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Oxygen Desorption from Polycrystalline Palladium: Thermal Desorption of O_2 from a Chemisorbed Layer of O_{ads} in the Course of the Decomposition of PdO Surface Oxide and in the Release of Oxygen from the Bulk of Palladium

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Abstract—The desorption of oxygen from polycrystalline palladium (Pd(poly)) was studied using temperature-programmed desorption (TPD) at 500–1300 K and the amounts of oxygen absorbed by palladium (*n*) from 0.05 to 50 monolayers. It was found that the desorption of O_2 from Pd(poly), which occurred from a chemisorbed oxygen layer (O_{ads}), in the release of oxygen from a near-surface metal layer in the course of the decomposition of PdO surface oxide, and in the release of oxygen from the bulk of palladium (O_{abs}), was governed by repulsive interactions between O_{ads} atoms and the formation and decomposition of O_{ads}–Pd*–O_{abs} structures (Pd* is a surface palladium atom). At $\theta \le 0.5$, the repulsive interactions between O_{ads} atoms (ε_{aa} = 10 kJ/mol) resulted in the desorption of O_2 from Pd(poly) at 650–950 K. At $0.5 \le n \le 1.0$, the release of inserted oxygen from a near-surface palladium layer occurred during TPD in the course of the migration of O_{abs} atoms to the surface and the formation–decomposition of O_{ads}–Pd*–O_{abs} structures. As a result, the desorption of O_2 occurred in accordance with a first-order reaction with a thermal desorption (TD) peak at $T_{max} \sim 700$ K. At $1.0 \le n \le 2.0$, the decomposition of PdO surface oxide occurred at a constant surface coverage with oxygen during TPD in the course of the formation–decomposition of O_{ads}–Pd*–O_{abs} structures. Because of this, the desorption of O_2 occurred in accordance with a zero-order reaction at low temperatures with a TD peak at $T_{max} \sim 675$ K. At $1.0 \le n \le 50$, oxygen atoms diffused from deep palladium layers in the course of TPD and arrived at the surface at high temperatures. As a result, O_2 was desorbed with a high-temperature TD peak at $T > 750$ K.

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INTRODUCTION

Because of their unique properties, platinum group metals are widely used as catalysts in chemical industry and in automotive exhaust gas neutralizers [1]. For example, palladium is used both in catalysts for the purification of automotive exhaust gases [1] and in catalysts for a number of industrially important catalytic processes such as ammonia oxidation [2] and methane combustion in gas turbines [3]. Palladium metal is used in these processes because of its high activity in the oxidation of hydrocarbons, CO, and H_2 and in the reduction of NO. Moreover, palladium oxide (PdO) is also highly active in oxidation reactions [3]. The wide use of palladium in industrial catalysis stimulated intense studies on the mechanisms of O_2, H_2, NO, CO, and CH_4 adsorption and catalytic reactions with the participation of these molecules on palladium single crystals with the use of current methods. Attention was focused on the interaction of oxygen with palladium because various PdO phases formed strongly affected the occurrence of catalytic oxidation reactions on palladium [3].

It is well known that the interaction of oxygen with transition metals involves the following three main steps: the dissociative chemisorption of O_2, the insertion of oxygen atoms into a metal lattice, and the formation of surface and bulk metal oxides. At elevated temperatures (≥500–600 K), the desorption of chemisorbed oxygen, the release of inserted oxygen, and the decomposition of metal oxides can occur along with these processes. These processes can strongly affect catalytic oxidation on metal catalysts. However, they are known less than the processes of oxygen adsorption and insertion and metal oxidation. In the Pd/O_2 system, the step of the associative desorption of chemisorbed oxygen on palladium single crystals is best understood. Thus, after the adsorption of O_2 at $T \ge 300$ K and low P_{O_2} ($\le 10^{-5}$ Pa), the desorption of O_2 was studied in detail using temperature-programmed desorption (TPD) on polycrystalline palladium (Pd(poly)) [4, 5], Pd(111) [6–11], Pd(100) [12–16], and Pd(110) [17–20]. An analysis of the TPD spectra indicated that the shapes and positions of O_2 thermal desorption (TD) peaks were almost independent of the surface structure of palladium and formed adsorption oxygen layers. Upon the adsorption of O_2 on Pd(111) at the surface coverage $\theta \le 0.25$ and $0.25 \le \theta \le 0.33$, $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30$ structures, respectively [6, 9–11], were formed; $p(2 \times 2)$ and $c(2 \times 2)$ were formed on Pd(100) at $\theta \le 0.25$ and $0.25 \le \theta \le 0.5$, respectively [12–16]; and (2×3)-1D and $c(2 \times 4)$ were formed on Pd(110) at $\theta \le 0.2$ and $0.2 \le \theta \le 0.5$, respectively [18, 19]. Therefore, the desorption of O_2 from Pd(111), Pd(100), and Pd(110) is accompanied by the decomposition of various adsorption structures: $p(2 \times 2)$ and (2×3)-1D at $\theta \le 0.25$ and $(\sqrt{3} \times \sqrt{3})R30$, $c(2 \times 2)$, and $c(2 \times 4)$, respectively, at $\theta \ge 0.25$. Nevertheless, a noticeable effect of these processes on the O_2 TPD spectra was not detected. On heating palladium samples, O_2 was desorbed from the surface of various palladium single crystals at 600–1000 K. The positions and shapes of TD peaks and changes in the spectra with increasing θ were found similar for Pd(poly) [4, 5], Pd(111) [6–11], and Pd(100) [12–16]. Moreover, the activation energies of O_2 desorption determined in various palladium samples at low θ were similar: 220 kJ/mol for Pd(poly) [4, 5]; 230, 200, and 222 kJ/mol for Pd(111) [6, 8, 9]; 210–250 kJ/mol for Pd(100) [15]; and 180 kJ/mol for Pd(110) [20].

At $T \ge 400$–500 K and elevated pressures of O_2 or NO_2 ($>10^{-5}$ Pa), a saturated chemisorbed oxygen layer (θ ~0.5) was formed in the course of the dissociative chemisorption of these molecules; in this layer, the insertion of chemisorbed oxygen (O_{ads}) into the near-surface layers of palladium occurred. It was found that, in the course of the insertion of O_{ads} atoms, palladium samples absorbed to ~3 monolayers (ML) of oxygen; ~1.8 ML was absorbed on Pd(poly) at 510 K [5]; ~1.0–3.1 ML was absorbed on Pd(111) at 500–623 K [8–11]; ~0.8 ML was absorbed on Pd(100) at 400–550 K [13–16]; and ~1.8 ML was absorbed on Pd(110) at 475 K [18, 19]. Note that the insertion of O_{ads} into near-surface metal layers can be accompanied by surface reconstruction. Thus, $p(5 \times 5)$ ($\theta = 0.64$) and $(\sqrt{5} \times \sqrt{5})R27$ ($\theta = 0.8$) reconstructive structures are formed on Pd(100) in the course of O_{ads} insertion; these structures were found similar to the structures of PdO faces, (110) and (001), respectively [13–16]. At small amounts of inserted oxygen (≤0.25 ML), the appearance of a narrow low-temperature peak was observed in the TPD spectra of O_2. Thus, a narrow peak was observed on Pd(poly) at 720 K [5], on Pd(111) at 700–725 K [8–11], on Pd(100) at 620–695 K [12–16], and on Pd(110) at 700–744 K [17–20]. It is believed that this peak can be due to the release of inserted oxygen from the near-surface region of the metal to the surface [5, 8–10, 18, 19] and the decomposition of reconstructive structures [11, 13–16]. At small amounts of inserted oxygen (≤0.25 ML), a gradual increase in the narrow TD peak was observed as the concentration of inserted oxygen was increased. The T_{max} of this peak remained almost unchanged; this suggests the desorption of O_2 from both Pd(poly) [5] and Pd(111) [8] in accordance with first order. As the amount of inserted oxygen was further increased (≥0.25 ML), a shift in the T_{max} of this peak toward high temperatures was observed as the intensity of the narrow peak increased. In this case, the ascending branches of the spectra coincided; this suggests the zero order of O_2 desorption from Pd(poly) [5] and Pd(111) [8, 9]. It was hypothesized that the zero order of O_2 desorption can be due to the exchange of oxygen atoms between the near-surface region and the surface [8] or between surface phases with different oxygen concentrations [9].

Thus, as a result of the study of O_2 desorption from various palladium samples, were found that, at $\theta \le 0.5$, oxygen was desorbed from the chemisorbed layer of O_{ads} at $T = 600$–1000 K. The surface structure of palladium samples and the chemisorbed layers of O_{ads} had almost no effect on the desorption of O_2. At $\theta \ge 0.5$, a narrow low-temperature TD peak with $T_{max} \sim 700$ K due to the release of oxygen from the near-surface region of palladium was observed in the course of TPD. However, the desorption of O_2 from palladium samples was studied only at small concentrations of oxygen absorbed in palladium (the number of monolayers $n \le 3.0$ ML), whereas to ~350 ML of oxygen can be accumulated in palladium [21].

The aim of this work was to study the thermal desorption of O_2 containing 0.05–50 ML of oxygen as a chemisorbed layer of O_{ads}, oxygen dissolved in a near-surface metal layer, PdO surface oxide, and oxygen dissolved in the bulk of palladium, and to determine the effect of oxygen atom diffusion in palladium on the desorption of O_2.

EXPERIMENTAL

The study was performed using a LEED-240 ultra-high-vacuum spectrometer (Varian) with an HCVA-850 AES analyzer (VG) and a Q-7 quadrupole mass spectrometer (VG). The measurement chamber of the spectrometer was evacuated with an ion pump to a residual gas pressure of $(1–2) \times 10^{-8}$ Pa. The spectrometer was additionally equipped with a catalytic chamber evacuated with a diffusion pump. This chamber allowed us to treat the samples over wide ranges of O_2 pressures (10^{-5}–10^3 Pa) and temperatures (300–1600 K). Polycrystalline palladium (Pd(poly)) foil of size $10 \times 5 \times 0.1$ mm was used as a sample. The sample temperature was measured with a W–Re thermocouple (W/Re 5%–W/Re 20%), which was welded to the outer surface of the sample. To remove carbon impurities from the sample, it was treated in O_2 at $P_{O_2} = 1$ Pa and $T = 500$–600 K followed by vacuum heating to 1300 K. The surface microstructure of the sample was analyzed by scanning electron microscopy (SEM). It

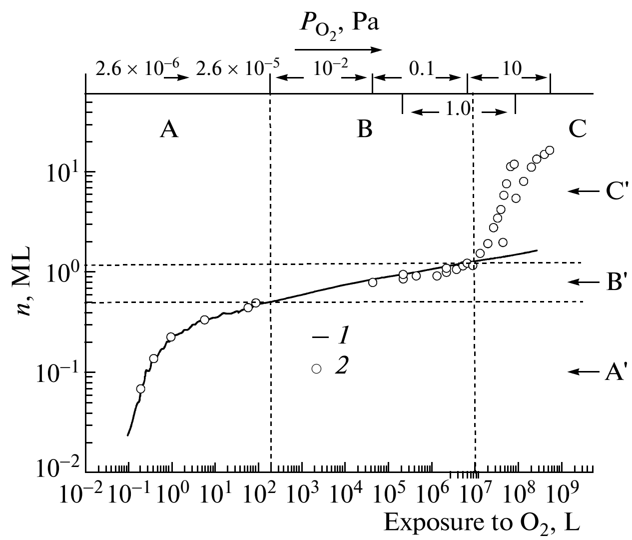

Fig. 1. Dependence of the number of oxygen monolayers (n) absorbed in Pd(poly) at (*1*) 500 and (*2*) 600 K on exposure in O_2. A–C are the ranges of P_{O_2} in which the corresponding exposures were obtained. A'–C' are the ranges of n in which various phases were formed in the Pd–O system (see the text for details).

was found that the sample surface consisted of crystallites of sizes from 10 to 100 μm; ~32, ~18, ~34, and ~15% of the crystallites had the (100), (111), (311), and (331) surface orientations, respectively [22].

The desorption of O_2 from Pd(poly) was studied by TPD. The TPD spectra were obtained at 500–1300 K and a sample heating rate of 10 K/s. The use of this rate allowed us to reliably detect the main features of the TPD spectra of O_2 obtained upon the release of up to ~50 ML of oxygen absorbed by palladium. The amount of absorbed oxygen was determined from the ratio of the area of a TPD spectrum obtained after the treatment of a sample at certain P_{O_2} and exposure to the area of a TPD spectrum obtained after the saturation of an adsorption layer of oxygen at $T = 500$ K and an exposure of 180 L (1 L = 10^{-6} Torr s) for the surface coverage θ of 0.5. Upon the surface saturation of (111), (100), and (110) palladium single crystals with chemisorbed oxygen, the $(\sqrt{3} \times \sqrt{3})$R30, $c(2 \times 2)$, and $c(2 \times 4)$ structures with oxygen coverages of 0.33, 0.5, and 0.5 ML, respectively, were formed [6, 9–16, 18, 19]. The Pd(poly) sample used in this work mainly included crystallites with (111) and (100) faces; therefore, we assumed that a saturated adsorption layer of oxygen on this sample at 500 K was formed at an exposure of 180 L in O_2 with θ = 0.5. The setup, sample preparation procedure, and experimental procedure were described in more detail elsewhere [22, 23].

RESULTS AND DISCUSSION

Interaction of Oxygen with Polycrystalline Palladium at $P_{O_2} = (2.6 \times 10^{-6})$–10 Pa

Previously [23], we studied the interaction of oxygen with Pd(poly) at T = 500–700 K and $P_{O_2} = (2.6 \times 10^{-6})$–10 Pa using TPD. We found that the interaction of O_2 with Pd(poly) depends on the pressure of O_2 and the temperature of the sample. At low P_{O_2} (≤1.3 × 10^{-5} Pa), O_2 was dissociatively chemisorbed on the surface of Pd(poly). The surface coverage with chemisorbed oxygen was θ = 0.5. At $P_{O_2} \geq 10^{-5}$ Pa and $T \leq 500$ K, the O_{ads} atoms inserted under a surface metal layer after the saturation of the layer of O_{ads} to θ ~ 0.5. The insertion of O_{ads} occurred because of a decrease in the bond energy D(Pd–O_{ads}) of chemisorbed oxygen atoms with the surface of palladium due to repulsive interactions between O_{ads} atoms. As a result, surface palladium oxide was gradually formed; in this case, to ~2 ML of oxygen was absorbed. The insertion of O_{ads} can occur by the formation of O_{ads}–Pd*–O_{abs} linear fragments, in which the inserted oxygen atom (O_{abs}) is strongly bound to both the surface Pd* atom and Pd atoms in the second layer of the metal [24]. At $P_{O_2} \geq 0.1$ Pa and $T > 500$ K, O_{ads} atoms inserted into the near-surface layer of palladium after the saturation of a surface oxide film (n ~ 2 ML). The inserted oxygen atoms gradually diffused deep into the bulk; as a result, ~50 ML of oxygen was absorbed at 700 K.

Figure 1 shows the dependence of the number of absorbed oxygen monolayers (n) in Pd(poly) on exposure in O_2 based on data obtained previously [23] for an exposure range from 10^{-1} to 10^9 L at O_2 pressures from 2.6 × 10^{-6} to 10 Pa and at temperatures of 500 and 600 K. Figure 1 demonstrates the effects of O_2 pressure and sample temperature on the absorption of oxygen by polycrystalline palladium. The top part of the figure shows the ranges of P_{O_2} in which the corresponding exposures in O_2 were obtained. Vertical dashed lines indicate the regions of P_{O_2} (A–C) in which various processes occurred. Horizontal dashed lines separate the regions of the amounts of oxygen absorbed by palladium (A'–C') in which various phase states of the Pd–O system were formed. Region A involved low O_2 pressures of ≤2.6 × 10^{-5} Pa, at which O_2 was dissociatively chemisorbed on the surface of palladium. In the course of chemisorption, a saturated adsorption layer was gradually formed with the coverage θ ~0.5 (region A') with chemisorbed oxygen. In region B, which included P_{O_2} from 10^{-5} to 0.1–1.0 Pa, at 500 and 600 K, O_{ads} oxygen atoms were inserted under the surface layer of palladium. In this case, the amount of absorbed oxygen increased from θ = 0.5 to n ~1.0 ML (region B'). At

$P_{O_2} \geq 0.1$–1.0 Pa (region C), the absorption of oxygen by palladium essentially depended on the temperature of the sample. At 500 K, surface PdO oxide was gradually formed. The amount of absorbed oxygen gradually increased to $n \sim 2.0$ ML. At 600 K, inserted oxygen atoms diffused deep under the surface layer of the metal and gradually accumulated in the bulk of palladium ($n > 1.0$ ML; region C'). Thus, at $P_{O_2} = 10$ Pa and $T = 600$ K, palladium absorbed ~20 ML of oxygen (Fig. 1). The insertion of O_{ads} occurred from the adsorbed layer $(O_2)_{ads}$. The steady-state surface coverage with $(O_2)_{ads}$ molecules was reached in the course of equilibration between $(O_2)_{gas}$ and $(O_2)_{ads}$, and it mainly depended on the value of P_{O_2}. Thus, an increase in P_{O_2} from 10^{-5} to 10 Pa resulted in a considerable increase in the coverage of $(O_2)_{ads}$, which accelerated the insertion of oxygen into the bulk of the metal and increased the amount of absorbed oxygen. An increase in the temperature (>500 K) accelerated the diffusion of oxygen atoms in palladium; because of this, inserted oxygen atoms penetrated deep under the surface layer of the metal and gradually accumulated in the bulk of palladium.

Desorption of Chemisorbed Oxygen from Pd(poly) at $\theta \leq 0.5$

The thermal desorption of O_2 from the chemisorbed layer of O_{ads} for Pd(poly) was studied in detail [22]. It was found that lateral repulsive interactions between the nearest O_{ads} atoms were responsible for the mechanism of O_2 desorption from Pd(poly). At low surface coverages with chemisorbed oxygen ($\theta \leq 0.25$), O_{ads} atoms are arranged far from each other. These atoms do not interact with one another and do not form ordered adsorption structures. As a result, the desorption of O_2 occurs from a disordered adsorption layer in accordance with second-order desorption with $E_{des} = 230$ kJ/mol. At $\theta \geq 0.25$, O_{ads} atoms began to occupy neighboring adsorption sites. Repulsive interactions between neighboring O_{ads} atoms resulted in a decrease in D(Pd–O_{ads}) from 364 to 324 kJ/mol. Because of this, the desorption of O_2 came into play at lower temperatures to cause O_2 TPD spectra broadening toward low temperatures. The TPD spectra of O_2 calculated at $\varepsilon_{aa} = 5$ kJ/mol and surface coverage $\theta = 0.1$–1.0 are consistent with those obtained after O_2 adsorption on Pd(poly) at 500 K and low values of P_{O_2} ($\leq 10^{-5}$ Pa). However, it is well known that the saturation of a chemisorbed layer with O_{ads} atoms at these pressures on various Pd samples occurred at $\theta \sim 0.5$ [6, 9–16, 18, 19]. Moreover, at $\theta \geq 0.5$, O_{ads} atoms were inserted into the near-surface layers of palladium [5, 8–11, 13–16, 18, 19]. It also follows from the dependence of E_{des} on θ that $\varepsilon_{aa} = 10$ kJ/mol [22].

In Fig. 1, it can be seen that, at $P_{O_2} \leq 2.6 \times 10^{-5}$ Pa (pressure region A), the amount of absorbed oxygen rapidly increased to 0.5 ML as the exposure in O_2 was increased to ~200 L (coverage region A'). Under these conditions, a chemisorbed layer of O_{ads} was formed on the surface of Pd(poly). To determine the lateral repulsive interactions between O_{ads} in the adsorption layer of oxygen on Pd(poly) and to study the effect of these interactions on the desorption of O_2 from palladium, we simulated the desorption of O_2 using various equations and compared calculated spectra with those obtained after the adsorption of O_2 on Pd(poly). Figure 2a shows the TPD spectra calculated from a second-order desorption equation at $E_{des} = 230$ kJ/mol, $k_0 = 0.2$ cm^2/s, and $\theta = 0.1$–0.9. Figure 2b shows the TPD spectra calculated from a desorption equation that took into account lateral repulsive interactions between the nearest adsorbed atoms [25]. The spectra were obtained at $\varepsilon_{aa} = 10$ kJ/mol and $\theta = 0.1$–0.9. Figure 2c shows the TPD spectra of O_2 obtained after the adsorption of O_2 on Pd(poly) at 500 K and O_2 exposures of 0.3–180 L (see the table for the conditions of adsorption). Vertical dashed lines indicate the temperatures of 700 and 825 K. In Fig. 2, it can be seen that, at $\theta \leq 0.3$, similar behaviors of the calculated spectra (Figs. 2a, 2b, spectra *1–3*) and the spectra obtained after the adsorption of O_2 on Pd(poly) (Fig. 2c, spectra *1–6*) were observed as θ was increased. In these spectra, an increase in the intensity of TD peaks and a shift in the T_{max} of these peaks to lower temperatures were observed as θ was increased. This behavior of TPD spectra is characteristic of the second-order desorption of O_2 from a disordered adsorption layer [5, 11–13, 16]. At $\theta = 0.3$–0.5, similar behaviors of the spectra calculated with consideration for repulsive interactions between O_{ads} atoms (Fig. 2b, spectra *3–5*) and the spectra obtained after the adsorption of O_2 (Fig. 2c, spectra *6–10*) were observed with increasing θ. In these spectra, the intensity of TD peaks changed insignificantly; however, a considerable broadening of these peaks toward low temperatures occurred in this case with increasing θ. In Fig. 2, it can be seen that these spectra are dramatically different from the spectra calculated by a second-order desorption equation (Fig. 2a, spectra *3–5*). This can be indicative of the effect of repulsive interactions between O_{ads} atoms with $\varepsilon_{aa} = 10$ kJ/mol on the desorption of O_2 from Pd(poly) at $\theta = 0.3$–0.5 because O_{ads} atoms gradually appeared at neighboring adsorption sites at the above values of θ. The repulsion between these O_{ads} atoms resulted in a decrease in D(Pd–O_{ads}) and, correspondingly, the desorption of O_2 at lower temperatures. At $\theta \geq 0.5$, considerable differences in the behaviors of spectra shown in Figs. 2a–2c were observed as θ was increased. Thus, the spectra calculated from the second-order desorption equation exhibited $T_{max} \sim 825$ K

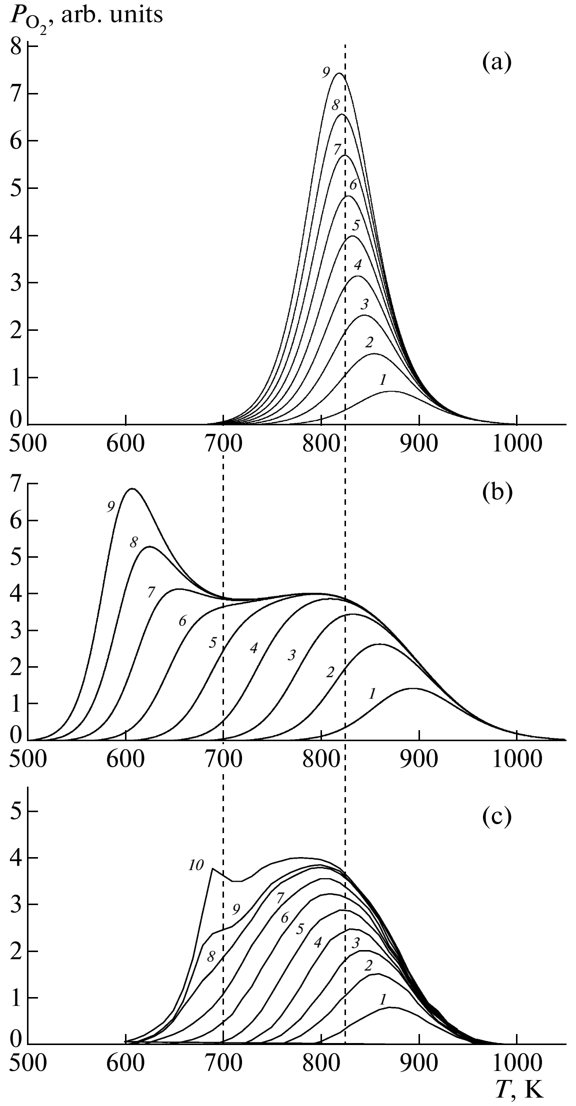

Fig. 2. TPD spectra of oxygen: (a) spectra calculated from a second-order desorption equation at E_{des} = 230 kJ/mol, (b) spectra calculated using a model with consideration for lateral repulsive interactions between O_{ads} atoms [25] at ε_{aa} = 10 kJ/mol, and (c) spectra obtained after the adsorption of O_2 on Pd(poly) at 500 K. (a, b) The oxygen coverage of the surface for spectra *1–9* varied from 0.1 to 0.9 ($\Delta\theta$ = 0.1). (c) See the table for adsorption conditions. Spectrum numbers are specified in the table.

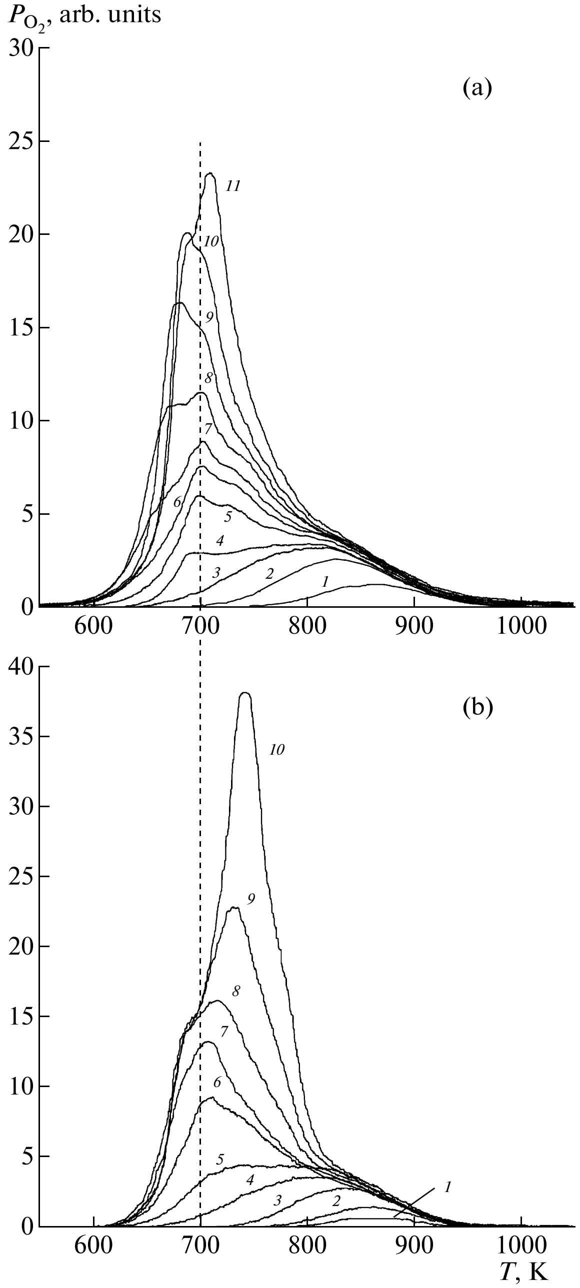

Fig. 3. TPD spectra of oxygen obtained after the treatment of Pd(poly) in O_2 at (a) 500 and (b) 600 K. See the table for adsorption conditions. Spectrum numbers are specified in the table.

(Fig. 2a, spectra *5–9*), whereas an individual low-temperature peak with $T_{max} \sim 600$ K appeared and increased in the spectra obtained with consideration for lateral interactions (Fig. 2b, spectra *5–9*). This peak was due to a considerable decrease in D(Pd–O_{ads}), which resulted from a considerable increase in the lateral environment of O_{ads} as a consequence of the adsorption of oxygen atoms at neighboring adsorption sites at $\theta \geq 0.5$. At $\theta \geq 0.5$, a gradual increase in the TD peak with $T_{max} \sim 700$ K was observed in the spectra obtained after the adsorption of O_2 on Pd(poly) (Fig. 2c, spectrum *10* and Fig. 3a, spectra *5–7*). This peak was due to the release of oxygen from a near-surface layer (see next section). Thus, we can conclude that, at $\theta \leq 0.3$ O_2 desorbed from Pd(poly) from a disordered adsorption layer in accordance with second order with E_{des} = 230 kJ/mol. At $0.3 \leq \theta \leq 0.5$, the desorption of O_2 was determined by lateral repulsive

Parameters of oxygen adsorption on Pd(poly)

Spectrum number*	P_{O_2}, Pa	Exposure time in O_2	Exposure to O_2, L**	Absorption of O atoms (n, ML)
Fig. 2c				
1	2.6×10^{-6}	10 s	0.2	0.06
2	2.6×10^{-6}	15 s	0.3	0.10
3	2.6×10^{-6}	20 s	0.4	0.15
4	2.6×10^{-6}	30 s	0.6	0.19
5	2.6×10^{-6}	60 s	1.2	0.23
6	2.6×10^{-5}	15 s	3.0	0.30
7	2.6×10^{-5}	1 min	12.0	0.35
8	2.6×10^{-5}	3 min	36.0	0.40
9	2.6×10^{-5}	6 min	72.0	0.43
10	2.6×10^{-5}	15 min	180.0	0.50
Fig. 3a				
1	2.6×10^{-6}	15 s	0.3	0.12
2	2.6×10^{-6}	40 s	0.8	0.25
3	2.6×10^{-5}	1 min	12.0	0.39
4	2.6×10^{-5}	15 min	180.0	0.5
5	10^{-2}	1 min	4.5×10^{3}	0.71
6	10^{-1}	1 min	4.5×10^{4}	0.87
7	1	1 min	4.5×10^{5}	1.01
8	10	1 min	4.5×10^{6}	1.24
9	10	5 min	2.25×10^{7}	1.38
10	10	15 min	6.75×10^{7}	1.48
11	10	60 min	2.70×10^{8}	1.67
Fig. 3b				
1	2.6×10^{-6}	10 s	0.2	0.05
2	2.6×10^{-6}	15 s	0.3	0.11
3	2.6×10^{-6}	30 s	0.6	0.2
4	2.6×10^{-5}	30 s	6.0	0.34
5	2.6×10^{-5}	15 min	180.0	0.5
6	10^{-1}	15 min	6.75×10^{5}	0.71
7	1	15 min	6.75×10^{6}	0.9
8	5	15 min	3.37×10^{7}	1.13
9	6	15 min	4.05×10^{7}	1.42
10	7	15 min	4.73×10^{7}	1.92

* The TPD spectra are shown in Figs. 2c, 3a, and 3b.
** L = Langmuir.

interactions between the nearest O_{ads} atoms (ε_{aa} = 10 kJ/mol). At $\theta \geq 0.5$ O_2 desorbed from Pd(poly) as a low-temperature TD peak with T_{max} ~ 700 K. This peak was due to the release of oxygen from a near-surface layer of palladium.

Desorption of O_2 Localized in a Near-Surface Layer of Palladium at $0.5 \leq n \leq 1.0$

In Fig. 1, it can be seen that the amount of absorbed oxygen gradually increased from $\theta = 0.5$ to n ~1.0 ML (region B') at 500 and 600 K and O_2 pressures from 10^{-5} to 10^{-1}–1.0 Pa (pressure region B) as the exposure in O_2 was increased from 200 to 10^7 L. Under these conditions, after the saturation of the adsorption layer of O_{ads} at $\theta = 0.5$, the O_{ads} atoms are inserted under the surface layer; as a result, oxygen is gradually accumulated in the near-surface layer of palladium. Previously [5, 8–11, 13–16, 18, 19], it was found that O_{ads} atoms can be inserted under the surface layer of palladium at $\theta \geq 0.5$. Figure 3a shows the TPD spectra of oxygen obtained after the adsorption of O_2 on Pd(poly) at 500 K, $P_{O_2} = 2.7 \times 10^{-6}$–10 Pa, and exposures of 0.3–2.7 × 10^8 L in O_2. Spectra *1–4* were obtained after adsorption at low P_{O_2} ($\leq 2.6 \times 10^{-5}$ Pa) and exposures of 0.3–180 L in O_2. These spectra are related to the desorption of O_2 from a chemisorbed O_{ads} layer. TPD spectrum *4* was obtained after surface saturation with O_{ads} atoms at an exposure of 180 L; it corresponds to $\theta = 0.5$. This spectrum was used to determine the amount of absorbed oxygen in Pd(poly) [23]. Spectra *5–7* were obtained after O_2 adsorption at $P_{O_2} = 10^{-2}$, 10^{-1}, and 1.0 Pa. For these spectra, the amounts of absorbed oxygen were 0.71, 0.87, and 1.01 ML, respectively. It can be seen that, as n was increased from 0.5 to 1.01 ML, the low-temperature peak at T ~ 700 K in TPD spectra increased (Fig. 3a, spectra *4–7*). The T_{max} of this peak remained almost unchanged with n; this suggests the first-order desorption of O_2. This peak was due to the release of oxygen from the near-surface layer of palladium because it is well known that, at $\theta \geq 0.5$, chemisorbed oxygen was inserted under a surface metal layer on Pd(111), Pd(100), and Pd(110) [5, 8–11, 13–16, 18, 19]. A TD peak at T ~ 700 K due to the first-order desorption of O_2 from Pd(poly) and Pd(111) was also observed [5, 8]. It was hypothesized that this peak resulted from the release of inserted oxygen.

On heating the sample, oxygen atoms inserted into near-surface palladium layers can diffuse to the surface. For the diffusion of oxygen atoms in a palladium lattice by the interstitial mechanism, E_{dif} was estimated at 150–200 kJ/mol [23]. Therefore, at $T \geq 600$ K, the diffusion of oxygen atoms in palladium is significant. Diffusing oxygen atoms can arrive at the surface, penetrate through a surface metal layer, and undergo chemisorption on the surface. Thereafter, they can undergo associative desorption. The mechanism of the penetration of inserted O atoms through a surface metal layer to the surface can be similar to the mechanism of the interstitial of chemisorbed O_{ads} atoms under the surface metal layer. Todorova et al. [24] used density functional theory (DFT) calculations to demonstrate that O_{ads} atoms can penetrate into a near-surface layer of palladium by the insertion mechanism after the saturation of the adsorption layer of O_{ads} on Pd(111) at θ ~ 0.5. At θ ~ 0.5, the values of E_b for O_{ads} and O atoms in tetrahedral cavities between the first and second metal layers became similar because of a decrease in E_b for Pd–O_{ads}. The decrease in E_b was due to lateral repulsive interactions between O_{ads}. As a result of this, at $\theta > 0.5$, the insertion of O atoms under the surface layer became predominant, as compared with the subsequent chemisorption of oxygen on the surface. In the course of O_{ads} insertion, a stable linear O_{ads}–Pd*–O_{abs} structure was formed, where O_{ads} is the O atom chemisorbed on the surface; Pd* is the surface atom of palladium; and O_{abs} is the oxygen atom in a tetrahedral cavity between the first and second metal layers, which is bound to both the Pd* atom and Pd atoms from the second layer. The formation of these structures considerably decreased an energy barrier for the insertion of O_{ads} atoms into a near-surface layer of palladium. Under certain conditions, O_{abs} atoms can diffuse into deeper metal layers.

Upon the absorption of oxygen in an amount of $0.5 \leq n \leq 1.0$ in Pd(poly) at 500 K, the surface of palladium was covered with a saturated chemisorption layer of O_{ads} with $\theta = 0.5$. The other oxygen atoms were inserted into the near-surface layer of the metal. On heating the sample, O_{abs} atoms distributed in the near-surface layer of palladium diffused to the surface. At $T \geq 600$ K, they arrived at the surface layer, and the O_{ads}–Pd*–O_{abs} structure can be formed in the course of the diffusion of O atoms. The formation of this structure suggests that O_{abs} atoms penetrated through the surface metal layer to the surface and underwent chemisorption. These structures can undergo decomposition along with formation. Upon decomposition, O_{abs} atoms left the O_{ads}–Pd*–O_{abs} fragments and diffused back to the near-surface metal region. The O_{ads} atoms remained on the surface. The O_{ads}–Pd*–O_{abs} structures can decompose because the number of vacant interstitial sites through which oxygen atoms can diffuse was sufficient at the given concentrations of inserted oxygen in the near-surface layers. Consequently, the surface coverage with O_{ads} atoms increases as a result of the formation–decomposition of the O_{ads}–Pd*–O_{abs} structures. At $T \geq 650$ K, the rates of O_{abs} diffusion and the formation–decomposition of the O_{ads}–Pd*–O_{abs} fragments increased considerably to result in a considerable increase in θ. At $\theta > 0.5$, O_{ads}

atoms began to occupy neighboring adsorption sites; because of this, the lateral interactions of O_{ads} with other adsorbed oxygen atoms increased considerably. As a consequence, $D(Pd-O_{ads})$ decreased considerably because of repulsive interactions between O_{ads} atoms. The decrease in $D(Pd-O_{ads})$ resulted in an increase in the rate of O_2 desorption, which led to the appearance of a low-temperature TD peak at $T \sim 700$ K (Fig. 3a, spectra *4–7*). Figure 2b shows the TPD spectra calculated with consideration for repulsive interactions between O_{ads} atoms. It can be seen that O_2 began to desorb at lower temperatures (<700 K) at $\theta > 0.5$ because of repulsions between O_{ads} atoms. Thus, an increase in the coverage of O_{ads} because of the migration of O_{abs} atoms from the near-surface layer to the surface at 650–700 K leads to a considerable increase in the rate of O_2 desorption and the appearance of a low-temperature TD peak at $T \sim 700$ K (Fig. 3a, spectra *4–7*). The T_{max} of this peak remained unchanged as the concentration of inserted oxygen was increased; this suggests the first order of O_2 desorption. We believe that, in the course of the release of inserted oxygen, the step of the formation–decomposition of the $O_{ads}-Pd^*-O_{abs}$ structure is a crucial step. The desorption of O_2 from the chemisorption layer of O_{ads} at $\theta \geq 0.5$ occurred much more rapidly. Because of this, the first-order desorption of O_2 was observed in the release of inserted oxygen.

Desorption of O_2 from Pd(poly) in the Decomposition of Surface Palladium Oxide at $1.0 \leq n \leq 2.0$

In Fig. 1, it can be seen that the amount of absorbed oxygen in Pd(poly) gradually increased from ~1.0 to ~2.0 ML (region C') at 500 K, O_2 pressures of ≥0.1–1.0 Pa (pressure region C), and exposures of $>10^7$ L in O_2. Under these conditions, along with the insertion of O_{ads} atoms under the surface layer of palladium, the formation of reconstructive oxide-like structures can occur. Previously [13–16], it was found that, in the course of the reaction of O_2 with Pd(100) at $\theta \sim 0.8$, the $(\sqrt{5} \times \sqrt{5})R27$ reconstructive structure, which is close to the structure of the PdO(001) face, was formed. This reconstructive structure can be considered as a surface oxide. Figure 3a shows the TPD spectra of O_2 obtained after the adsorption of O_2 on Pd(poly) at 500 K and $P_{O_2} \geq 1.0$ Pa (spectra *7–11*). Spectrum *7* was obtained after the adsorption of O_2 at $P_{O_2} = 1.0$ Pa, and spectra *8–11*, after adsorption at $P_{O_2} = 10.0$ Pa. In these spectra, the amounts of absorbed oxygen were 1.01, 1.24, 1.38, 1.48, and 1.67 ML, respectively. It can be seen that, as n was increased from 1.01 to 1.67 ML, a low-temperature peak with $T_{max} \sim 675$ K appeared in the TPD spectra (Fig. 3a, spectra *7–11*). In these spectra, the ascending branches were similar; this suggests the zero order of O_2 desorption. The coincidence of ascending branches in the TPD spectra of O_2 from Pd(poly) and Pd(111) at the amounts of inserted oxygen of >0.25 ML was also observed [5, 8, 9]. Previously [26], we studied the thermal decomposition of thin oxide films on Rh(100) and Rh(poly) and found the coincidence of the ascending branches of O_2 TD peaks at $n = 2–10$ ML. We assumed that the desorption of O_2 occurred at the constant coverage of a surface oxide layer with oxygen because of the rapid exchange of oxygen atoms between oxide layers. The TPD spectra of O_2 calculated using this model were consistent with experimental spectra.

The coincidence of the ascending branches of the TD peaks of O_2 from Pd(poly) in spectra *7–11* in Fig. 3a can be due to the desorption of O_2 from the surface at constant coverage with oxygen. It is likely that the constant coverage of the palladium surface with oxygen can be due to the rapid diffusion of O_{abs} atoms from near-surface metal layers to the surface. At the amount of absorbed oxygen $1.0 \leq n \leq 2.0$, the desorption of O_2 from Pd(poly) was analyzed with consideration for the decomposition–reduction of $O_{ads}-Pd^*-O_{abs}$ structures. Upon oxygen absorption by palladium at $n \sim 1.0$ ML and 500 K, the surface of palladium was coated with a saturated chemisorption layer of O_{ads} with $\theta = 0.5$. The other oxygen atoms were inserted under the surface metal layer. As oxygen was absorbed at $n > 1.0$ ML, O_{abs} atoms occupied free interstitial sites in the near-surface metal region. However, oxygen atoms did not penetrate deep into the bulk because E_{dif} is ~150–200 kJ/mol for oxygen in palladium [23]; consequently, the diffusion of oxygen atoms at 500 K is considerably restricted. Because of this, at 500 K, the inserted atoms of oxygen will be concentrated in the near-surface layers of the metal at the surface. An increase in the concentration of O_{abs} atoms under the surface layer considerably increased the stability of the resulting $O_{ads}-Pd^*-O_{abs}$ linear structures. The stability of these structures increased because of both a decreased ability of O_{abs} atoms to diffusion at 500 K and a decrease in the concentration of free interstitial sites in near-surface layers, which are required for the diffusion of oxygen atoms. Thus, at 500 K and $n > 1.0$ ML, O_{ads} atoms as the constituents of the $O_{ads}-Pd^*-O_{abs}$ structures gradually accumulated at the surface. Correspondingly, the surface coverage with O_{ads} gradually increased (>0.5 ML). It is believed that, at 500 K, a surface oxide film was gradually formed in the course of oxygen absorption by polycrystalline palladium at $n > 1.0$ ML. For example, in the course of the surface reconstruction of Pd(100) under the action of O_2, the resulting $(\sqrt{5} \times \sqrt{5})R27$ reconstructive structure was close to the structure of the PdO(001) face; in this case, the surface coverage with oxygen was 0.8 ML [13–16]. At a surface coverage of $O_{ads} > 0.5$ ML, the binding energy of these atoms with the surface considerably decreased as a result of repulsive interactions between O_{ads}. Therefore, at $n > 1.0$ ML, the desorption of O_2 came into play in the course of sample heating at $T \geq 600$ K; this desorption resulted from the decomposition of the O_{ads}–Pd*–O_{abs} structures. However, at the specified temperatures, these structures rapidly recovered by the rapid exchange of oxygen atoms between metal layers. As a result, the desorption of O_2 in the course of surface oxide decomposition occurred at the surface permanently occupied by O_{ads} atoms, that is, in accordance with zero order. This resulted in the coincidence of ascending branches in the TPD spectra of O_2 at n ~1.0–2.0 ML (Fig. 3a, spectra *7–11*).

In the course of O_2 desorption, the amount of absorbed oxygen gradually decreased. In Fig. 3a (spectra *7–11*), it can be seen that, in the course of O_2 desorption, a peak appeared at $T \sim 700$ K after a TD peak with $T_{max} \sim 675$ K. The T_{max} of this peak coincided with the T_{max} of a peak observed on the release of oxygen from the near-surface layers of palladium at low concentrations of inserted oxygen (Fig. 3a, spectra *5–7*). In the course of O_2 desorption, the value of n gradually decreased and the concentration of O_{abs} in the near-surface layers of palladium considerably decreased at $n \sim 1.0$ ML. As a consequence, the stability of the O_{ads}–Pd*–O_{abs} structures decreased, and they began to decompose. The O_{abs} atoms left these structures and diffused to the near-surface layers of the metal through unoccupied interstitial sites. In this case, O_{ads} atoms remained in the chemisorption layer. Because of the decomposition of these structures, the surface coverage with O_{ads} atoms that are the constituents of the O_{ads}–Pd*–O_{abs} structures considerably decreased, whereas the coverage with O_{ads} atoms bound to only the surface atoms of Pd increased. Thus, in the course of desorption at $n \leq 1.0$ ML, O_2 desorbed from the chemisorbed layer of O_{ads}, whose coverage was ≥0.5 ML because of the formation–decomposition of the O_{ads}–Pd*–O_{abs} structures. At $\theta \geq 0.5$, E_b for Pd–O_{ads} considerably decreased because of repulsions between O_{ads} atoms. As a result of this, the rate of O_2 desorption increased and a TD peak at $T \sim 700$ K appeared in the TPD spectra (Fig. 3a, spectra *8–11*).

Desorption of O_2 from the Bulk of Palladium at $1 \leq n \leq 50$

In Fig. 1, it can be seen that the amount of oxygen absorbed by palladium at $P_{O_2} \geq 0.1$–1.0 Pa (pressure region C) and exposures of $>10^7$ L in O_2 at 600 K considerably increased, as compared with that obtained at 500 K. Thus, at $P_{O_2} = 10$ Pa, ~20 ML of oxygen was absorbed at 600 K for 120 min, whereas only ~1.5 ML was absorbed at 500 K. Based on an analysis of the time dependence of the amount of absorbed oxygen obtained at 600 K and $P_{O_2} = 10^{-1}$, 1.0, and 10 Pa, we hypothesized that, under these conditions, oxygen atoms diffused deep into the metal lattice under the surface layer and gradually accumulated in the bulk of palladium [23].

Figure 3b shows the TPD spectra of O_2 adsorbed on Pd(poly) at 600 K and various pressures of O_2. Spectra *1–5* were obtained after O_2 adsorption at low P_{O_2} ($\leq 2.6 \times 10^{-5}$ Pa). They are related to the desorption of O_2 from a chemisorbed layer at $\theta \leq 0.5$. Spectra *6–10* were obtained after adsorption at $P_{O_2} = 10^{-1}$, 1, 5, 6, and 7 Pa, respectively. For these spectra, the amounts of absorbed oxygen were 0.71, 0.90, 1.13, 1.42, and 1.92 ML, respectively. In spectra *6–8*, peaks with $T_{max} \sim 710$ K were due to O_2 desorption in the course of oxygen release from the near-surface layer of palladium because O_{ads} atoms inserted under the surface layer of palladium at $\theta \geq 0.5$ (see the previous section). In spectra *7–10*, low-temperature branches coincided at $T \leq 700$ K. They were related to the desorption of O_2 in the course of the decomposition of surface palladium oxide because a film of surface palladium oxide was formed at $n \geq 1.0$ ML (see the previous section). In Fig. 3, it can be seen that, at $n \leq 1.0$ ML, the TPD spectra of O_2 obtained after the adsorption of O_2 at 600 K (Fig. 3b, spectra *1–8*) and 500 K (Fig. 3a, spectra *1–8*) are close to each other. This suggests a weak effect of temperature over the range of 500–600 K on the processes of O_2 chemisorption, O_{ads} insertion under the surface metal layer, and surface oxide formation. However, at $n \geq 1.0$ ML, the TPD spectra of O_2 obtained after adsorption at 500 and 600 K essentially differ from each other. Thus, after adsorption at 500 K and $n \geq 1.0$ ML, an increase in both of the low-temperature peaks with $T_{max} \sim 675$ and 700 K was observed in the TPD spectra (Fig. 3a, spectra *8–11*), whereas an increase in the new high-temperature peak with $T_{max} \geq 750$ K was observed in the TPD spectra obtained after adsorption at 600 K (Fig. 3b, spectra *8–10*). This considerable difference in the TPD spectra of O_2 obtained after the adsorption of O_2 at 500 and 600 K at $n \geq 1.0$ ML can be due to the acceleration of the diffusion of oxygen atoms in the lattice of palladium as the sample temperature was increased. Because E_{dif} is 150–200 kJ/mol for oxygen atoms in palladium [23], the diffusion of oxygen atoms in palladium can be considerable at 600 K. In the course of the interaction of O_2 with Pd(poly), an acceleration of the diffusion of oxygen atoms can cause an increase in the penetration depth of O atoms in the bulk of the metal. Thus, at 500 K, oxygen atoms were inserted only under the surface layer of palladium, in which they were mainly accumulated. In this case, reconstructive oxide-like structures (surface oxide) can be formed. On heating, because of the release of inserted oxygen and the decomposition of a surface oxide, O_2 is desorbed at a low temperature (TD peaks with $T_{max} \sim 675$ and 700 K; Fig. 3a, spectra *5–11*). At 600 K, oxygen atoms can penetrate

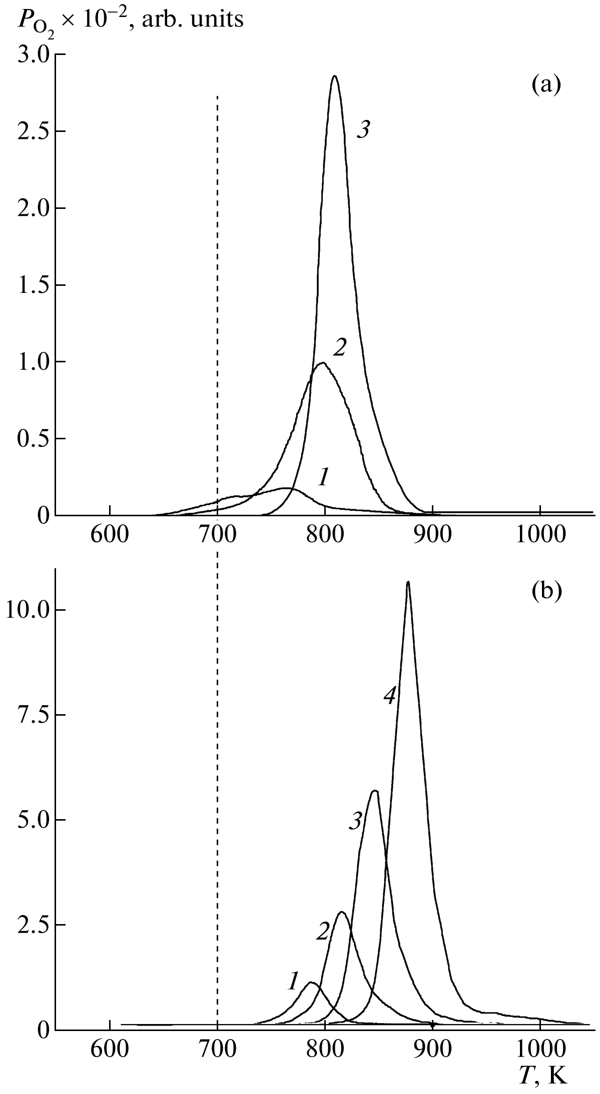

Fig. 4. TPD spectra of oxygen obtained after the treatment of Pd(poly) in O_2 for 2 h: (a) at 600 K, P_{O_2} = (*1*) 10^{-1}, (*2*) 1.0, and (*3*) 10 Pa and n = (*1*) 1.7, (*2*) 7.69, and (*3*) 16.65 ML; (b) at P_{O_2} = 10 Pa and T = (*1*) 550, (*2*) 600, (*3*) 650, and (*4*) 700 K and n = (*1*) 8.26, (*2*) 15.76, (*3*) 31.04, and (*4*) 50.91 ML.

into deeper metal layers and gradually accumulate in the bulk. On heating, in the course of their diffusion to the surface, the desorption of O_2 occurred in the form of a high-temperature TD peak with $T_{max} \geq 750$ K (Fig. 3b, spectra *8–10*). Figure 4a shows the TPD spectra of O_2 obtained after the adsorption of O_2 on palladium at 600 K and $P_{O_2} = 10^{-1}$, 1.0, and 10 Pa for 120 min. For these spectra, the amounts of absorbed oxygen were 1.17, 7.69, and 16.65 ML, respectively. It can be seen that, as n was increased from 1.17 to 16.65 ML, the TD peak intensity considerably increased and the T_{max} of the peak shifted toward higher temperatures. Thus, for spectra *1–3* in Fig. 4a, T_{max} = 760, 800, and 810 K, respectively. Figure 4b shows the TPD spectra of O_2 obtained after the adsorption of O_2 on Pd(poly) at 10 Pa for 120 min at temperatures of 550, 600, 650, and 700 K. For these spectra, the amounts of absorbed oxygen were 8.26, 15.76, 31.04, and 50.91 ML, respectively. In Fig. 4b, it can be seen that, as n was increased from 8.26 to 50.91 ML, the TD peak intensities increased considerably and the T_{max} of peaks gradually shifted toward higher temperatures. Thus, T_{max} = 790, 820, 850, and 880 K for spectra *1–4* in Fig. 4b, respectively. Thus, at $T > 500$ K and $P_{O_2} \geq$ 0.1–1.0 Pa, oxygen atoms inserted into the metal lattice and diffused deep into the bulk of palladium in the course of the interaction of O_2 with Pd(poly). On heating the sample in the course of thermal desorption, oxygen atoms diffused to the surface, penetrated through a surface metal layer, and underwent chemisorption on the surface and associative desorption in the form of a high-temperature TD peak with $T_{max} >$ 750 K.

CONCLUSIONS

An analysis of the TPD spectra of O_2 from polycrystalline palladium, which were obtained as the amount of oxygen absorbed by palladium was increased from 0.05 to 50 ML, allowed us to better understand the desorption of O_2 both from a chemisorbed layer of O_{ads} and in the release of oxygen from near-surface layers in the course of surface oxide decomposition and in the release of oxygen from the bulk of the metal.

At low P_{O_2} ($\leq 1.3 \times 10^{-5}$ Pa) and temperatures (500–600 K), a saturated chemisorption layer with $\theta \sim$ 0.5 was formed on the surface of Pd(poly). At low coverages with O_{ads} ($\theta \leq 0.3$), a gradual shift of the T_{max} of peaks toward lower temperatures (approximately from 900 to 800 K) was observed in the TPD spectra of O_2 as θ was increased. This suggests the second-order desorption of O_2 from a disordered adsorption layer of O_{ads} atoms with E_{des} = 230 kJ/mol. At $0.3 \leq \theta \leq 0.5$, a considerable broadening of the TD peak toward lower temperatures to ~700 K was observed with increasing θ. This suggests a decrease in E_b for Pd–O_{ads} because of repulsive interactions between O_{ads} atoms with ε_{aa} = 10 kJ/mol.

At the pressures $P_{O_2} = 10^{-5}$–(0.1–1.0) Pa and T = 500–600 K after the saturation of a chemisorbed oxygen layer with $\theta \sim 0.5$ on the surface of Pd(poly) as a result of a decrease in E_b for Pd–O_{ads}, the O_{ads} oxygen atoms inserted under the near-surface layer of palladium. The insertion of O_{ads} was accompanied by the formation of O_{ads}–Pd*–O_{abs} structures, in which the inserted oxygen atom O_{abs} was strongly bound to both the surface Pd* atom and Pd atoms in the second layer of the metal [24]. At the specified values of P_{O_2} and temperatures, to ~0.5 ML of oxygen was gradually accumulated in the near-surface layer of palladium. At these concentrations of O_{abs}, a low-temperature TD peak at $T \sim 700$ K appeared and increased in the TPD spectra of O_2 from Pd(poly). The T_{max} of this peak did not shift with increasing n; this fact suggests the first order of O_2 desorption. This peak was related to the desorption of O_2 in the course of the release of inserted oxygen from the near-surface layer of palladium. On heating the sample, the O_{abs} atoms migrated to the surface, penetrated through a surface layer, and underwent chemisorption on the surface. The penetration of O_{abs} atoms to the surface occurred through the formation of O_{ads}–Pd*–O_{abs} fragments. These fragments can decompose in the course of the removal and diffusion of O_{abs} atoms back to the near-surface metal layer. As the sample was heated (600–700 K), the diffusion of O_{abs} atoms to the surface accelerated and the rate of formation–decomposition of the O_{ads}–Pd*–O_{abs} fragments increased. As a result of these processes, the surface coverage with O_{ads} atoms increased. At $\theta \geq 0.5$, repulsive interactions between them appeared to result in the low-temperature desorption of O_2 and the appearance of a TD peak at $T \sim 700$ K. In the course of the release of inserted oxygen, the formation–decomposition of the O_{ads}–Pd*–O_{abs} structures was a rate-determining step. The desorption of O_2 from the chemisorption layer of O_{ads} at $\theta \geq 0.5$ and $T \sim 700$ K occurred much more rapidly. Because of this, the first-order desorption of O_2 was observed on the release of inserted oxygen; that is, the T_{max} of the TD peak of O_2 did not change with the concentration of inserted oxygen.

At $P_{O_2} \geq 0.1$–1.0 Pa and $T = 500$ K, the concentration of oxygen inserted into the near-surface layer of Pd(poly) gradually increased ($n \geq 1.0$ ML). At $n \geq 1.0$ ML, O_{abs} atoms were mainly concentrated under the surface metal layer. Because of this, stable O_{ads}–Pd*–O_{abs} fragments were formed, which gradually formed a surface oxide layer of PdO, and a low-temperature TD peak at $T \sim 675$ K appeared and increased in the TPD spectra of O_2. This peak was due to the desorption of O_2 in the course of the decomposition of the surface oxide PdO. In the TPD spectra of O_2, ascending branches were similar; this suggests the zero order of O_2 desorption on the decomposition of the surface oxide. On heating the sample in the course of the decomposition of O_{ads}–Pd*–O_{abs} structures, the desorption of O_2 occurred at low temperatures (600–675 K) because of repulsive interactions between O_{ads} atoms. The O_{ads} atoms distributed in the near-surface region of the metal rapidly migrated to the surface and reconstructed the O_{ads}–Pd*–O_{abs} structures. As a result of the rapid reconstruction, O_2 was desorbed at a constant surface coverage with oxygen. Consequently, the coincidence of the ascending branches of TPD spectra was observed; that is, the zero-order desorption of O_2 occurred on surface oxide decomposition.

At $P_{O_2} \geq 0.1$–1.0 Pa and elevated temperatures (>500 K), the absorption of oxygen in polycrystalline palladium was strongly accelerated. Thus, at 700 K and $P_{O_2} = 10$ Pa, ~50 ML of oxygen was absorbed for 120 min. Oxygen atoms inserted into the lattice of palladium and diffused deep into the bulk. An increase in P_{O_2} (≥0.1–1.0 Pa) caused in increase in the steady-state coverage of the palladium surface with O_{ads} atoms, which inserted into the near-surface metal layer and diffused to the bulk. An increase in the sample temperature (>500 K) accelerated the diffusion of oxygen atoms in the palladium lattice and, correspondingly, led to a deeper penetration of O atoms into the bulk. As a consequence, a considerable amount of oxygen was accumulated in the metal lattice. On heating the sample in the course of thermal desorption, oxygen atoms diffused from the bulk to the surface, penetrated through the surface layer of the metal, and underwent chemisorption on the surface and associative desorption. Because of diffusion from deep metal layers, O atoms penetrated onto the surface at elevated temperatures (≥700 K). Therefore, on the release of oxygen from the bulk of palladium, the desorption of O_2 occurred at high temperatures ($T_{max} \geq 750$ K).

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