2 on Pd(poly)
at Low Pressures of $P_{O_2} \leq 1.3 \times 10^{-5}$ Pa*

Oxygen adsorption and desorption at low pressures ($P_{O_2} \leq 1.3 \times 10^{-5}$ Pa) on the polycrystalline palladium (Pd(poly)) surface consisting of 10- to 100- μ m crystallites with (100), (111), (311), and (311) faces (~32, ~18, ~34, and ~15%, respectively) were studied in detail in an earlier work [31]. It was found that the main kinetic features of O_2 adsorption and desorption on Pd(poly) are determined by the formation and decomposition of the oxygen adsorption structures $p(2 \times 2)$ and $c(2 \times 2)$ on the (100) and (111) crystallite faces. These processes are governed by the repulsive lateral interactions between chemisorbed oxygen atoms. The repulsion between O_{ads} atoms reduces the chemisorbed oxygen atom–palladium surface bond energy ($D(\text{Pd–O})$). As a consequence, the initial stages of O_2 chemisorption on the (100) crystallites yields the simple structure $p(2 \times 2)$, in which O_{ads} atoms occupy third-nearest neighbor (3NN) adsorption sites and do not interact with one another; accordingly, $D(\text{Pd–O})$ takes its maximum value [31]. As the O_{ads} coverage of the surface increases, the denser structure $c(2 \times 2)$ forms, in which O_{ads} atoms occupy next-nearest neighbor (2NN) adsorption sites. Repulsive interactions arise between these atoms, causing a decrease in $D(\text{Pd–O})$.

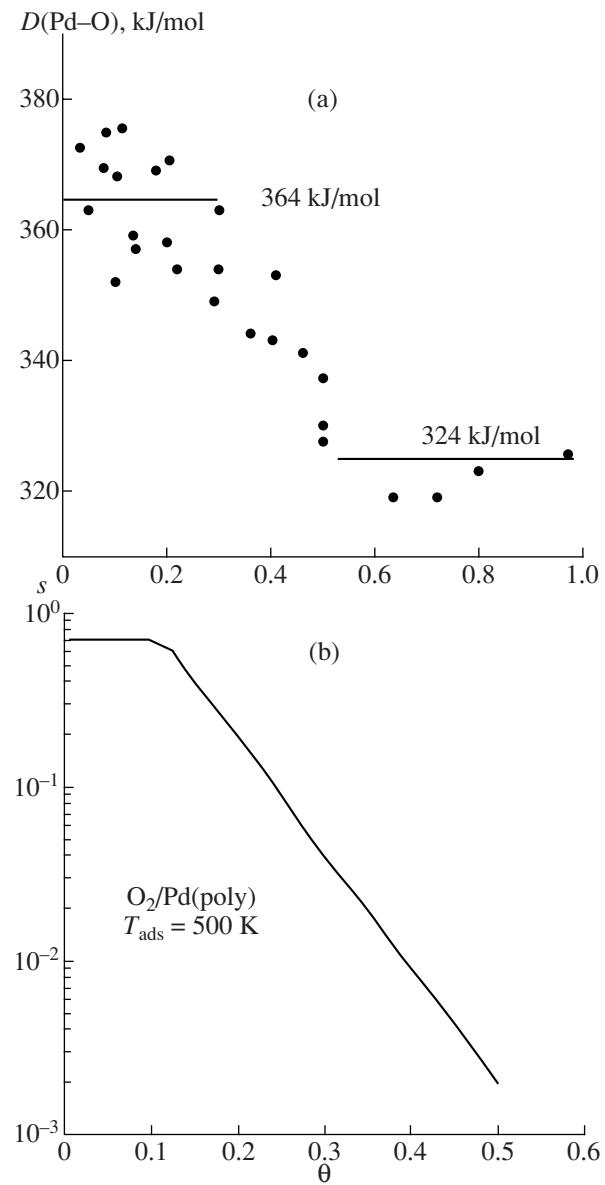


Fig. 3. (a) O_{ads} –Pd(poly) surface bond energy and (b) the sticking coefficient versus the oxygen coverage of the surface.

Figure 3a plots $D(\text{Pd–O})$ as a function of the O_{ads} coverage of the surface. The $D(\text{Pd–O})$ values were determined from the equation $2D(\text{Pd–O}) = D(\text{O–O}) + q$, where $D(\text{O–O})$ is the dissociation energy of the O_2 molecule (498 kJ/mol) and q is the heat of adsorption of O_2 . Since $q = E_{\text{des}} - E_{\text{ads}}$ (E_{des} is the activation energy of O_2 desorption) and the activation energy of adsorption (E_{ads}) is low (<10 kJ/mol), it can be assumed that $q \sim E_{\text{des}}$. In the calculation of $D(\text{Pd–O})$, which depends on the oxygen coverage of the surface, we used E_{des} data for different θ values, which were derived from O_2 TD spectra [31]. As is clear from Fig. 3a, $D(\text{Pd–O})$ is about 364 kJ/mol for $\theta \leq 0.2$ –0.3, decreases rapidly at $\theta \geq 0.2$ –0.3, and reaches its minimum value of ~ 324 kJ/mol

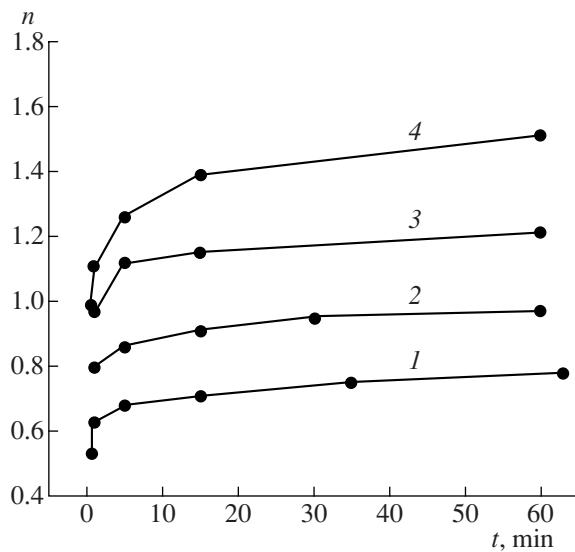


Fig. 4. Amount of oxygen (n , ML) sorbed by Pd(poly) at 500 K as a function of the O_2 exposure time at P_{O_2} = (1) 10^{-2} , (2) 10^{-1} , (3) 1, and (4) 10 Pa.

at $\theta \sim 0.5$. From the $D(Pd-O)$ values at $\theta \sim 0$ ($D(Pd-O)_0$) and $\theta \sim 0.5$ ($D(Pd-O)_{0.5}$), it is possible to determine the energy of the repulsive lateral interaction between chemisorbed atoms (ϵ_{aa}). Taking into account the lateral surroundings of O_{ads} at $\theta = 0$ and 0.5, we obtain $\epsilon_{aa} = (D(Pd-O)_0 - D(Pd-O)_{0.5})/4 = 10$ kJ/mol. Figure 3b plots the dependence of the oxygen sticking coefficient (s) on the chemisorbed oxygen coverage of the surface. The $s(\theta)$ dependence was calculated from O_2 chemisorption kinetic data obtained earlier [31]. At $\theta < 0.15$, s is invariable and is 0.7 (Fig. 3b). This may be due to the formation of the $p(2 \times 2)$ structure on the (100) and (111) faces [31]. At $\theta \geq 0.15$, s decreases rapidly to become $\sim 10^{-3}$ at $\theta \sim 0.5$. This is possible due to the formation of the $c(2 \times 2)$ structure on the (100) face [31]. It was also found for O_2 chemisorption on Pd(111) that s decreases rapidly as θ increases and that $s < 10^{-3}$ at $\theta \geq 0.3-0.4$ [27]. At the pressures examined ($\leq 1.3 \times 10^{-5}$), longer exposure to O_2 does not cause any increase in θ . This is likely due to the substantial decrease in the O_2 adsorption rate upon the saturation of the adsorption layer ($s \leq 10^{-3}$). For this reason, a wide range of O_2 pressures (2.6×10^{-6} –30 Pa) was used in our study of oxygen insertion into palladium.

Formation of a Surface Oxide on Pd(poly)

Figure 4 illustrates the kinetics of oxygen sorption by Pd(poly) at O_2 pressures of 10^{-2} to 10 Pa at $T = 500$ K. For all of these pressures, the oxygen uptake increases rapidly at the early stages of the process ($t \leq 1-2$ min). At $t \geq 1-2$ min, n increases insignificantly, gradually reaching the saturation level. Raising P_{O_2} causes an increase in the oxygen uptake at saturation.

For example, at $P_{O_2} = 10^{-2}$, 10^{-1} , 1.0, and 10 Pa, the oxygen uptake in 65 min is 0.8, 1.0, 1.2, and 1.5 ML, respectively. At these P_{O_2} values, extending the exposure time from 65 to 150 min does not cause any significant change in the oxygen uptake. Thus, the time-dependent oxygen uptake data ($n(t)$) for the interaction between O_2 and Pd(poly) at $T = 500$ K and $P_{O_2} = 10^{-2}$ –10 Pa (Fig. 4) indicate a rapid stage (<1–2 min) and a slow stage (>1–2 min). In an earlier study [32], a similar time dependence of the oxygen uptake was observed for the growth of an oxide film on Rh(poly). An analysis of the $n(t)$ data suggested the following growth mechanism for the oxide film on Rh(poly). A layer of physically adsorbed $(O_2)_{ads}$ molecules forms on the oxide film surface in an O_2 atmosphere. The heat of adsorption of these molecules is ~ 20 kJ/mol. The dissociation of the oxygen molecules in this layer yields O_{ads} atoms, which penetrate into the oxide film, diffuse to the oxide/metal interface, and interact with Rh atoms. This is how the oxide film grows. Because the heat of adsorption of $(O_2)_{ads}$ is low, the adsorption–desorption equilibrium between the O_2 molecules in the gas and the $(O_2)_{ads}$ molecules and, accordingly, the steady-state $(O_2)_{ads}$ coverage of the oxide film surface at $T = 400$ –600 K are established quite rapidly. Thus, the O_2 pressure determines the $(O_2)_{ads}$ coverage of the surface, which is a factor in the rate of O atom insertion into the oxide film and, accordingly, in the film growth rate. It is likely that, after the saturation of the O_{ads} layer ($\theta \sim 0.5$) during the interaction between O_2 and Pd(poly) at $T = 500$ K and $P_{O_2} = 10^{-2}$ –10 Pa, further oxygen uptake proceeds via the above mechanism. A layer of physically adsorbed $(O_2)_{ads}$ molecules forms on the surface of the saturated O_{ads} layer. The O_2 pressure determines the $(O_2)_{ads}$ coverage of the Pd(poly) surface, which, in turn, determines the rate of the insertion of O_{ads} into the subsurface layer and, accordingly, the amount of oxygen sorbed by palladium. From the oxygen uptake data as a function of O_2 exposure (Fig. 1) and from O_2 TD spectra (Fig. 2), it follows that, at $n = 0.5$ –2.0, a reconstruction structure or a surface oxide forms on Pd(poly). A simultaneous analysis of these data and the data presented in [32] suggests that the $n(t)$ dependence plotted in Fig. 4 indicates the growth of a surface oxide on Pd(poly) at 500 K and $P_{O_2} = 10^{-2}$ –10 Pa. It was demonstrated earlier that oxide-like reconstruction structures form on Pd(111) and Pd(100) at $\theta \geq 0.5$ [10, 11, 13–15].

The penetration of O_{ads} into the subsurface layers of palladium may take place via the insertion mechanism. This mechanism was deduced for O_{ads} on Pd(111) from the results of DFT calculations of the bond energy for O_{ads} on the surface and for O atoms in the tetrahedral and octahedral holes between the first and the second layers of the metal [30]. It was demonstrated that, in the

chemisorbed O_{ads} layer on Pd(111) at $\theta \sim 0.5$, the E_{bond} values for O_{ads} and for O atoms in the tetrahedral holes between the first and second layers of the metal are similar because of the decrease in E_{bond} for Pd– O_{ads} . This bond weakening arises from the repulsive lateral O_{ads} – O_{ads} interactions. As a result, at $\theta > 0.5$, the insertion of O atoms under the surface layer is energetically more favorable than further oxygen chemisorption on the surface. The insertion of O_{ads} yields a linear O_{ads} –Pd*– O_{abs} structure, where O_{ads} is an O atom chemisorbed on the surface, Pd* is a surface atom of the metal, and O_{abs} is an oxygen atom occupying a tetrahedral hole between the first and the second layers of the metal. The O_{abs} atom is bonded both with the Pd* atom and with a Pd atom from the second layer. This O_{ads} –Pd*– O_{abs} structure is stable owing to O_{ads} and O_{abs} being strongly bonded to the surrounding Pd atoms. The strength of these bonds is due to the fact that the Pd* atoms partially screen the repulsive interactions between O_{ads} and O_{abs} and the relaxation shifts of the Pd atoms surrounding O_{abs} result in the optimization of the Pd– O_{abs} bond.

Insertion of Oxygen into the Pd(poly) Bulk

Figure 5 plots the amount of oxygen sorbed by Pd(poly) as a function of the time of exposure to O_2 at 600 K and different P_{O_2} values. For all O_2 pressures, n initially increases to ~ 1.0 ($t \leq 1$ –2 min), and this is followed by an induction period, in which n grows only slightly with time. The induction period is followed by a comparatively rapid increase in n until saturation. As P_{O_2} is raised, the induction period shortens and the oxygen uptake at saturation increases markedly (curves 1–3). At $P_{O_2} = 10^{-1}$ Pa, the induction period is 120 min and no significant increase in n is observed over this time ($n \sim 1$, curve 1). At $P_{O_2} = 1$ Pa, the induction period has a shorter duration of 60–80 min and is followed by a rapid growth of n to ~ 12 (curve 2). At $P_{O_2} = 10$ Pa, the induction period is as short as 5–10 min and ~ 17 ML of oxygen is sorbed in 120 min (curve 3). It follows from the dependence of n on the O_2 exposure (Figs. 1, 4) and from O_2 TD spectra (Fig. 2) that, at $n = 0.5$ –2.0, a surface reconstruction structure or a surface oxide forms on Pd(poly); at $n \geq 2$, O atoms penetrate deep into the subsurface layers of palladium. In the $n(t)$ curves shown in Fig. 5, which were obtained at 600 K, n varies between 1 and ~ 17 ; therefore, these curves correspond to the formation of a surface oxide on Pd(poly) and to the insertion of O atoms into the palladium bulk. At a low pressures of P_{O_2} (10^{-1} Pa), the $(O_2)_{ads}$ coverage of the surface is very low and, accordingly, the rate of O_{ads} insertion into the subsurface layer of palladium and the rate of subsequent surface oxide formation are slow. As a consequence, the oxygen uptake at this P_{O_2} value is $n = 0.8$ –1.2, so curve 1 in Fig. 5 describes the formation

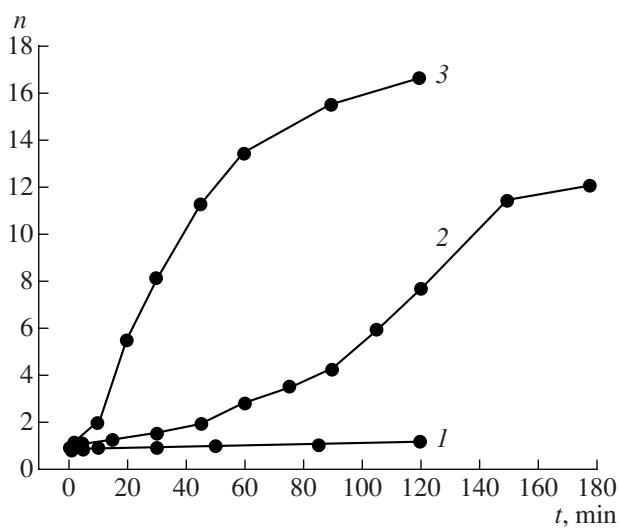


Fig. 5. Amount of oxygen (n , ML) sorbed by Pd(poly) at 600 K as a function of the O_2 exposure time at $P_{O_2} =$ (1) 10^{-1} , (2) 1, (3) 10 Pa.

of the surface oxide on Pd(poly). Raising P_{O_2} to 1.0 Pa causes a marked increase in the $(O_2)_{ads}$ coverage of the surface and, accordingly, accelerates the formation of the surface oxide. On the surface of the oxide film, O_{ads} atoms form in the $(O_2)_{ads}$ layer. These atoms penetrate into the surface oxide and then into the subsurface layers of the metal. No data concerning the activation energy of diffusion (E_{diff}) of oxygen atoms in palladium have been found in the literature. It is likely that E_{diff} for O atoms in palladium is similar to E_{diff} for oxygen in rhodium, because oxygen diffuses in all metals via the same insertion mechanism [33]. Estimation of E_{diff} for oxygen in rhodium led to a value of ~ 200 kJ/mol [33]. Therefore, E_{diff} for O atoms in the palladium lattice can be 150–200 kJ/mol, so there is significant diffusion of O atoms in palladium at $T = 600$ K. As a result, the O atoms penetrate deep under the surface layer and build up progressively in the subsurface zone of palladium. This is why palladium sorbs as much as ~ 12 ML of oxygen at 600 K and $P_{O_2} = 1.0$ Pa in 140 min, as demonstrated by curve 2 in Fig. 5. The shape of this curve is determined by the superposition of the oxygen sorption curves referring to oxide film formation and to the insertion of O atoms into deep subsurface layers of palladium. As a consequence, curve 2 in Fig. 5 indicates an induction period of 60–80 min followed by an increase in the oxygen uptake. Raising P_{O_2} to 10 Pa causes a further increase in the $(O_2)_{ads}$ coverage of the surface and accelerates the formation of the surface oxide film and the insertion of O atoms into the subsurface layers of palladium. As a result, the surface oxide is formed in 5–10 min and ~ 17 ML of oxygen are sorbed in 120 min (Fig. 5, curve 3).

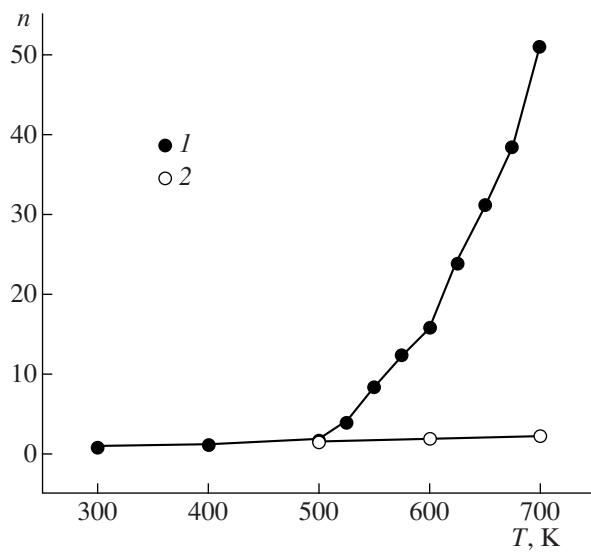


Fig. 6. Temperature dependences of the amount of oxygen (n , ML) sorbed by Pd(poly) at an O_2 exposure time of 2 h and $P_{O_2} = 10$ Pa derived (1) from TD spectra and (2) from $O-KL_{23}L_{23}$ Auger spectra obtained using the XPS technique.

In order to study the effect of the sample temperature on oxygen sorption by palladium, we treated Pd(poly) with O_2 in a wide temperature range (300–700 K). Figure 6 plots the temperature dependences of the amount of oxygen sorbed by Pd(poly) for samples exposed to oxygen at $P_{O_2} = 10$ Pa for 2 h at a given temperature between 300 and 700 K. Curve 1 was derived from TD spectra; curve 2, from Auger spectra of oxygen ($O-KL_{23}L_{23}$) obtained using the XPS technique. The concentration of sorbed oxygen was determined using $O-KL_{23}L_{23}$ spectra with $E_{kin} = 514$ eV because the main photoelectron peak of oxygen ($O 1s$, BE = 529.3 eV) is overlapped with the stronger Pd $3p_{3/2}$ peak [34]. It is clear from curve 1 that, as the temperature is raised from 300 to 700 K, the oxygen uptake increases to $n \sim 50$. Two characteristic portions can be distinguished in this curve. The first is between 300 and 500 K, in which n changes only slightly (from 0.8 at 300 K to 1.8 at 500 K). The second portion is between 500 and 700 K, in which n grows markedly (from 1.8 at 500 K to 50 at 700 K). Since $n = 0.5$ –2.0 is the range in which the surface oxide forms on Pd(poly), oxygen sorption at 300–500 K is due to the formation of an oxide film. No further oxygen sorption takes place at 300–500 K, because the diffusion rate of O atoms in palladium at these temperatures is extremely low. At $T > 500$ K, the diffusion of O atoms in palladium is much more rapid. As a consequence, as the sample temperature is raised, the O atoms penetrate deeper into the metal bulk and, accordingly, the oxygen uptake at $T > 500$ K is higher (Fig. 6, curve 1). For example, ~2 ML of oxygen is sorbed in

2 h at $P_{O_2} = 10$ Pa and 500 K, while the oxygen uptake at 700 K is $n \sim 50$. The temperature dependence of the oxygen uptake derived from the $O-KL_{23}L_{23}$ spectra (curve 2) differs significantly from the same dependence derived from the TD spectra. According to curve 2, n increases only slightly with increasing temperature (from 1.5 at 500 K to 2.2 at 700 K). This radical difference between the oxygen uptake data obtained by XPS and TD is due to the small analytical depth of the XPS method. Under the conditions examined, the analytical depth of XPS is < 15 –20 Å [34, 35]. In the TD method, oxygen can be released from deeper layers of the metal at a sample temperature of $T = 500$ –1300 K. The same fact that n from TD spectra is much larger than n from XPS data was observed for oxygen sorbed in the subsurface layers of Pd(110) [34, 35].

CONCLUSIONS

The interaction between O_2 and Pd(poly) at O_2 pressures of 10^{-6} –10 Pa at temperatures of 300–700 K includes O_2 chemisorption, the formation of a surface oxide film, and the insertion of oxygen atoms deep into the subsurface layers of palladium. The interaction between O_2 and Pd(poly) is governed by the O_2 pressure and the sample temperature. At low pressures of $P_{O_2} \leq 1.3 \times 10^{-5}$ Pa, oxygen undergoes dissociative chemisorption on the (111), (100), and (110) crystallite faces of polycrystalline palladium. During chemisorption, as the O_{ads} coverage of the surface (θ) increases, the O_{ads} –surface bond energy $D(Pd–O)$ gradually decreases from 364 kJ/mol for $\theta \sim 0$ to 324 kJ/mol for $\theta \sim 0.5$ because of the repulsive lateral interactions between O_{ads} atoms ($\epsilon_{aa} = 10$ kJ/mol). Because of the decrease in $D(Pd–O)$, the O_2 sticking coefficient (s) for Pd(poly) falls from 0.7 at $\theta \leq 0.15$ to $\sim 10^{-3}$ at the point of surface saturation with O_{ads} ($\theta \sim 0.5$).

At higher O_2 pressures of $\geq 10^{-2}$ Pa and $T \leq 500$ K, after the oxygen chemisorption layer is saturated ($\theta \sim 0.5$), O_{ads} atoms penetrate under the surface layer of the metal and form a palladium oxide film on the surface because of the decrease in $D(Pd–O)$ for O_{ads} . The insertion of O_{ads} may be due to the formation of linear O_{ads} –Pd*– O_{abs} structures in which the inserted oxygen atom (O_{abs}) is strongly bonded both with the surface palladium atom Pd* and with a Pd atom in the second layer of the metal [30]. The resulting O_{ads} –Pd*– O_{abs} structures may be fragments of the surface oxide. The O_{ads} penetrating into the subsurface layers come from the adsorbed $(O_2)_{ads}$ layer. The steady-state $(O_2)_{ads}$ coverage is established during the equilibration between $(O_2)_{gas}$ and $(O_2)_{ads}$ and is determined primarily by P_{O_2} . As a consequence, raising P_{O_2} from 10^{-2} to 10 Pa causes an increase in the $(O_2)_{ads}$ coverage, thereby accelerating the formation of the surface oxide. This

leads to an increase in the oxide film thickness from $n = 0.8$ at 10^{-2} Pa to $n = 1.5$ at 10 Pa. The thermal decomposition of the surface oxide gives rise to a low-temperature O_2 peak ($T_{\max} = 715$ K) in the TD spectrum.

In the interaction between O_2 and Pd(poly) at $P_{O_2} \geq 1$ Pa and $T > 500$ K, after the formation of the saturated surface oxide film with $n \sim 2$, the O_{ads} atoms that form in the $(O_2)_{\text{ads}}$ adsorption layer penetrate into the oxide film and then into the subsurface layer of palladium and diffuse deep into the metal bulk. Raising the O_2 pressure (≥ 1 Pa) and the sample temperature (> 500 K) accelerates oxygen sorption. The O_{ads} atoms penetrating the oxide film again come from the $(O_2)_{\text{ads}}$ layer, the $(O_2)_{\text{ads}}$ coverage being determined by the O_2 pressure. As a consequence, raising P_{O_2} causes an increase in the $(O_2)_{\text{ads}}$ coverage and, accordingly, in the oxygen insertion rate. The activation energy of the diffusion of O atoms in palladium is between 150 and 200 kJ/mol [33]. Accordingly, raising the sample temperature (> 500 K) enhances the diffusion of O atoms in palladium; as a result, the O atoms penetrate deep under the palladium surface and build up in the metal bulk. At 700 K and $P_{O_2} = 10$ Pa, the oxygen uptake in 120 min is ~ 50 ML. Upon heating, the oxygen inserted in the subsurface layers of palladium gives rise to a distinct high-temperature TD peak with $T_{\max} \geq 750$ K.

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