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Abstract

Full Text

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STUDY BY THE E.P.R. METHOD OF THE RADICAL FORM OF ADSORPTION OF MOLECULAR OXYGEN ON REDUCED TITANIUM DIOXIDE

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One of the main shortcomings of current ideas about chemisorption on semiconductors is the almost complete absence of any experimental information on the chemical nature of the adsorbed particles and on the character of their bond with the surface ([1]). In this connection, comprehensive investigations of chemisorption by electrophysical methods and by the e.p.r. method, which makes it possible to analyze radical forms of chemisorption, are very promising. As the first stage of such investigations, we studied the spectra of electron paramagnetic resonance of oxygen chemisorbed on partially reduced titanium dioxide.

Fig. 1. E.p.r. spectra of titanium dioxide with oxygen adsorbed on the surface. *a*—initial pressure of O_2 during adsorption 0.12 mm Hg; *b*—initial pressure of O_2 0.5 mm Hg; *c*—initial pressure of O_2 70 mm Hg.

An anatase preparation was used in the work; the nature of its surface and adsorption properties had been studied previously ([2]). Before the measurements, the sample was evacuated for six hours in a vacuum of 10^{-5} mm Hg at 500°. The specific surface area of the calcined sample was 56 m^2/g. As was shown in ([3]), at these temperatures a noticeable rearrangement of the anatase lattice into the rutile structure occurs at the surface (the extent of the phase transformation is 12-14%). At the same time, as a result of partial reduction, titanium dioxide

acquires the properties of an n-type semiconductor ([4]). Oxygen chemisorption was studied at room temperature. The e.p.r. spectra were recorded on an IKhF EPR-2 radiospectrometer ([5]) with an operating wavelength of 3.2 cm.

After calcination in vacuum at 500°, partial reduction of the anatase samples occurred ([2,4,6,7,8]): they acquired a gray-blue color. We did not, however, observe e.p.r. signals from Ti^{3+} ions, which is in accord with the literature data ([7,8]). When ampoules with the samples were introduced into the resonator of the e.p.r. spectrometer, its quality factor decreased appreciably, indicating the high electrical conductivity of the samples. After adsorption of oxygen, the color of the titanium dioxide became lighter and its electrical conductivity decreased, which is also in agreement with the literature data ([6,9]).

After oxygen was admitted into the ampoules with the samples, the appearance of a complex e.p.r. signal was observed, the form of which depended on the oxygen pressure.

oxygen at which the adsorption was carried out. At an initial pressure lower than 0.1 mm Hg, the spectrum consists mainly of a single symmetric line 6 oersteds wide with a g-factor equal to 2.002 (Fig. 1, a). In what follows we shall call this signal "narrow." If, after adsorption is completed, the oxygen pressure is increased, the amplitude of the narrow signal decreases, and at pressures above 20 mm Hg it is not observed. The decrease in the signal amplitude is accompanied by an increase in its width. The area of the signal, however, does not change. The broadening effect of oxygen on the EPR signal is reversible. If the oxygen is rapidly pumped out of the ampoule containing the sample, the initial width and amplitude of the signal are restored practically instantaneously. Apparently, we are dealing here with dipole–dipole broadening of the resonance signal by the local magnetic field created by physically adsorbed paramagnetic oxygen molecules, i.e., with the typical "oxygen effect" previously observed for EPR signals in coals and supported oxide catalysts ([10,11]).

If, after the initial thermal treatment, oxygen adsorption is carried out at a pressure above 0.1 mm Hg, then in the EPR spectrum, in addition to the narrow signal, a broad asymmetric line also appears, lying on the low-field side (Fig. 1, b). When the oxygen pressure is increased, this line, like the narrow line, undergoes dipole–dipole broadening. The most intense broad signals were obtained in the case where the initial oxygen pressure during adsorption was several hundred mm Hg. In this case, after completion of the adsorption process, the oxygen was pumped out of the gas phase before the EPR measurements in order to eliminate the broadening effect on the signal. The spectrum observed in this case (Fig. 1, b) consists practically of one broad line. The characteristic asymmetric shape of the signal indicates anisotropy of the g-factor. From the spectrum shown in Fig. 1, b, the following characteristics of the "broad" signal were obtained: $g_{\perp} = 2.010$; $g_{\parallel} = 2.021$; $g_{\text{avg}} = 2.014$.

After storage of TiO_2 samples with oxygen adsorbed on the surface at room temperature for several days, the intensity of the broad signal decreased strongly,

while the intensity of the narrow signal did not change. Pumping the samples at room temperature for several hours also led to a decrease in the intensity of the broad signal. After pumping for 30 min, the line decreased by approximately a factor of two. If pumping is carried out with simultaneous heating of the sample to 50–60°, then after several minutes the broad signal disappears completely. If the sample is then cooled to room temperature and oxygen is adsorbed again, the broad signal reappears; however, its intensity is much lower than after the first adsorption of oxygen on a sample heated in vacuum at 500°. Thus, the effect of the appearance of the broad signal in the EPR spectrum upon adsorption of oxygen is partially reversible. In contrast to this, the narrow signal does not disappear after heating the samples in vacuum for one hour even at 200°.

The decrease in the electrical conductivity of titanium dioxide observed upon adsorption of oxygen evidently indicates capture of conduction electrons by adsorbed oxygen molecules (or atoms), with the formation of charged adsorbed forms. At the same time, upon oxygen adsorption, two characteristic lines appear in the EPR spectrum, probably also associated with adsorbed forms of oxygen. The magnitude of the g-factor and the presence of pronounced anisotropy of the g-factor make it possible to assign one of them (the broad one) to a peroxide-radical form of adsorption of oxygen molecules.

It is well known that peroxide radicals formed in polymers irradiated in air give characteristic anisotropic EPR signals, the shape of which depends on the nature of the averaging motion of the polymer chains ([12]). The signal parameters depend little on the group bonded to the peroxide-

grouping part of the molecule; usually even hyperfine structure from a proton located at the nearest carbon atom is not observed. This circumstance makes it possible to assert that the unpaired electron of the free radical is almost entirely localized in the O–O group and that the EPR signals of peroxide groups in other compounds and, in particular, on the surface of solids should have similar parameters. Indeed, the observed values of the g-factors ($g_{\parallel} = 2.021$, $g_{\perp} = 2.010$, and $g_{\text{av}} = 2.014$) of the broad signal are close to the corresponding parameters of the signal of a peroxide radical in irradiated Teflon ($g_{\text{av}} = 2.017 \pm 0.003$) (12). The appearance of the broad signal upon adsorption of oxygen can be explained by the following scheme:

$$\text{O–O} + e \longrightarrow \text{O–O}^{-}$$

Chemisorption occurs as a result of localization of conduction electrons on adsorbed O_2 molecules. The bond of the chemisorbed oxygen molecules with the surface may have a homeopolar or ionic character. In the latter case, the adsorbed O_2 molecules are ion radicals O_2^-. The interpretation of the narrow signal appearing in the EPR spectrum upon adsorption of oxygen is less unambiguous. As one of the possible explanations, it may be assumed that it is associated with dissociative adsorption of oxygen in the form O^-. Another possible explanation is that this signal is associated with impurity donor levels in

Fig. 2. Comparison of oxygen adsorption with the change in the EPR spectrum. a—pressure drop in the ampoule with the sample during adsorption; b—successive change of the EPR spectrum in the same experiment.

Figure 2: Fig. 2. Comparison of oxygen adsorption with the change in the EPR spectrum. a—pressure drop in the ampoule with the sample during adsorption; b—successive change of the EPR spectrum in the same experiment.

reduced titanium dioxide. According to literature data (4, 13), such impurity levels may be Ti^{3+} ions or electrons trapped by oxygen vacancies (F centers). These levels are located, however, so close to the bottom of the conduction band (several hundredths of an electron-volt) that at room temperature they are practically unoccupied and the reduced titanium dioxide is a degenerate semiconductor with pseudometallic conductivity (4, 6, 13). Free electrons in the conduction band, however, are not observed by the EPR method, since they give very broad signals. It is possible that, as a result of the negative charging of the TiO_2 surface occurring during oxygen adsorption, the bands bend, the depth of occurrence of the impurity donor levels increases, and they capture free electrons from the conduction band. As a result, a narrow signal with a g-factor close to two appears in the EPR spectrum.

Fig. 2. Comparison of oxygen adsorption with the change in the EPR spectrum. **a**—pressure drop in the ampoule with the sample during adsorption; **b**—successive change of the EPR spectrum in the same experiment.

The peroxide-radical form of adsorbed oxygen is unstable, since storage of the samples at room temperature and especially their heating in vacuum lead to a decrease in the intensity of the broad EPR signals. Upon heating in vacuum, apparently, partial reoxidation of the surface or transition of oxygen into a more firmly bound nonradi-

radical form of adsorption: upon repeated adsorption of oxygen the intensity of the broad signal is not fully restored.

Of great interest is the study of the chemical properties (reactivity) of the various forms of adsorbed oxygen. In this connection we studied the change in the EPR spectra upon treating titanium dioxide with oxygen adsorbed on the surface with reducing agents: ethylene, hydrogen, and acetaldehyde. It turned out that at room temperature ethylene and hydrogen do not cause a change in the intensities of the broad and narrow EPR signals. When a stronger reducing agent—acetaldehyde—is admitted into the ampoule with the sample, the broad signal disappears instantaneously, while the narrow one does not change. Apparently, oxidation of acetaldehyde by adsorbed oxygen takes place here—a reaction that proceeds at room temperature with molecular oxygen at a very low rate. Thus, the adsorbed peroxide-radical form of oxygen possesses, in comparison with molecular oxygen, increased chemical activity.

Table 1

Experiment No.	Initial pressure O_2, mm Hg	Number of adsorbed O_2 molecules per 1 g TiO_2	EPR signal intensity, in unpaired electrons per 1 g TiO_2 "broad"	EPR signal intensity, in unpaired electrons per 1 g TiO_2 "narrow"
63	0.1	$3 \cdot 10^{18}$	$1 \cdot 10^{18}$	$2 \cdot 10^{18}$
70	0.1	$4 \cdot 10^{18}$	$1 \cdot 10^{18}$	$2 \cdot 10^{18}$

It was of interest to compare the intensity of the EPR signals arising upon adsorption of oxygen with the amount of chemisorbed oxygen. For this purpose experiments were carried out in which the pressure drop in the ampoule with the sample during adsorption was measured simultaneously and the EPR spectra were recorded. The data obtained in one of the experiments are presented in Fig. 2. From the horizontal section of the curve in Fig. 2, *a*, the number of adsorbed oxygen molecules was estimated; from the EPR spectrum observed at the end of the experiment, the intensities of the broad and narrow signals were calculated. The corresponding data for two parallel experiments are given in Table 1.

Because of the small weighed portions of TiO_2, the number of adsorbed molecules was determined very roughly, and the data given in Table 1 should be regarded only as rough estimates. There is no doubt, however, that the intensity of the observed EPR signals is close to the number of adsorbed oxygen molecules.

At present we have begun studies of the change in the work function upon adsorption of oxygen on titanium dioxide. The first experiments, carried out at Moscow State University by E. N. Figurovskaya, showed that the change in the work function $\Delta\varphi$ as a function of the temperature of calcination of TiO_2 in vacuum includes a reversible part ($\Delta\varphi_{\text{rev}}$), which decreases upon evacuation of oxygen, and an irreversible part ($\Delta\varphi_{\text{irrev}}$), which remains after evacuation. These data also indicate the presence of charged forms of oxygen chemisorption.

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