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Fig. 1

Figure 1: Fig. 1

Abstract

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STUDY OF THE SURFACE PROPERTIES OF CRYSTALLINE TITANIUM DIOXIDE

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In numerous studies of adsorption on titanium dioxide, questions concerning the nature of the surface have not been specially investigated. The authors (^{1,2}) consider the adsorption centers on the surface of TiO_2 to be lattice ions and, on this basis, calculate the energy of the van der Waals interaction of the adsorbed molecule with the ions, which they compare with the experimentally determined heat of adsorption. Considering dehydration and dehydrogenation reactions in the presence of TiO_2 as a catalyst, the authors (^{3}) also believe that the active centers are the O and Ti ions of the surface. On the other hand, studies (^{4}) of the irreversible adsorption of water vapor on titanium dioxide indicate that, in addition to physical adsorption of water, hydration processes are possible on the surface. The presence in titanium dioxide of a small amount of water not removed even at high temperatures is indicated by data (^{5}) on loss in weight upon ignition. However, the nature of this water in (^{5}) was not revealed. Hydration of the surface can substantially change the character of adsorption interactions as compared with the case of purely electrostatic and dispersion interactions considered in (^{1,2}). In all the works cited ($^{1-4}$), quantitative determinations of the degree of hydration of the surface were not carried out.

Fig. 1. Dependence of the structural-water content in TiO_2, calculated per unit mass (a), per unit surface area (v), and of the specific surface area (b), on the temperature of treatment of the sample.

In the present work we set ourselves the aim of investigating the degree of hydration of the surface of titanium dioxide subjected to various temperature treatments. In addition, measurements were made of the adsorption of water vapor. The latter, as was shown in (^{6}), is a sensitive indicator of the state of the surface. The few studies ($^{7-9}$) of the specific adsorption of water vapor on titanium dioxide were not accompanied by analysis of the surface of the sample on which the adsorption measurements were carried out. The object of investiga-

Fig. 2. Specific isotherms of primary adsorption on TiO_2 samples evacuated at 25° (1), 150° (2), and 260° (3), quartz kv-5 at 25° (I), and silica gel K-2 at 25° (II) (^{10}). The black symbols correspond to secondary adsorption.

Figure 2: Fig. 2. Specific isotherms of primary adsorption on TiO_2 samples evacuated at 25° (1), 150° (2), and 260° (3), quartz kv-5 at 25° (I), and silica gel K-2 at 25° (II) (^{10}). The black symbols correspond to secondary adsorption.

tion was a low-temperature modification of titanium dioxide—anatase—obtained by combustion of $TiCl_4$. To obtain maximum hydration of the surface, the sample was first kept for a long time in saturated water vapor. Measurements of the adsorption of water and nitrogen vapor were carried out on a volumetric adsorption apparatus. The specific surface areas were determined by the BET method from low-temperature adsorption of nitrogen. To determine structural water, the water released upon ignition of the sample was frozen out; the pressure of the noncondensed gases was determined, and then the total pressure of the gas and thawed water was determined on the volumetric apparatus. The results are shown in Figs. 1 and 2.

As is evident from Fig. 1c, the content of structural water per unit surface area of titanium dioxide evacuated at room temperature is very high. In terms of the degree of hydration, the TiO_2 surface approaches the surface of quartz (kv-5, degree of hydration 11.5 $\mu M/m^2$ (^{10})) treated under the same conditions. In the calcination-temperature interval 25–400°, the content of structural water, referred to unit mass of adsorbent (Fig. 1a) and to unit surface area (Fig. 1c), drops sharply. Titanium dioxide in this temperature interval loses three times more water than quartz (kv-5). The specific surface area increases somewhat as the temperature rises to 460° (Fig. 1b). One reason for this may be the liberation of part of the surface due to the removal of surface hydrate from surface defects and dislocations. A small increase in specific surface area at these temperatures was observed on films of titanium dioxide (^{11}). Adsorption of water vapor on a sample evacuated at 25° is reversible (Fig. 2).

Fig. 2. Specific isotherms* of primary adsorption on TiO_2 samples evacuated at 25° (1), 150° (2), and 260° (3), quartz kv-5 at 25° (I), and silica gel K-2 at 25° (II) (^{10}). Black symbols correspond to secondary adsorption.

It should be noted that the reproducibility of the initial state of the titanium dioxide surface is considerably poorer than for silica samples (^{6}); it depends substantially on the duration of evacuation of the sample. Apparently, this is also connected with the low stability of the surface hydrate of TiO_2. As is evident from Fig. 2, the reversible isotherm on titanium dioxide is very close to the corresponding isotherm on quartz having almost the same surface hydration (^{10}). At a high water content on the surface, the differences in the adsorption capacity of the oxides of titanium and silicon are smoothed out. Adsorption of water vapor on such surfaces is mainly due to the formation of hydrogen bonds between the adsorbed water molecules and the structural water on the surface. The supposition that the centers of adsorption of water on the TiO_2 surface are hydroxyl groups has been expressed by a number of authors (^{4}, ^{11}, ^{12}); however, no experimental confirmations of their existence or estimates of their quantity have been given. Recently (^{13}), bands of valence vibrations of OH groups and deformation vibrations of water were found in the IR absorption spectrum measured on TiO_2 films heated in the temperature interval 25–190°.

With an increase in the treatment temperature of the samples from 25 to 260°, the specific values of primary adsorption in the initial part of the isotherm increase (Fig. 2). Earlier, in studying the adsorption of water vapor on films of titanium dioxide, the authors (^{11}) also noted an increase in adsorption activity with increasing treatment temperature of the sample. From Fig. 2 it is evident that the isotherm on the TiO_2 sample calcined at 260° is almost three times higher than the corresponding isotherm on silica gel K-2, which has practically the same value of the degree of hydration (^{6}). After holding the samples for 2 days in saturated water vapor, as in work (^{4}), irreversible adsorption was observed. The values of irreversible adsorption increase with increasing treatment temperature of the samples (150°: 6.4 μM/m^2; 260°: 7.75 μM/m^2). In the temperature range considered, the values of irreversible adsorption on TiO_2 exceed the corresponding values for crystalline silica by more than 5–10 times (^{10}). The processes of dehydration and rehydration are reversible. As is evident from Fig. 2, the initial portions of the secondary-adsorption isotherms on the sample calcined at 260° fit satisfactorily onto the reversible isotherm for the initial sample. It is interesting to note that rehydration of the surface dehydrated at the considered

···temperatures of the samples proceeds completely even at low vapor pressures. As is seen from Fig. 2, practically at zero pressure the adsorption isotherms on samples treated at 150 and 260° reach values close to the above-noted magnitudes of irreversible adsorption. No noticeable decrease in the rate of absorption of water vapor in this part of the isotherm was observed, in contrast to the rehydration of calcined silica gels, where the rehydration process at low pressures proceeded extremely slowly (^{14}). The ease with which the surface gives up its water and is rehydrated again indicates the absence of any substantial rearrangement of the surface lattice in this temperature range.

With an increase in the calcination temperature above 460°, the specific surface area of the sample undergoes a sharp decrease. A considerable reduction of the surface at high temperatures was observed earlier in works (^{3,15}). The authors (^{3}) see the cause of such a reduction in a phase transformation occurring in the sample. As is known, the phase transition of the low-temperature modification of TiO_2—anatase—into the more stable modification—rutile—takes place at high temperature. In the literature (^{16}) various values are given for the temperature of this transition (from 825 to 1000°). The authors (^{3,5}) justly note that the rearrangement of the lattice into the rutile structure begins on the surface at considerably lower temperatures*. In the temperature interval corresponding to the fourfold abrupt change in specific surface area (Fig. 1b), the content of structural water in 1 g of the sample decreases only slightly (Fig. 1a). The content of structural water calculated per unit surface area, however, increases somewhat (Fig. 1c). The observed increase in the concentration of structural water on the surface is probably connected with the rearrangement of the anatase surface into the denser rutile structure. It should be noted that at these same temperatures sharp changes were observed in the catalytic activity and selectivity of catalysis on TiO_2 (3). Our experimental results agree well with the data (3) and confirm the view of the authors (3) concerning the role of polymorphic transformations in TiO_2 on its physicochemical surface properties. These data show that surface properties are a sensitive indicator of phase transformations occurring in the solid.

With an increase in the calcination temperature above 600°, further dehydration of the surface occurs. At a calcination temperature of 400° the TiO_2 sample begins to turn noticeably gray. In the dehydration products, a small amount (0.2-0.3 μM/m^2) of gas is then found which does not freeze out in a trap with liquid nitrogen. As shown in investigations (15,18), during calcination of TiO_2 oxygen is evolved, and, conversely, oxygen can be absorbed by the sample at high temperatures. The authors (15) believe that at high temperatures oxygen is evolved as a result of the transition of TiO_2 into titanium oxide TiO. Chemical analysis of our sample calcined at 1100° showed the presence of about 0.3% trivalent titanium; ions of divalent titanium, in contrast to (15), were not detected. Measurements (19) of magnetic properties showed that upon reduction of TiO_2 a fairly high concentration of Ti^{3+} ions is formed on the surface. The latter is a constituent of the natural mineral anosovite (20,21).

At present it is difficult to give any complete interpretation of the nature of the water evolved from titanium dioxide during its calcination. The authors (5) call the water contained in titanium dioxide "osmotically" bound water. However, dissolution of water in the dense lattice of anatase seems unlikely. Crystallohydrate forms in the anatase–rutile series are not known. A surface origin of the water evolved from TiO_2 is more probable. This is indicated by the absence of a retarded kinetics of absorption of water, which occurs during the diffusion of vapor into the lattice of the solid. Ti atoms in the structure of TiO_2 have coordination number 6. At the surface the coordination sphere of the titanium-oxygen octahedra will be unsaturated. According to (22), optimal screening of Ti ions can be effected, in particular, both by saturating them with valence-bound hydroxyl groups and by water molecules, as occurs in the case of the oxides SiO_2 and Al_2O_3 (10, 17). As the temperature is raised during calcination of the sample, coordination water will be removed first. With a further increase in temperature, when a phase transition begins at the surface, accompanied by deformation and then rearrangement of the anatase lattice (3), hydroxyl groups more strongly bound

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* In the study of the phase transition γ-Al_2O_3 into α-Al_2O_3 it was shown that the transition begins on the surface at considerably lower temperatures than in the bulk (17).

to the surface will also be removed. In the region of high temperatures, the decrease in the degree of hydration of the surface may also be connected to some extent with a change in the valence of the Ti^{4+} ion. The presence of structural water on the surface up to the temperatures at which catalytic processes proceed must be taken into account when considering the elementary catalytic act. It is possible that, along with the schemes considered in ([3]) for the catalytic reactions of alcohol decomposition on surface oxygen and titanium atoms, the alcohol dehydration reaction may also proceed by the formation of surface ethers upon interaction of alcohol molecules with surface hydroxyls, as, for example, occurs in reactions of alcohol dehydration on aluminosilicates ([23]). Ether compounds of Ti are well known. In the theoretical calculations of the energies of adsorption interactions, which the authors ([1], [2]) compared with the values of heats of adsorption measured on samples (treated at comparatively high temperatures), the hydration processes occurring on the surface and changes in the valence of some of the Ti^{4+} ions were not taken into account. It should be noted that treating the adsorption energy as local interactions of an adsorbed molecule with ions of the TiO_2 lattice is hardly rigorous. In the case of TiO_2, which is a semiconductor ([18]), the adsorbed molecules and the lattice of the adsorbent must be considered as a single quantum-mechanical system ([24]).

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