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TDS AND XPS STUDY OF OXYGEN DIFFUSION INTO SUBSURFACE LAYERS OF Pd(110)

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Abstract

The interaction of O_2 with Pd(110) has been studied by TDS and XPS at T = 400 K and at pressures P_{O_2} from 2.6×10^{-6} to 10 Pa. At low exposures in O_2 ($\varepsilon \leq 1$–5 L), an adsorption layer with θ of *ca.* 0.5 and with the O1s peak at BE = 529.3 eV has been found to form on the surface. When ε grows from 5 to 10^8 L, the position and intensity of the oxygen O1s peak remain practically constant. At the same time, as much as 5 mL of oxygen is absorbed according to the TDS data. The results obtained by TDS and XPS indicate that oxygen penetrates deep into the subsurface layers of palladium (≥ 15–20 Å) and is distributed in its bulk in a low concentration.

Keywords: Oxygen, palladium, diffusion

INTRODUCTION

Palladium is one of the main components of catalysts for automobile exhaust neutralizers [1], deep oxidation of methane in gas turbines [2], and other important processes. Such a wide range of applications of Pd is based on its high activity both in the deep oxidation of hydrocarbons, CO, or H_2, and in the reduction of NO. An increased attention to the interaction of O_2 with palladium is related to the fact that various Pd-O phases formed in this interaction have a significant effect on catalytic oxidation reactions that proceed on Pd [2]. With the use of low energy electron diffraction (LEED) [3, 4], thermal desorption (TDS) [5-7], work function ($\Delta \varphi$) measurements [5, 7], and X-ray photoelectron

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spectroscopy (XPS) [7], it has been found that at low exposures ($\varepsilon \leq 1$–5 L), the interaction of O_2 with Pd(110) results in the formation of a surface reconstructive structure c(2×4) with 0.5 mL surface coverage (θ) with oxygen (1 mL = 9.4x10^{14} atoms·cm^{-2}). At higher exposures ($\varepsilon \geq 1$–5 L), oxygen has been found to penetrate into subsurface palladium layers. For example, about 1.8 mL of oxygen is absorbed by Pd(110) at $\varepsilon = 7228$ L and T = 475 K [5]. A further increase in the exposure to O_2 ($\varepsilon \geq 10^6$–10^7 L) leads to a shift of the Pd3d$_{5/2}$ peak from 335.2 to 336.3 eV, which indicates the formation of PdO [7]. The penetration of oxygen into subsurface layers of palladium and the formation of bulk PdO phase have a significant effect on catalytic oxidation reactions on Pd [2, 8]. For instance, during the oxidation of CO by O_2 on Pd(110) at $P_{O2} \geq 10^{-1}$ Pa and T of *ca.* 400 K, the oxygen diffusion into subsurface palladium layers leads to self-oscillations of the CO oxidation rate [8]. For the catalytic oxidation of methane over supported palladium catalysts, the formation and reduction of PdO determine the activity of the catalyst [2]. Therefore, to determine the effect of dissolved, or "subsurface" oxygen on catalytic reactions, it is necessary to investigate in detail the oxygen diffusion into palladium. The goal of this study was to investigate the oxygen diffusion into subsurface layers of Pd(110) and oxygen distribution in the metal by means of TDS and XPS in a wide range of O_2 pressures (2.6x10^{-6}–10 Pa) at T = 400 K.

EXPERIMENTAL

The experiments were carried out using ultra high vacuum spectrometers LEED-240 (Varian) and ESCALAB-HP (VG) with residual gas pressure of *ca.* 10^{-8} Pa. A Pd(110) single crystal with dimensions 10×7×1 mm was used in all the experiments. The surface of the palladium sample was cleaned from carbon impurities by bombardment with Ar$^+$ ions and annealing in oxygen. XPS, LEED and TDS methods were used in this study. The X-ray diffraction analysis indicated that the deviation of the sample plane from the (110) plane was about 1 degree. The XPS was used to control the sample surface cleanliness from contaminations and to determine the chemical state of adsorbed oxygen on the Pd(110) surface. The XPS spectra were obtained using primary X-ray irradiation AlKα (hν = 1486.6 eV). The spectrometer was calibrated against reference lines Au4f$_{7/2}$ (BE = 84.0 eV) and Cu2p$_{3/2}$ (BE = 932.7 eV). The position of the Pd3d$_{5/2}$ peak in bulk palladium was at BE = 335.2 eV. The XPS spectra were recorded with the analyzer located at 55° with respect to the sample surface. This angle provided an analysis depth of about 15–20 Å. LEED was used to control the structure of the sample surface. The total amount of absorbed oxygen in monolayers (mL) was determined using TDS.

RESULTS AND DISCUSSION

The interaction of O_2 with Pd(110) was studied by TDS and XPS at T = 400 K and at pressures $P_{O2} = 2.6 \times 10^{-6}$–10 Pa. Figure 1 presents TD spectra of
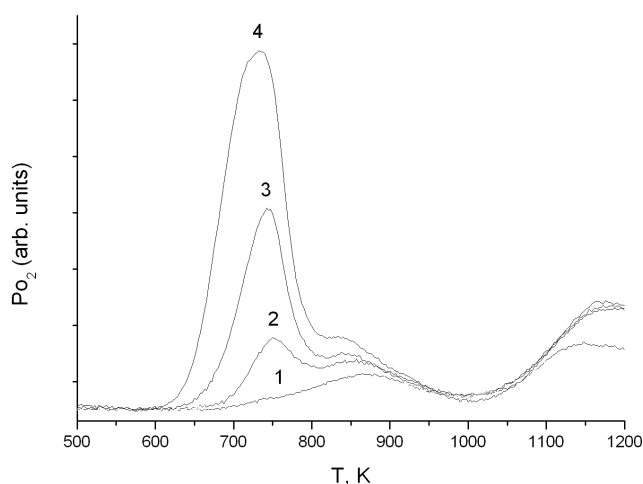

Fig. 1. TD spectra of O_2 from Pd(110) after various exposures at 400 K: 1 – 3, 2 – 60, 3 – 6×10^3, and 4 – 6×10^4 L. Heating rate = 5 K s^{-1}

O_2 obtained after various oxygen exposures at 400 K. There are three main peaks around 1150, 850 and 750 K, which can be attributed to the diffusion of dissolved oxygen from the bulk of the metal, to the decomposition of the c(2×4) structure, and to the desorption of oxygen located within the subsurface palladium layers, respectively [5-7, 9]. The dependence of the total amount of absorbed oxygen in monolayers (mL) over Pd(110) on exposure to O_2 at 400 K is shown in Fig. 2, curve 1. The data were obtained in the O_2 exposure range 0.6–10^8 L and O_2 pressure range 2.6×10^{-6}–10 Pa. The total amount of absorbed oxygen was determined from the O_2 TD spectra.

The LEED data show that the c(2×4) reconstructive structure with 0.5 mL surface coverage with oxygen was formed on the Pd(110) surface after 1–5 L O_2 exposure at T = 304–475 K [3, 4]. Therefore, an O_2 TD spectrum obtained at $\varepsilon = 3$ L and T = 400 K (spectrum 1, Fig. 1) was used to determine the amount of oxygen absorbed by Pd(110). For this spectrum, it was assumed that $\theta = 0.5$. During the calculations of the oxygen amount, the high temperature peak withT $\geq$ 1000 K was subtracted from the O_2 TD spectra. It does not depend on

the O_2 exposure and may be a result of the diffusion of dissolved oxygen from the bulk of the metal [9]. The exposure to O_2 was varied by changing the O_2 pressure in the range from 2.6×10^{-6} to 10 Pa and by changing the exposure time from 0.5 to 10 min. Figure 2, curve 1 shows that the character of the oxygen amount
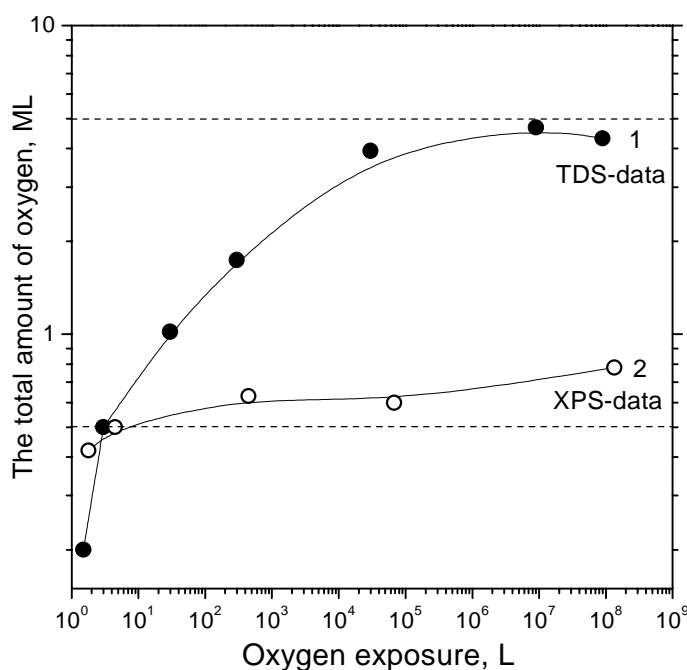

Fig. 2. Dependence of the total amount of oxygen absorbed by Pd(110) at 400 K on exposure in O_2 obtained from the TDS data (1) and from O1s spectra (2)

dependence on exposure in O_2 at 400 K changes with the increase in ε. At low ε ($\leq$ 5 L), the growth of ε from 0 to 5 L is accompanied by a fast increase in θ from 0 to 0.5 due to the formation of a c(2×4) chain reconstructive structure [3, 4]. As ε grows from 5 to 10^5 L, the amount of absorbed oxygen gradually increases from 0.5 to *ca.* 5 mL. This growth may be caused by gradual diffusion of oxygen into subsurface layers of palladium [4-6]. At $\varepsilon \geq 10^5$ L, the amount of absorbed oxygen remains practically constant (*ca.* 5 mL). About 1.8 mL of oxygen is absorbed by Pd(110) at T = 475 K and ε = 7228 L [5], which is close to the value shown in Fig. 2, curve 1.

The chemical state of absorbed oxygen and its concentration over Pd(110) were determined from the O1s spectra. Since the O1s peak is overlapped with a

more intense $Pd3p_{3/2}$ peak, the O1s line was isolated by subtracting the $Pd3p_{3/2}$ spectrum of clean metal from the composed ($Pd3p_{3/2}$ + O1s) spectrum. Before the subtraction, the XPS spectra were smoothed and the ($Pd3p_{3/2}$ + O1s) spectra were normalized to the background and the maximum of the $Pd3p_{3/2}$ peak of clean metal. This procedure results in restoring the most correct O1s line of the adsorbed oxygen on the palladium surface.
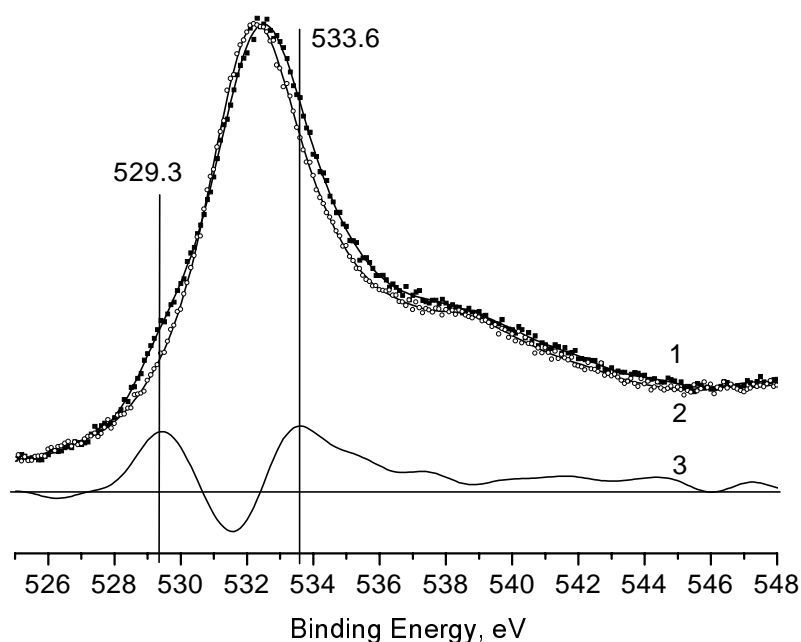
Fig. 3. $Pd3p_{3/2}$ XPS spectra of clean Pd(110) (2 – open circles) and composed spectra ($Pd3p_{3/2}$ + O1s) obtained after treating the sample in O_2 at T = 400 K and $\varepsilon = 1.35 \times 10^8$ L (1 – filled squares)

Figure 3 shows the original and smoothed $Pd3p_{3/2}$ XPS spectra for clean Pd(110) (spectrum 2 – open circles) and the composed ($Pd3p_{3/2}$ + O1s) spectrum obtained after treating the sample in O_2 at T = 400 K and $\varepsilon = 1.35 \times 10^8$ L (spectrum 1 – filled squares). Figure 3 shows also the difference spectrum (spectrum 3), which was obtained as the subtraction of spectrum 2 from spectrum 1. In the difference spectrum, one can see the peak with BE = 529.3 eV due to oxygen on the Pd(110) surface and the peak with BE = 533.6 eV that is associated with shifts of the $Pd3p_{3/2}$ peak due to the O_2 adsorption. The XPS spectra with BE = 529.3 eV, resulting from the subtraction of the $Pd3p_{3/2}$ spectrum of clean Pd(110) from the composed ($Pd3p_{3/2}$ + O1s)

spectra obtained after treating the sample in O_2 at T = 400 K and $P_{O2} = 2.6 \times 10^{-6}$–10 Pa, are related to oxygen adsorbed on Pd(110). Thus, the oxygen O1s peak was extracted by subtracting the contributions of the metal and background to the O1s spectrum. This procedure made it possible to determine the exact position and intensity of the O1s peak, which give information on the chemical state of oxygen on Pd(110) and the surface coverage with oxygen, respectively.
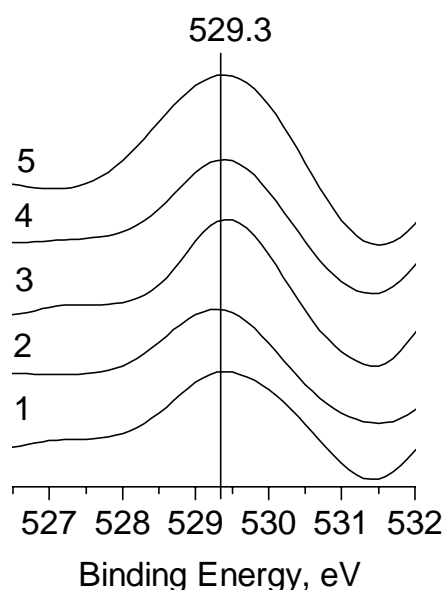
Fig. 4. Difference O1s peaks obtained after treatment of Pd(110) at T = 400 K and at the following exposures in O_2: 1 – 1.8, 2 – 4.5, 3 – 4.5×10^2, 4 – 6.75×10^4, 5 – 1.35×10^8 L, which respectively correspond to the following amounts of absorbed oxygen: 0.3, 0.5, 1.9, 5.0, 4.5 mL

Figure 4 presents the difference O1s spectra obtained after the sample treatment at 400 K and at O_2 exposure varied in a wide range: ε = 1.8 (1), 4.5 (2), 4.5×10^2 (3), 6.75×10^4 (4), 1.35×10^8 L (5), which resulted in absorption of 0.3, 0.5, 1.9, 5.0 and 4.5 mL of oxygen, correspondingly. One can see that the position and intensity of the O1s peak practically do not change, despite the fact that the amount of absorbed oxygen grows from 0.3 to 4.5 mL. It indicates that the chemical state and the coverage of oxygen on the Pd(110) surface remain constant within this range of the amount of absorbed oxygen. Since the c(2×4) reconstructive structure is formed on the Pd(110) surface at θ of *ca.* 0.5 [3, 4], one can assume that this structure does not change on the palladium surface

when the amount of absorbed oxygen grows from 0.3 to 4.5 mL. The LEED diffraction pattern of the c(2×4) structure is constant in the range of the amount of absorbed oxygen from 0.5 to 1.8 mL [5]. The reconstructive structures formed after the interaction of O_2 with Pd(111) at $\theta \geq 0.25$ [10] and with Pd(100) at $\theta \geq 0.5$ [11] are characterized by the O1s peaks with BE = 529.5 and 529.3 eV, respectively, which are close to those presented in Fig. 4. Thus, these O1s peaks with BE = 529.3 eV clearly show the formation on Pd(110) of a layer of chemisorbed oxygen. Note, we failed to detect any peak with BE = 530.3 eV. This indicates that, under the conditions studied, palladium oxides, such as PdO, do not form [12].

The difference O1s spectra obtained were used to determine the amount of oxygen absorbed by Pd(110). The oxygen amount was calculated as a ratio of the areas of the O1s peaks after treating the sample in the pressure range $P_{O2} = 2.6 \times 10^{-6}$–10 Pa to the area of the O1s peak obtained after 4.5 L exposure in O_2, which corresponds to 0.5 mL surface coverage with oxygen. Figure 2, curve 2 presents the amount of oxygen absorbed by Pd(110) as a function of exposure in O_2 at 400 K as determined from the O1s spectra. One can see that the amount of oxygen obtained by this method change only slightly in the exposure range from 1.8 to 10^8 L. For example, with the increase in the exposure from 4.5 to 10^8 L, the amount of oxygen increased from 0.5 to only *ca.* 0.8 mL. Thus, the data shown in Fig. 2, curve 2 indicate that *ca.* 0.8 mL of oxygen is absorbed according to the XPS data by Pd(110) at 400 K when exposure in O_2 grows from 0.6 to 10^8 L. This value is approximately 10 times lower than that obtained from the TD data (*ca.* 5 mL, Fig. 2, curve 1). Similar results were obtained by Banse and Koel [13], who found that the intensity of the oxygen O_{KLL} signal grows linearly with the growth of the amount of absorbed oxygen determined from the TD data during the O_2 absorption on Pd(110) at the amount of oxygen ≤ 1.4 mL. At the same time, at the amount of oxygen ≥ 1.4-2.1 mL, the intensity of the O_{KLL} signal practically did not change. This indicates that oxygen penetrates into deep layers of palladium, so that absorbed oxygen has little contribution to the O_{KLL} signal.

Thus, oxygen penetrates into subsurface palladium layers during O_2 interaction with Pd(110) at 400 K when ϵ grows from 1–5 to 10^8 L. As a result, the amount of oxygen absorbed by palladium grows gradually to *ca.* 5 mL according to the TD data (Fig. 2, curve 1). From the XPS data, it was found that under these conditions, the position of the O1s peak (529.3 eV, Fig. 4) and the amount of oxygen on Pd(110) (0.4–0.8 mL, Fig. 2, curve 2) remain practically constant. This indicates invariability of the chemical state and amount of oxygen on the palladium surface. Since in our experiments the XPS analysis depth was *ca.* 15–20 Å, the penetrated oxygen appears to be distributed deeply in the subsurface layers of the metal (≥ 15-20 Å) with a low concentration. As a result, it gives a very small contribution to the O1s peak. This agrees well with

the data on low solubility of oxygen in palladium, *ca.* 0.5 at.% at 1200°C [14].

During the chemisorption of O_2 on Pd(110) at T = 400 K and $\varepsilon \leq$ 1–5 L, O_2 molecules react with the surface Pd atoms. The resulting –O–Pd–O– chains form gradually the c(2×4) reconstructive structure with θ = 0.5 [3-4]. As the exposure in O_2 grows to $\varepsilon \geq$ 1–5 L, O_2 molecules, which strike unoccupied adsorption sites between the –O–Pd–O– chains, become captured into a weakly bound precursor state $(O_2)_{ads}$ and migrate over the surface. When $(O_2)_{ads}$ molecules dissociate, the resulting O_{ads} atoms may diffuse into the subsurface palladium layers. However, at low P_{O2} ($\leq 10^{-5}$ Pa), the oxygen diffusion is very slow because the surface coverage with $(O_2)_{ads}$ and O_{ads} particles is low due to fast desorption of $(O_2)_{ads}$ molecules weakly bound to the surface. The desorption rate of the $(O_2)_{ads}$ molecules is high due to low adsorption energy of physically adsorbed molecules on metals, *ca.* 20 kJ/mol [15]. When P_{O2} grows above 10^{-5} Pa, the surface coverage with $(O_2)_{ads}$ and O_{ads} particles gradually increases. This leads to the growth of the oxygen penetration rate into the subsurface palladium layers and, consequently, to the growth of the amount of oxygen absorbed by palladium. Thus, the surface reconstructive structure c(2×4) with θ = 0.5 is formed during the O_2 interaction with Pd(110) at T = 400 K and low ε ($\leq$ 1–5 L). At $\varepsilon \geq$ 1–5 L, when P_{O2} grows to 10 Pa, oxygen penetrates into the subsurface palladium layers. As a result, the sample becomes gradually enriched with oxygen to *ca.* 5 mL.

CONCLUSIONS

The interaction of O_2 with Pd(110) at T = 400 K and $P_{O2} = 2.5 \times 10^{-6}$–10 Pa is studied by TDS and XPS. At low exposures in O_2 ($\leq$ 1–5 L), an adsorption layer with θ = 0.5 and with the oxygen O1s peak at BE = 529.3 eV is formed on the Pd(110) surface. The XPS analyzer located at 55° with respect to the sample surface provided the analysis depth about 15–20 Å. According to the XPS data, when ε grows from 1–5 to 10^8 L, the position (529.3 eV) and intensity of the oxygen O1s peak remain approximately constant, which indicates the invariability of the chemical state and coverage of oxygen on the Pd(110) surface under these conditions. Meanwhile, according to the TDS data, the sample gradually absorbs *ca.* 5 mL of oxygen. On the basis of the insignificant change in the chemical state of oxygen and its coverage (*ca.* 0.4–0.8 mL according to the XPS data) and the substantial growth of the amount of absorbed oxygen (up to *ca.* 5 mL according to the TDS data), it has been supposed that at $\varepsilon \geq$ 5 L oxygen from the adsorption layer diffuses deep into the subsurface palladium layers ($\geq$ 15–20 Å) and is distributed in its bulk with a low concentration. As a result, the "dissolved" oxygen has only a weak contribution

to the O1s peak. The results of the detailed analysis of the O_2 adsorption on Pd(110) that are needed for understanding the mechanism of the oxygen diffusion in palladium will be presented in the nearest future.

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