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Abstract

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FORMS OF ADSORPTION OF OXYGEN ON TITANIUM DIOXIDE AND ITS PHOTOACTIVATION

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In a previous paper (^{1}) it was reported that hydrogen is irreversibly absorbed by titanium dioxide under illumination at the edge of its intrinsic absorption (~400 mμ). The phenomenon was called photosorption of hydrogen. Photosorption was observed only after preliminary calcination of the samples in oxygen at T = 600–800°K. The absorption of oxygen was not monitored in this process, but it was noted that such treatment decreases the electrical conductivity of the samples (σ) by approximately two orders of magnitude. It is known (^{2}) that adsorption of oxygen decreases σ of TiO_2 (an acceptor gas on an electronic semiconductor); therefore it may be assumed that the appearance of photosorption is caused by prior adsorption of oxygen. However, it was found that adsorption of oxygen at T = 293°K on a "photoactive" sample,* while decreasing σ by 4 orders of magnitude, did not affect the photoactivity. Evidently, at different temperatures oxygen is adsorbed in different forms, which affect photoactivity in different ways.

The present work is devoted to the study of the forms of adsorption of oxygen on TiO_2 and their influence on photoactivity. Oxygen adsorption was studied manometrically and simultaneously by its influence on σ in the temperature range 90–600°K. The work was carried out on the same manometric apparatus as in (^{1}). The pressure was continuously recorded with a Pirani manometer. The conductivity was measured with an MOM-3 megohmmeter. The powder sample was usually placed in a flat glass cuvette provided with silver contacts for measuring σ.

The working volume (about 20 cm^3), in which the pressure was measured, was separated from the rest of the high-vacuum system by a greaseless valve with a fluoroplastic seal; by cautiously opening it, the desired amount of oxygen could be admitted into the working volume, which was monitored by the decrease in pressure in the buffer volume from which the oxygen was admitted. The sample was illuminated with an SVD-120 mercury lamp with a mirror condenser. In the experiments, samples of TiO_2 in the anatase modification were used, prepared by the method described in (^{3}), with a specific surface area of 70 m^2/g.

It is known that appreciable chemisorption of oxygen is observed only on titanium dioxide samples reduced relative to the stoichiometric composition, and at

Figure 1

Figure 1: Figure 1

300°K 30—50% of the oxygen removed during reduction is irreversibly absorbed (^{4}). In our experiments, samples freed of organic impurities by calcination in oxygen were reduced in hydrogen. The composition of the reduced samples, judging from the adsorption capacity with respect to oxygen, which corresponded to a surface coverage (θ) of 0.1—0.2%, was approximately $TiO_{1\cdot 999}$.

If oxygen is admitted in small portions at 90°K onto such a sample, then the first portions (10—20% of the maximum coverage at 300°K) are adsorbed irreversibly already at this temperature, which is accompanied by an irreversible decrease in σ. If a sample with such oxygen is heated to 500°K, the pressure remains at zero, and after cooling σ returns to the value before heating; i.e., no additional irreversible processes occur during heating. Evidently, the first portions occupy surface oxygen vacancies and already at 90°K are incorporated into the lattice in the form $O^{2-}_{\text{latt.}}$.

The subsequent portions of oxygen behave quite differently. Figure 1 shows the curves of the change in pressure in the volume (curve 1—1, consisting of three separate peaks) and of σ upon heating a sample with oxygen adsorbed at 90°K ($\theta = 0.1\%$). Curve 1—2 shows the change in σ of the sample before adsorption of oxygen (but after filling of the surface oxygen vacancies). Admission of oxygen at 90°K does not change σ, although all the oxygen is immediately adsorbed. After admission the valve was closed, and the amount of gas in the volume no longer changed. Upon heating to $T_1 = 130$°K, gas is released into the volume, and σ changes in the same way as before adsorption of oxygen (curve 1—3a). At T_1 sharp adsorption begins, and all the gas is absorbed by $T_2 = 170$°K, while σ falls by approximately 3 orders of magnitude. Evidently, oxygen physically adsorbed at 90°K is released upon heating and is adsorbed again at T_1, already in a charged form. The transition is irreversible: cooling transfers σ to branch 1—3b, and upon a second heating in this temperature region gas is not released, and there is no anomalous drop in σ. With further heating, the pressure again begins to rise from $T_3 = 200$°K and again falls to zero at $T_4 = 260$°K. Secondary cooling transfers σ to branch 1

Fig. 1. Heating of TiO_2 with oxygen adsorbed at 90°K.
1 —pressure in the volume during the first heating, 2 —change in σ during heating of the adsorption of O_2, 3 —change in σ during heating after adsorption of O_2 at 90°K

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* Here and below, photoactivity is understood as the activity with respect to photosorption of hydrogen. The initial rate of photosorption is taken as the measure of activity (A).

Figure 2

Figure 2: Figure 2

—3v, thereby showing that the second irreversible drop in σ, not directly visible during warming, corresponds to the second peak in pressure. Indeed, upon the second heating in the interval T_3—T_4, σ rises more rapidly, while the pressure remains at zero. With further heating, gas is released at $T_5 = 370^\circ$K and is again completely adsorbed by $T_6 = 500^\circ$K; with the onset of gas release, σ begins to fall, and cooling transfers σ to branch 1—3g. This transition is also irreversible, like the first two; therefore, to repeat the experiment it is necessary to reduce the sample again in hydrogen.

Fig. 2. Dependence of the photoactivity of TiO_2 on the form of oxygen adsorbed on it.
1 —before adsorption of oxygen, 2 —$O_{2\,\mathrm{ads}}$, 3 — "O_{ads}" , 4 —O^{2-}_{ads}

Thus, during the first heating of a sample with oxygen adsorbed at 90°K up to $T = 500^\circ$K, gas release is observed three times

into the bulk with subsequent readsorption, with each evolution corresponding to an irreversible drop in conductivity. These phenomena can be explained by a threefold transition of adsorbed oxygen into more highly charged forms, with localization at the surface of an ever larger number of conduction electrons. The following scheme of transitions may be proposed:

$$\begin{aligned} &1)\quad O_{2\,\mathrm{gas}} + e^- \to O^-_{2\,\mathrm{ads}} \quad (130\text{–}170^\circ\ \mathrm{K}),\\ &2)\quad O^-_{2\,\mathrm{ads}} + e^- \to 2O^-_{\mathrm{ads}} \quad (200\text{–}260^\circ\ \mathrm{K}),\\ &3)\quad O^-_{\mathrm{ads}} + e^- \to O^{2-}_{\mathrm{ads}} \quad (370\text{–}500^\circ\ \mathrm{K}). \end{aligned}$$

These forms are usually accepted for the adsorption of oxygen on oxides (5).

During transitions (2) and (3), no more than 15% of the adsorbed gas is evolved into the bulk, and, probably, this evolution is only a consequence of the recharge that has begun on the surface.*

Depending on the form of the oxygen adsorbed on the specimen, the photoactivity of the specimen changes. Figure 2 presents barograms of the photosorption of hydrogen under identical conditions (pressure in the dark 10^{-3} torr, $T = 170^\circ$ K) with the same amount of oxygen on the specimen, but adsorbed in different forms: 1—before oxygen adsorption, 2—after the first transition (O_2^-), 3—after the second transition (O^-), 4—after the third transition (O^{2-}). From a comparison of the barograms it is evident that the photoactivity is associated with the presence on the surface of adsorbed oxygen in the high-temperature form (O^{2-}_{ads}), appearing after the third transition, but some activity appears already after the second transition (maximum heating temperature 293° K).

Fig. 3. Change in the photoactivity of TiO_2 with filling of the surface by oxygen at $T = 573°$ K

Fig. 4. Dependence of photoactivity on the filling of the surface by oxygen in the form O^{2-}_{ads} (initial portion)

It is important that before reduction in hydrogen the specimen be cleaned of organic contaminants; otherwise, on passing through the temperatures corresponding to transition 3, σ does not fall but, on the contrary, irreversibly increases, and on further heating a gas freezing out at 90° K, most likely CO_2, begins to be evolved; evidently, the adsorbed oxygen is consumed in the oxidation of organic contaminants. After this, even the weak photoactivity that appears on heating to 293° K disappears.

An attempt was made to find a quantitative relation between photoactivity and the filling of the surface with oxygen in the form O^{2-}_{ads}. Into a preliminarily reduced specimen at $T = 573°$ K, corresponding to the form O^{2-}_{ads}, oxygen was admitted in small portions ($\theta = 0.01\%$), which was immediately absorbed completely. After the admission of each portion of oxygen, the temperature was lowered to 293° K, hydrogen was admitted, and under standard conditions a brief illumination was carried out—a test for photoactivity. Then the hydrogen was pumped out, the temperature was again raised to 573°K and the next portion of oxygen was added. Fig. 3 presents the results of the experiment described. The entire curve can be divided into 3 regions: 1—up to θ_0—activity does not appear; evidently, the first portions, as at 90°K, occupy surface oxygen vacancies and do not give photoactivity. 2—from θ_0 to Q_1—activity increases in proportion to the square of the coverage, as is seen from Fig. 4, where the activity in region 2 is plotted against $(\theta - \theta_0)^2$ (θ_0 is the onset of activity growth, found by extrapolation of the parabola). 3—$\theta > \theta_1$—activity is proportional to coverage.

The following model of hydrogen photosorption may be proposed: a quantum of light creates an electron-hole pair; some of the holes are drawn to the surface and are captured by ions O^{2-}_{ads}, which should serve as effective traps for holes because of their double negative charge. For a certain time the hole remains in the trap, and if during this time a molecule of H_2 from the gas phase reaches this formation, it can supply an electron in place of the one neutralized by the hole, and thus the hydrogen molecule will become bound to the surface center (photosorption).

In this model the rate of photosorption (A) must be determined by the number of holes simultaneously present in surface traps (at constant hydrogen pressure). It may be assumed that at constant temperature the number of captured holes is proportional to the number of traps (i.e., to the coverage of the surface by O^{2-}_{ads} ions) and therefore of holes to the surface: $A = a_1 \theta \eta$, where a_1 is a constant, η

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* The desorption mechanism is described in a paper by Yu. P. Slonitsyn, in preparation.

is the flux of holes to the surface. If it is assumed that η is proportional to the surface barrier, which increases linearly with coverage*, then $A = a_2\theta^2$, which is observed in region 2 of the curve in Fig. 3. The change in the dependence at θ_1 can be explained by saturation of η.

It is usually believed that capture of a photohole by an ion of adsorbed oxygen leads to desorption (“photodesorption of oxygen”). In our case, when a hole is captured by the ion O^{2-}_{ads}, not the entire charge is neutralized; therefore oxygen is not desorbed, but for some time passes into a reactive state; thus photodesorption of oxygen is replaced by its photoactivation through partial discharge. Indeed, attempts to find photodesorption of oxygen from TiO_2 by a direct manometric method were unsuccessful (^{7}), although discharge of the TiO_2 surface under illumination was observed from the change in the contact potential difference and was explained by photodesorption of oxygen (^{8}).

Photoactivated adsorbed oxygen is capable of reacting not only with hydrogen. Under the same conditions as for photosorption of H_2, photosorption of methane on TiO_2 was detected. Photosorptions of H_2 and CH_4 were also detected on ZnO after saturation of the surface with oxygen at 600–700°K. It is possible that the same mechanism of photoactivation of adsorbed oxygen, reacting with an organic binder, underlies the chalking of paints containing TiO_2 or ZnO.

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* A linear increase of the surface barrier with coverage was observed, for example, in adsorption of O_2 on ZnO (^{6}).

Note: Figure translations are in progress. See original paper for figures.

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