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PHOTOSORPTION OF HYDROGEN ON TITANIUM DIOXIDE

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The study of the photosorption of hydrogen on titanium dioxide was carried out in an apparatus similar to that described previously ([1]); however, in order to improve purity, instead of the mercury seal separating the working vessel from the pumping and gas-admission system, a brass valve with a fluoroplastic seal was used. The pressure in the working vessel was measured with a Pirani gauge with automatic recording. The maximum sensitivity of the manometer for hydrogen was about 1×10^{-4} torr over the instrument scale; for oxygen and water vapor, about 1×10^{-3} torr over the scale; the noise level was approximately 1% of the measurement limit. The sample was illuminated with an SVD-120 mercury lamp with a mirror condenser or with a light-intensity monochromator. A powdered titanium dioxide sample weighing $0.03 \div 0.04$ g was poured into a flat cuvette of uviol glass measuring $1 \times 10 \times 20$ mm^3 and was usually conditioned for 3 hours at 350–400°C in a vacuum of 1×10^{-6} torr. Electrolytic hydrogen and oxygen obtained by thermal decomposition of potassium permanganate were used for adsorption measurements; in most experiments, the oxygen for calcining the samples was obtained by evaporation of liquid oxygen.

Chemically pure titanium dioxide from the "Krasnyi khimik" plant, from two different batches, was used as the samples. In all, 6 samples were studied: 2 samples without any additional treatment; 2 samples before and after additional calcination in oxygen (0.5 atm, 350°, 2 hours, followed by the usual conditioning to remove adsorbed oxygen); and 2 samples only after calcination in oxygen. Apparently, calcination in oxygen plays an essential role, since photosorption of hydrogen was observed only on samples subjected to such calcination. Since the character of the photosorption was qualitatively the same in all cases, a more detailed study of it was carried out on only one of the samples, this sample being placed in a cuvette equipped with silver electrodes for measuring resistance (MOM-3 megohmmeter together with a PS1-02 self-recording potentiometer). At room temperature the resistance of the conditioned sample before calcination in oxygen was approximately 3×10^5 ohm; the resistance of the sample after calcination in oxygen and additional conditioning was approximately 4×10^7 ohm and depended substantially on temperature. No photoconductivity could be detected in this sample; the slight decrease in the sample resistance upon

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Fig. 2. Dependence of the average rate of photosorption on the resistance of the sample, varied by adsorption of oxygen. Resistance $R > 10^{11}$ ohm is attained upon saturation of the sample surface with adsorbed oxygen

Figure 2: Fig. 2. Dependence of the average rate of photosorption on the resistance of the sample, varied by adsorption of oxygen. Resistance $R > 10^{11}$ ohm is attained upon saturation of the sample surface with adsorbed oxygen

illumination observed in the experiment is, in this case, explained by heating of the sample by the light. No change in resistance upon admission of hydrogen (usually about 1×10^{-3} torr) was detected either; moreover, adsorption of hydrogen at room temperature in the absence of illumination is not observed, unless it occurs instantaneously at the moment of admission.

Illumination of the sample in the presence of hydrogen leads to a sharp irreversible drop in pressure (Fig. 1). No change in the resistance of the sam-

the sample is still not detected. From Fig. 1 it is seen that the photosorption of hydrogen gradually approaches saturation; pumping at room temperature and introducing a new portion of hydrogen do not restore the photosorption, but brief heating of the sample to 400° is sufficient for its complete restoration. It is essential to note that in this case no evolution of any gases into the volume is observed; consequently, the photosorbed hydrogen cannot be released in the form of hydrogen even upon such heating. It remains to assume that upon heating the photosorption centers are freed either as a result of hydrogen migration over the grain surface from illuminated sites to unilluminated ones, or as a result of diffusion into the crystal lattice, or as a result of reaction with the surface of titanium dioxide with formation of water, which, however, in such small amounts in a well-degassed working vessel, at the indicated sensitivity of the manometer, cannot be detected.

Fig. 1. Typical barogram of hydrogen photosorption on titanium dioxide. $p_0 \simeq 10^{-3}$ torr

Fig. 2. Dependence of the average rate of photosorption on the resistance of the sample, varied by adsorption of oxygen. Resistance $R > 10^{11}$ Ω is attained upon saturation of the sample surface with adsorbed oxygen.

A calculation shows that, when the sample is illuminated with strongly absorbed ultraviolet light, when it may be considered that the dimensions of the sample surface participating in photosorption differ little from the geometrical dimensions of the illuminated cuvette surface (allowing for roughness), saturation occurs upon filling 0.001–0.01 of a monolayer. This circumstance does not permit one to assert with certainty that hydrogen photosorption occurs specifically on the surface of titanium dioxide and not on its defects. Preliminary experiments with illumination of the sample by individual lines of the mercury spectrum in the region 313–577 mμ show that the spectral characteristic of photosorption has a distinct maximum at the edge of the intrinsic absorption band of titanium dioxide (about 400 mμ), so that titanium dioxide in the phenomenon described at least plays the role of a sensitizer.

To prove the nonthermal nature of the photosorption, a series of experiments was carried out at different temperatures in the interval 0–200°, as a result of which it was established that, as the temperature is raised, the rate of photosorption decreases. In addition, heating of the sample equivalent to its heating under illumination causes no change in pressure (the resistance of the sample served as the measure of temperature in this case).

On the basis of the electronic theory of photoadsorption processes(2), one may expect that one of the conditions necessary for observing photoadsorption is a definite ratio of the concentrations of free current carriers of different signs in the near-surface layer. By changing this ratio in one way or another, one may hope to change, if not the sign, then in any case the magnitude of the observed phenomena. We attempted to change this ratio by preliminary adsorption of oxygen. By careful admission of oxygen the resistance of the sample could be

was arbitrarily increased from 4×10^7 ohms to values greater than 1×10^{11} ohms (the limit of our measurement capability), i.e., by at least four orders of magnitude. Although such a change in resistance undoubtedly corresponds to a significant decrease in the concentration of free electrons, no change in the character of the photosorption of hydrogen is observed in this case (Fig. 2). It follows from this that, first, the change in the electronic state of the surface in our experiments did not affect the photosorption of hydrogen; second, the photosorption of hydrogen is not a photochemical reaction of hydrogen with adsorbed oxygen.

The independence of this process from the electronic state of the surface and its complete irreversibility make it difficult to explain from the point of view of the theory of photoadsorption (2). Therefore, the decrease in the pressure of hydrogen over titanium dioxide under illumination observed by us is called not photoadsorption, but photosorption, thereby emphasizing that the mechanism of the phenomenon remains as yet unknown.

It should be noted that the literature (3) reports the sorption of hydrogen on thorium dioxide upon illumination of the system with a cold mercury quartz lamp in the presence of mercury vapor. In that case the phenomenon is explained (3,4) by mercury-vapor-photosensitized dissociation of hydrogen with subsequent strong adsorption. The photosorption of hydrogen on titanium dioxide observed by us undoubtedly has a different mechanism, since the presence of mercury vapor in the working volume in our experiments is unlikely and, moreover, photosorption is observed equally successfully both when the sample is illuminated with a mercury lamp and with an incandescent lamp.

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