Kinetics and Catalysis, Vol. 43, No. 6, 2002, pp. 868–873. Translated from Kinetika i Kataliz, Vol. 43, No. 6, 2002, pp. 934–939.

Study of Oxygen Adsorption and Reoxidation of Reduced Titanium Dioxide by Thermal Desorption Mass Spectrometry

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Received February 7, 2002

Abstract—The adsorbed oxygen species formed upon the reoxidation of reduced titanium dioxide (Degussa P-25) and oxygen adsorption on the reduced and reoxidized titanium dioxide are studied by thermal desorption mass spectrometry. The reoxidation of the oxide in the presence of O_2 at $P \geq 2 \times 10^{-3}$ Pa and $T \geq 500$ K is shown to result in the appearance of a peak with a maximum at ~700 K in the thermal desorption spectrum. The desorption of oxygen corresponding to this peak occurs via the recombination mechanism with the activation energy $E_{des} = 1.4$ eV. The dynamic model of reoxidation occurring through the adsorption and desorption of oxygen is suggested for the explanation of the temperature dependences of the concentration of surface oxygen that were obtained earlier for the process of reoxidation of rutile single crystal.

INTRODUCTION

The intrinsic local defects of reduced titanium dioxide remain the focus of extensive research, since the properties of these defects determine the adsorption behavior and catalytic activity of TiO_2 [1]. Much attention is paid to both the analysis of the defect surface and the elucidation of the mechanism of its reoxidation [2–6]. Presently this process attracts considerable interest because the reoxidation of the surface (001) of a rutile single crystal is accompanied by the formation and decomposition of different subatomic periodic structures [2, 4, 6]. Moreover, the annealing of titanium dioxide doped with metal ions in an atmosphere of O_2 induces surprisingly high photocatalytic activity in the visible region [7]. However, the detailed mechanism of the reoxidation process is not quite clear yet. The main question on the adsorbed oxygen species formed during reoxidation still remains debatable [3, 4, 6]. Therefore, the purpose of this work was to investigate the reoxidation of reduced TiO_2 and the adsorption of oxygen using the method of thermal desorption (TD) mass spectrometry. Previous studies of powdered [8, 9] and single crystal TiO_2 [10] using this technique focused on the study of oxygen adsorption.

EXPERIMENTAL

The experimental setup consisted of an MI-1201 mass spectrometer equipped with a secondary ion multiplier VEU-1, an ultra high vacuum system, and a data acquisition system and control for the programmed heating of the sample. The wall of a quartz cell was coated with a thin (~20 mg/cm^2) layer of TiO_2 (Degussa P-25, $S_{sp} = 50$ m^2/g). For this purpose, the cell with a suspension of TiO_2 powder in doubly distilled water was gradually heated in air to 600 K and then kept at this temperature for 4 h. The cell with the sample was pretreated in an ultra-high vacuum system alternately in an O_2 flow (130 Pa) and in a vacuum (10^{-6} Pa) at 850 K for 30 h. The heating element provided a constant heating rate $\beta = 0.1$–0.25 K/s within the interval 290–850 K. Oxygen of natural isotope composition was purified by diffusion through the walls of a silver capillary. A DRT-120 mercury lamp equipped with a quartz thermal filter filled with water was used as a source of UV radiation.

RESULTS

Before each study, the sample treated was calcined at 850 K in a vacuum (10^{-6} Pa) for 30 min. Such a treatment leads to the reduction of TiO_2. The TD spectra of such a sample exhibit several special features: (1) if oxygen was not adsorbed (evacuation for 1 h), the desorption of oxygen started only at $T \geq 700$ K (Fig. 1, curve *1*); (2) if oxygen was adsorbed at 290 K and $P =$ 5–10 Pa (Fig. 1, curve *2*), peaks at $T_{max} = 410$ and $T_{max} = {\sim}490$ K, corresponding to chemisorbed oxygen, appeared in the TD spectra. At 290 K, the adsorption of oxygen on the reduced sample ceased when the concentration of chemisorbed oxygen $c \approx 0.8 \times 10^9$ cm^{-2} was achieved. Oxygen adsorption corresponding to the peak at ~490 K is an activated process, because the intensity of this peak increased more than three times if O_2 was adsorbed at 350 K. No special thermal evacuation is required for obtaining reproducible TD spectra (and the degree of the sample reduction). It was sufficient to heat the samples during the TD experiments to 820 K and then cool them under vacuum conditions.

Reoxidation of the reduced TiO_2 sample was carried out in O_2 ($P = 2 \times 10^{-3}$–13 Pa) at $T =$ 500–820 K. At temperatures above 700 K, reoxidation was followed by slow ($\beta = 0.2$–0.3 K/s) cooling in oxygen to ~500 K with further evacuation at $T \leq 500$ K. The reoxidized

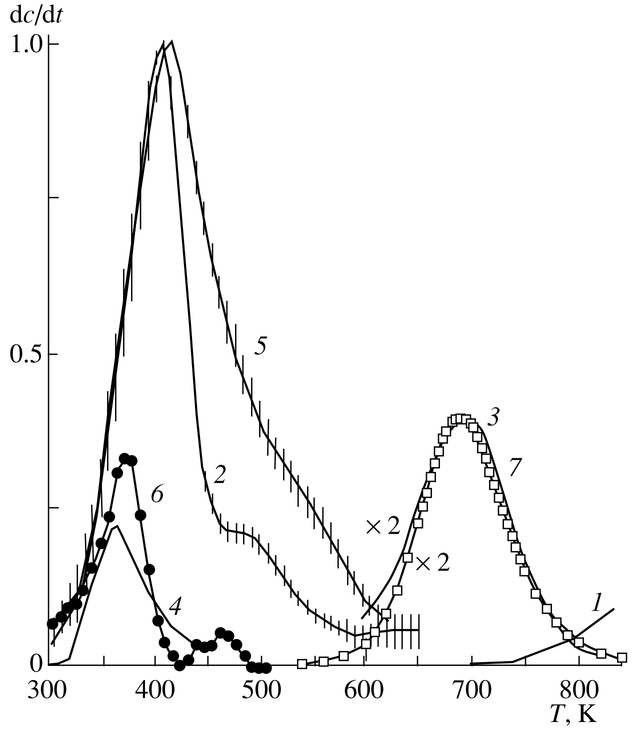

Fig. 1. TD spectra of oxygen desorption from the TiO_2 surface: (*1*) after reduction in a vacuum at 850 K; (*2*) after O_2 adsorption at 290 K on the reduced sample; (*3*) after reoxidation at $T \le 600$ K; (*4*) after O_2 adsorption at 290 K on the reoxidized sample; and (*5*) after UV irradiation in O_2 (TD spectra *2* and *5* are averaged for different adsorption conditions and normalized to $(dc/dt)_{max}$); $\beta = 0.2$ K/s; (*6*) the difference between the normalized TD spectra after O_2 chemisorption at 290 and 350 K; (*7*) the calculated peak at 700 K (for details see the text).

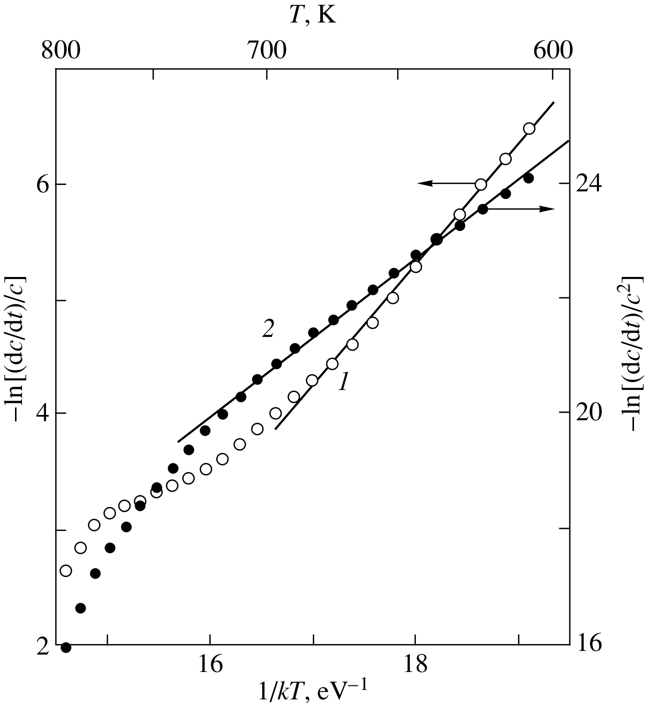

Fig. 2. TD spectra with a maximum at 700 K in the coordinates of the equation of (*1*) first- and (*2*) second-order desorption kinetics and referred to the concentration of adsorbed oxygen *c*. The values of the desorption activation energy and the preexponential factor for the case of the linear approximation are (*1*) $E_{des} = (1.04 \pm 0.03)$ eV, $k^0_{des} = (7 \pm 3) \times 10^5$ s^{-1} and (*2*) $E_{des} = (1.39 \pm 0.03)$ eV, $k^0_{des} = (6 \pm 3)$ cm^2/s.

sample is characterized by: (1) the presence of the TD peak with $T_{max} \sim 700$ K (Fig. 1, curve *3*) and (2) very weak (more than ten times lower as compared with the reduced sample) oxygen adsorption. The amount of oxygen corresponding to the TD peak at 700 K did not exceed 10^8 cm^{-2}.

The reoxidized state of the sample was preserved if the evacuation of the sample was carried out at $T \le 600$ K. Heating the sample in a vacuum at $T \le 600$ K (in this work to 800–820 K) is necessary to restore the adsorption ability of the sample.

The typical TD spectrum of oxygen adsorbed under UV irradiation in O_2 ($P = 6$ Pa) is presented in Fig. 1 (curve *5*). The concentration of photoadsorbed O_2 molecules after 10 min of irradiation reached $\sim 6.0 \times 10^{10}$ cm^{-2}. This value is more than 70 times higher than *c* for chemisorbed oxygen (Fig. 1, curve *2*). It should be noted that the shape of the TD spectrum and the concentration of photoadsorbed molecules were almost independent of the degree of reoxidation (reduction) of the sample.

The TD curve corresponding to the peak at 700 K is presented in Fig. 2 in the coordinates of $\ln[(dc/dt)/c]$ and $\ln[(dc/dt)/c^2]$ vs. $1/kT$ (where *k* is the Boltzmann constant). Such a linearization corresponds to the first- and second-order desorption kinetics referring to the concentration of chemisorbed oxygen *c* (curves *1* and *2*, respectively). Figure 2 shows that linear approximation of curves *1* and *2* enables one to determine the desorption activation energy (E_{des}) with an appropriate accuracy (~3%) for both types of equations. However, in the case of the first-order desorption, the value $E_{des} = 1.0$ eV is considerably lower than the value of 1.5 eV obtained using the formula for the estimate $E_{des} \approx 25kT_{max}$ [11]. Moreover, the value of the preexponential factor k^0_{des} in this equation (7×10^5 s^{-1}) is considerably lower than the value assumed usually for the case of monomolecular desorption (10^{13} s^{-1}) [12, 13]. At the same time, in the case of second-order desorption kinetics, the value k^0_{des} = 6 cm^2/s is in good agreement with the values estimated in [12, 13] for the case of associative desorption, while the value $E_{des} = 1.4$ eV is close to the estimate. The equation of second-order desorption was solved by numerical integration. The results of calculations performed at the initial concentration of oxygen molecules $c = 10^8$ cm^{-2}, $E_{des} = 1.42$ eV, $k^0_{des} = 3$ cm^2/s, and $\beta = 0.25$ K/s are shown in Fig. 1 (curve *7*; curves *3* and *7* are presented in a single scale). It is seen from Fig. 1 that satisfactory agreement between the calculated and experimental TD peaks can be obtained for the experimental values of E_{des} and k^0_{des}. Thus, we suppose that the TD peak at 700 K corresponds to the recombinative desorption of atomic oxygen. This hypothesis is confirmed by the TD data obtained for the photostimulated NO disproportionation on the same TiO_2 sample. In the case of reaction conditions ensuring desorption of N_2 in the gas phase, a TD peak of oxygen at 700 K similar to that presented in Fig. 1 (curve *3*) is observed along with the peaks corresponding to NO and N_2O desorption. In this case, the atomically adsorbed oxygen is the product of the photodecomposition of NO [14].

DISCUSSION

The TD spectrum of chemisorbed oxygen obtained earlier for the TiO_2 (Degussa P-25) sample reduced by heating in the presence of H_2 or CO [15] is similar to the spectrum presented in Fig. 1 (curve *2*). Two peaks with maxima at 415 and ~445 K [8] and 450 and ~520 K [9] were observed in TD spectra of oxygen chemisorbed on dispersed rutile reduced in a vacuum at 873 [8] and 1000 K [9], respectively. The TD spectrum of oxygen chemisorbed on the surface of a reduced (850 K, vacuum) rutile single crystal also exhibits a maximum at 410 K [10]. The fact that the peak with T_{max} at 410 K is independent of the concentration of chemisorbed oxygen in enough wide concentration interval from 0.8×10^9 cm^{-2} (Fig. 1, curve *2*) to $\sim 3.0 \times 10^{11}$ cm^{-2} [15] is an indication of monomolecular desorption of adsorbed oxygen molecules. The same peak is observed in the TD spectra after UV irradiation of TiO_2 in O_2 (Fig. 1, curve *5*). Photoadsorption is usually attributed [1, 7] to the process of the capturing of a photoinduced electron by an O_2 molecule. Thus, the peak at 410 K can be assigned to the adsorption species O_2^-. The same assignment was made for a similar peak in the TD spectrum of oxygen chemisorbed on the surface of a rutile single crystal [10].

According to the data obtained in [10], the values of E_{des} and k^0_{des} calculated from the first-order desorption equation for the peak at 410 K are equal to 1.12 eV and 10^{13} s^{-1}, respectively. The same value of $E_{des} = 1.12$ eV was obtained in [8] ($T_{max} = 415$ K). The value $E_{des} = 0.65$ eV [9] and the value $E_{des} \approx 0.45$ eV ($T_{max} = 410$ K) obtained in this paper (Fig. 1, curves *2*, *5*) do not correlate with the estimated value of ~0.9 eV obtained using the formula $E_{des} \approx 25kT_{max}$ [11]. Such a disagreement can be explained by the presence of an additional low-temperature peak overlapping with the peak at 410 K (Fig. 1, curves *2*, *5*). The same peak probably contributed to the TD spectra observed in [9]. Such a peak with $T_{max} \approx 370$ K can be separated by subtracting the normalized TD spectra obtained after oxygen adsorption at different temperatures (Fig. 1, curve *6*). The TD spectrum of oxygen chemisorbed upon reoxidation (at $P \geq 10$ Pa) and cooling of the sample in O_2 to 290 K (Fig. 1, curve *4*) also shows a peak at ~370 K. Moreover, a well-resolved shoulder at ~380 K close to the main peak at 410 K was observed in [10]. The authors, however, did not succeed in unequivocally assigning the peak at ~380 K because of uncertainty in the conditions necessary for the appearance of this peak. The peak at ~370 K is predominant in the TD spectra of oxygen adsorbed on the reoxidized samples (Fig. 1, curve *4*); therefore, it can be attributed to oxygen adsorption on the TiO_2 nondefect surface. The same idea was suggested in [10].

The assignment of the peak at 490 K in the TD spectra is not quite obvious. According to our data, the adsorption of oxygen responsible for this peak is an activated process. Moreover, oxygen that desorbs at this temperature can participate in the isotopic exchange with oxygen of the oxide [8, 9]. (The maximum at ~520 K was not observed in the TD spectrum in [9], but the products of isotopic exchange $O^{16}O^{18}$ and O_2^{16} were detected in this temperature range after adsorption of O_2^{18}). These results indicate that the peak at 490 K corresponds to a new type of oxygen adsorption that differs from the molecular species O_2^-. It was found earlier [3] that the adsorption of O_2 on reduced rutile single crystal leads to the formation of atomic adsorption species along with the molecular form. Such a type of adsorbed species can be observed within a wide temperature interval, but at $T > 500$ K the concentration of oxygen adatoms noticeably decreases. In our experiments, the intensity of the TD peak at 490 K also should be decreased in the case of O_2 adsorption at $T \geq 500$ K. Thus, this peak could be ascribed to the atomic form, and these species can be more active in the process of isotopic exchange with oxygen of the oxide than with the molecular form.

The phase composition of the TiO_2 sample used in this work is not uniform. The Degussa Grade P-25 samples contain 20 [16] to 30% rutile [7] (the rest is anatase). The TD spectrum of chemisorbed oxygen for this sample (Fig. 1, curve *2*) is quite similar to the spectra obtained for dispersed [8, 9] and single crystal rutile [10]. So the adsorption properties of reduced Degussa P-25 TiO_2 toward oxygen are mainly determined by the defects in the rutile structure. It was reported in [17] that prolonged vacuum annealing at 800 K does not lead to any considerable reduction of dispersed anatase, which was preliminarily purified from organic admixtures. No clear trend toward the formation of stable defects was observed for single crystals of anatase after treating in a vacuum at 930 K [18]. As compared with anatase, reduction of rutile occurs at a higher rate both in a vacuum [19] and in H_2 [20]. This difference can be explained by the lower binding energy of surface oxygen and consequently by the lower desorption activation energy for rutile (1.66 eV) than for anatase (2.5 eV) [19].

Hence, the data of TD experiments on the forms of chemisorbed oxygen and on the influence of the thermal evacuation on the capability of TiO_2 to adsorb oxygen, which were obtained in this work, are in good agreement with the results reported earlier for the dispersed and single crystal samples. At the same time, it was found in this work that the reoxidation of TiO_2 in O_2 results in the formation of the atomic form of adsorbed oxygen. Desorption of these species under the reduction in a vacuum is responsible for the appearance of the peak at ~700 K in the TD spectra.

Analysis of the TD curve of a peak at ~700 K indicates that desorption of oxygen occurs according to the recombination mechanism, although desorption in atomic form cannot be excluded at a low oxygen coverage (~10^8 cm^{-2}). The direct experimental confirmation of these findings is possible with the use of a mass spectrometer that is capable of detecting primary products of the thermal activated desorption (the MI-1201 mass spectrometer used in this study was not suitable for this purpose). At present, the thermal desorption of atomic oxygen was observed only in [21] with the use of time-of-flight mass spectrometer for ZnO, the adsorption properties of which are very similar to those of TiO_2 [22]. The maximum amount of desorbed oxygen atoms at ~350 K is equal to ~1%, while at $T > 600$ K (the temperature of desorption of structural oxygen and formation of surface vacancies), it does not exceed 0.2% [21]. The results of direct-flight mass spectrometric analysis of the products of thermal decomposition of BaO and SrO [23, 24] also indicate the evolution of lattice oxygen in molecular form. All these results lend support for the hypothesis of the associative mechanism of the desorption at 700 K of oxygen atomically adsorbed on TiO_2.

Our conclusion that the reoxidation of TiO_2 in O_2 is related with the formation of the adsorbed atomic species characterized by the peak at 700 K in the TD spectra is indirectly confirmed by the data on the changes in the concentration of surface oxygen observed in studying the restructuring of the surface of rutile single crystal [4, 6]. As was shown by tunneling microscopy, the reoxidation at 460–~700 K causes the formation of surface structures, such as pseudohexagonal atomic groups (rosettes) that transform at $T > 700$ K into linear-type structures (strands) [4, 6]. It is important that the process of reoxidation ($P_{O_2} = 10^{-4}$ Pa) is accompanied by an increase (at $T > 480$ K) and a decrease (at $T > 670$ K) in the surface oxygen concentration with the maximum at ~630 K [4]. The authors explain this increase by the process of dissociative oxygen adsorption with the activation energy of ≈0.82 eV at 477–530 K, while the decrease in the concentration is probably accounted for by the desorption of oxygen that was atomically adsorbed during the reoxidation step. The same conclusion was drawn in [6] in the study of the process of reoxidation of a rutile single crystal at $P_{O_2} = 10^{-4}$ Pa and $T = 550$–570 K with further reduction by heating at different temperatures in a vacuum. It should be noted that oxygen desorption was not measured in [4, 6], and the contribution of oxygen desorption to the process of surface reconstruction can only be assumed. The presence of a peak at 700 K in TD spectra can be considered as experimental evidence for the occurrence of the desorption of oxygen atomically adsorbed during reoxidation at temperatures of the TiO_2 surface reconstruction.

The process of the reoxidation of the TiO_2 surface in the presence of gaseous oxygen can be considered as a dynamic process of formation and decomposition of atomically adsorbed species. The rate law of the process, including the step of dissociative adsorption of O_2 molecules with the occupation of two vacancies and further associative desorption, can be presented as follows:

$$\mathrm{d}c_{\mathrm{ads}}/\mathrm{d}t = k_{\mathrm{ads}}(C - c_{\mathrm{ads}})^2 - k_{\mathrm{des}}c_{\mathrm{ads}}^2, \qquad (1)$$

where c_{ads} is the current concentration of adsorbed atoms, C is the initial concentration of surface defects, k_{ads} and k_{des} are the constants of adsorption and desorption rates, and t is the time of heating in oxygen. Both stages of the process have an activation barrier; therefore, $k_{\mathrm{ads}} = k^0_{\mathrm{ads}}\exp(-E_{\mathrm{ads}}/k_{\mathrm{ads}}T)$ and $k_{\mathrm{des}} = k^0_{\mathrm{des}}\exp(-E_{\mathrm{des}}/k_{\mathrm{des}}T)$, where E_{ads} and E_{des} are the activation energies of adsorption and desorption, respectively.

The solution to Eq. (1) at the initial conditions $c_{\mathrm{ads}} = 0$ at $t = 0$ is

$$c_{\mathrm{ads}} = C \times \left\{ \frac{k_{\mathrm{ads}}}{k_{\mathrm{ads}} - k_{\mathrm{des}}} + \left(\frac{\sqrt{k_{\mathrm{ads}}k_{\mathrm{des}}}}{k_{\mathrm{ads}} - k_{\mathrm{des}}} \frac{\exp(-2C\sqrt{k_{\mathrm{ads}}k_{\mathrm{des}}}t) + A}{\exp(-2C\sqrt{k_{\mathrm{ads}}k_{\mathrm{des}}}t) - A} \right) \right\}, \qquad (2)$$

where $A = (k_{\mathrm{ads}} + \sqrt{k_{\mathrm{ads}}k_{\mathrm{des}}})/(k_{\mathrm{ads}} - \sqrt{k_{\mathrm{ads}}k_{\mathrm{des}}})$. Expression (2) can be used for the calculation of the temperature dependence of the concentration of adsorbed atoms c_{ads} (or the coverage of surface defects, i.e., the reoxidation degree, c_{ads}/C). The same dependence discussed in [4] has a maximum at $T \sim 625$ K with a half-width $\Delta T_{1/2} \approx 250$ K; the reoxidation time was $t = 260$ and 900 s (two series of experiments). The values of $E_{\mathrm{des}} = 1.4$ eV and $k^0_{\mathrm{des}} = 6$ cm^2/s obtained for the TD peak at 700 K and the value $E_{\mathrm{ads}} = 0.82$ eV estimated in [4] were used for the calculations.

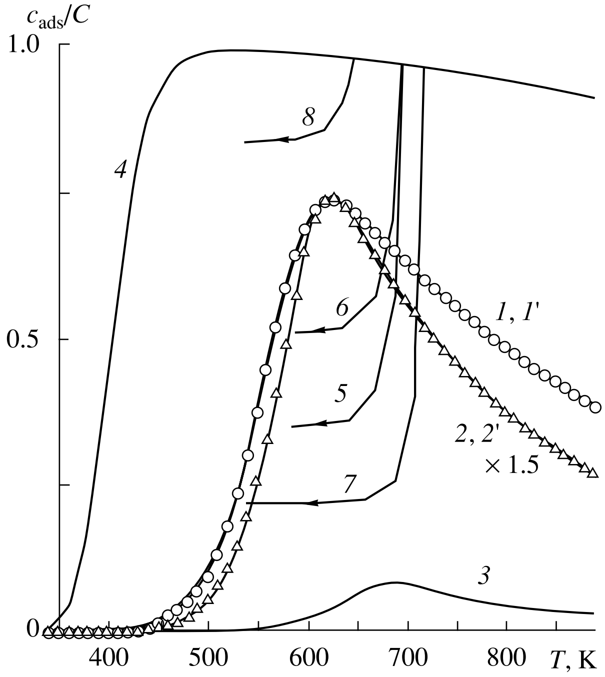

Fig. 3. Dependence of the relative concentration of adsorbed oxygen [c_{ads}/C] responsible for the peak at 700 K on the temperature in the case of the simultaneous process of dissociative adsorption (E_{ads} = 0.82 eV) and associative desorption (E_{des} = 1.4 eV and k^0_{des} = 6 cm^2/s) at (*1*) t = 260 s, k^0_{ads} = 1.2×10^{-3} cm^2/s, $C = 7 \times 10^7$ cm^{-2}; (*1'*) 900 s, 1.2×10^{-3} cm^2/s, 1.8×10^7 cm^{-2}; (*2*) 260 s, 1.5×10^{-4} cm^2/s, 1.8×10^8 cm^{-2}; (*2'*) 900 s, 1.5×10^{-4} cm^2/s, 5×10^7 cm^{-2}; (*3*) 500 s, 3.2×10^{-6} cm^2/s, 10^8 cm^{-2}; (*4*) 500 s, 3.2×10^{-1} cm^2/s, 10^8 cm^{-2}. The dependence of [c_{ads}/C] on the temperature for the sample reoxidized as in (*4*) and cooled in a vacuum (k^0_{ads} = 3.2×10^{-6} cm^2/s) at (*5*) the starting temperature of evacuation 700 K and cooling rate 0.5 K/s; (*6*) 700 K, 1.0 K/s; (*7*) 720 K, 0.5 K/s; and (*8*) 650 K, 0.5 K/s.

The dependence of [c_{ads}/C](T) on the temperature at different values of t, k^0_{ads}, and C is shown in Fig. 3. At t equal to 260 and 900 s, this dependence has a maximum at T = 630 K with a half-width $\Delta T_{1/2} \geq 250$ K, and $(c_{ads}/C)_{max}$ = 0.5–0.75 (Fig. 3, curves *1*, *1'* and *2*, *2'*) at k^0_{ads} = 1.2×10^{-3}–1.5×10^{-4} cm^{-2}/s and $C = 1.8 \times 10^7$–1.8×10^8 cm^{-2}, respectively. Thus, the adsorption–desorption model of reoxidation satisfactorily agrees with the dependences of the concentration of surface oxygen on the temperature during reoxidation of TiO_2 in O_2, which were obtained earlier in [4]. It should be emphasized that the proposed model is based on the examination of the process of formation and decomposition of specific adsorption forms of surface oxygen responsible for the peak at 700 K in the TD spectra. The lattice oxygen species desorb at $T > 700$ K with a monotonously increasing rate (Fig. 1, curve *1*).

The calculated value of C is considerably lower than the concentration of oxygen vacancies on the surface of a rutile single crystal (110) (~10^{13} cm^{-2}) found after evacuation at 850–930 K [10, 18]. One should take into account in comparing these values that the main part of defects (including oxygen vacancies) in reduced TiO_2 are active in the interaction with O_2 molecules even at room temperature [10, 15]. Complete reoxidation can be achieved in the process of activated adsorption at $T > 400$–500 K (E_a = 0.82 eV) [4]. Additional studies are required to answer the question of the nature and concentration of oxygen vacancies filled during reoxidation.

The presentation of Eq. (1) used in this work implies that the preexponential factor k^0_{ads} is directly proportional to the oxygen pressure P_{O_2}. The dependences [c_{ads}/C](T) on the temperature (Fig. 3, curves *1*, *1'* and *2*, *2'*) obtained for k^0_{ads} = 10^{-3}–10^{-4} cm^2/s are in good agreement with the results of the experiment carried out at $P_{O_2} = 10^{-4}$ Pa. The dependences of the degree of reoxidation proportionally to oxygen pressures on the temperature can be calculated by changing k_{ads} at different P_{O_2}. The results of the calculation at $C = 10^8$ cm^{-2} and t = 500 s are shown in Fig. 3. Almost no reoxidation occurs in a vacuum at $P_{O_2} = 10^{-6}$ Pa ($k_{ads} = 3.2 \times 10^{-6}$ cm^2/s), and $(c_{ads}/C)_{max} \approx 0.08$ (Fig. 3, curve *3*). At $P_{O_2} \geq 10^{-1}$ Pa ($k_{ads} \geq 3.2 \times 10^{-1}$ cm^2/s), 90% of all defects are occupied starting from ~490 K, and there is no sharp maximum on the dependence [c_{ads}/C](T) on the temperature (Fig. 3, curve *4*). It should be noted that the reoxidation of Degussa P-25 TiO_2 was achieved by varying the oxygen pressure only at the constant temperature 623 K in [25]. The results of calculations also show that, if the reoxidation is carried out under conditions providing almost complete filling of the surface defects (Fig. 3, curve *4*) and if the sample is further cooled in a vacuum, then the degree of reoxidation is strongly dependent on the starting temperature of evacuation and on the rate of cooling (Fig. 3, curves *5*–*8*).

The discovery of a new specific form of adsorbed atomic oxygen responsible for the peak at 700 K in TD spectra will contribute to a better understanding of the processes of reconstruction of the surface of titanium dioxide and will help in choosing optimal conditions for reaching and keeping the maximum degree of reoxidation of the oxide surface.

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