Spectral and Temperature Dependences of the Quantum Yield of the Photoadsorption of Simple Gases on Dispersed Titanium Oxide

A. V. Emelin, G. N. Kuz'min, D. Purevdorzh, and I. G. Shenderovich

Research Institute of Physics, St. Petersburg State University, Petrodvorets, 198904 Russia

Received November 3, 1995

Abstract—The dependences of the quantum yield of oxygen, hydrogen, and methane photoadsorption on the energy of exciting photons (1.7–4.4 eV) and temperature (100–700 K) are investigated using the "ideal black body" technique on a TiO_2 sample of the rutile modification. A band of photoadsorption activity with a maximum at 3.7 eV is revealed for the first time.

INTRODUCTION

Despite the fact that the properties of titanium dioxide have been comprehensively studied for a long time, so far there is no unified standpoint concerning the mechanism of the photocatalytic processes occuring on it. One possible way to elucidate the nature of these processes is to investigate the photostimulated adsorption of alien molecules on the catalyst surface as the necessary (as a rule) first stage of any photocatalytic reaction.

This work aims at measuring the quantum yield (φ) of photoadsorption that is one of the quantitative characteristics of the process. The quantum yield of photoadsorption comprises the ratio of the experimental maximum (virtually initial) photoadsorption rate (dQ/dt) to the intensity of photon absorption (dN/dt):

$$\varphi = \frac{dQ/dt}{dN/dt}.$$

However, the quantum yield is often determined by monitoring the incident light because of the difficulties with controlling the losses of light for reflection, dispersion, and transmission, especially in the experiments with dispersed samples. Furthermore, it is implicitly assumed that the zone–zone absorption is active in photoadsorption when the absorption coefficient is rather high and the φ value thus determined is close to the true value. Generally, measurements of the incident light give the lower estimate of the quantum yield, which, however, can markedly differ from the absolute values, thus causing the distortion of the spectral and temperature dependences.

Unfortunately, none of the available methods has a sensitivity permitting investigations of the photoadsorption effects on the single crystal surface because the surface coverage with photoadsorbed molecules does not exceed 10^{-4} monolayers. The quantitative measurements are possible only on dispersed samples using manometry. The photoadsorption rate on such samples is determined either analytically (using the equation of the photoadsorption kinetics) or by the direct differentiation of the photoadsorption barograms.

The more difficult problem encountered when using dispersed samples is measuring the number of absorbed photons that cause the adsorption effect. This problem is usually solved employing diffuse-reflectance spectroscopy (DRS) by determining the absorption coefficient of a virtually nontransparent sample of a sufficient thickness from the equation $K = 1 - R$, where R is the reflectivity. In this case, the absorption intensity is $I_{abs} = dN/dt = KI_{inc}$, where I_{inc} is the intensity of the incident light. The amount of absorbed photons is readily determined by DRS when observing photoadsorption in the fundamental absorption band of the adsorbent when the R coefficient is low (i.e., the K coefficient is high). However, in the region of the intrinsic absorption and near its edge, where noticeable photoadsorption effects are also observed, the reflectivity, on the contrary, is high ($R \approx 0.9$) and the absolute error in its determination, caused largely by the accuracy of the reference calibration, is ~0.05. This suggests that the error in determining the intensity of light absorption by DRS in this spectral region reaches 50%.

Taking into account that measurements of the incident light allows only the approximate estimation of the efficiency of the photoadsorption effect and that the use of DRS to determine the amount of absorbed photons does not provide sufficient accuracy, it was proposed [1–3] to measure the quantum yield of photochemical reactions (including photoadsorption) by monitoring the incident light in the visible and near UV regions. The luminous flux was directed through a small calibrated inlet to the interior cavity of a glass cell made in the form of a Dewar vessel (Fig. 1) with a sample studied placed between its walls. At a sufficient (ideally
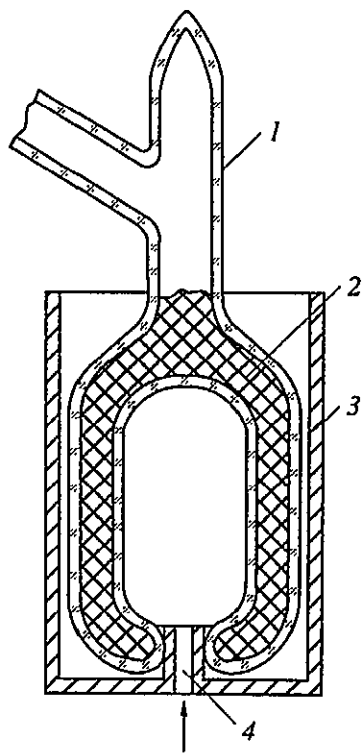
Fig. 1. A cell of the "ideal black body" type: (*1*) a cell, (*2*) a dispersed adsorbent; (*3*) an exterior aluminum screen, and (*4*) a calibrated inlet for introducing light.

infinite) thickness of the layer of the powdered adsorbent and a small (as compared to the geometric sizes of the cell) inlet for light and the absolute transparency of the cell material (quartz), the cell comprises an ideal black body with a sample studied acting as its walls. Thus, the light introduced into the cell (i.e., the incident light), the intensity of which is directly measured in the experiment, is virtually completely absorbed by the adsorbent ($K \approx 1$). The small ($\leq 5\%$) error in determining the quantum yield of the photoprocess may be attributed to both the losses of light on the cell walls and the reverse light reflection from the cell.

There are two works reporting the data on the spectral dependences of the quantum yield of the photoadsorption of simple molecules on TiO_2. The effect of hydrogen and methane photoadsorption on rutile (ultra-high purity grade) was examined in [4]. A similar investigation of the photoadsorption of oxygen and carbon oxide on anatase (ultra-high purity grade, A-2-14), approximately 2/3 of which was converted into rutile upon thermal treatment, was performed in [5]. Unfortunately, the use of different TiO_2 modifications and different gases in these works did not permit the correct comparison of the results obtained. Moreover, the line light sources (mercury lamps) were used in both works, which in principle limited the observation of the hyperfine structures in the spectrum.

This work was aimed at studying the photoadsorption of O_2, H_2, and CH_4 in a wide spectral region on the

same TiO_2 sample (rutile, ultra-high purity grade, $S_0 = 8$ m²/g) as in [4] using a continuous light source (a xenon lamp). The temperature dependences of the quantum yield of photoadsorption, which had been obtained earlier only for zinc oxide [6, 7], were also determined.

EXPERIMENTAL

The use of a high-vacuum oil-free stainless-steel setup ensured the high degree of removal of organic contaminations from the sample surface, which was attained by the successive oxygen and vacuum treatment for several hours at 770 K, and the sample regeneration between the runs [8, 9].

Oxygen and hydrogen were obtained directly in the setup by the thermal decomposition of potassium permanganate and titanium hydride, respectively. Methane (99.8%) from a standard set of hydrocarbons for chromatographic analysis was used. Prior to admission into the cell, gases were additionally purified by passing through a trap with liquid nitrogen to remove freezable admixtures.

The gas pressure in the reactor was measured with a Pirani gage with a sensitivity of $\sim 5 \times 10^{-4}$ Pa (the maximum sensitivity of determining the rate was 10^{-7} Pa/s).

The optical part contained a light source, a two-lens quartz condenser, and a wide-aperture (1 : 3.5) monochromator on a concave diffraction grating (1200 lines per one millimeter, the maximum energy concentration at a wavelength of 300 nm). This allowed us to perform measurements in the spectral region of 1.7–4.9 eV, the width of the chosen spectral interval did not exceed 0.1 eV at $E_h = 3.0$ eV. A DKsSh-120 lamp was usually employed as a light source, and a DRSh-100-2 lamp was used for measuring weak effects. The intensity of the luminous flux incident on a sample was 10^{12}–10^{13} photon cm⁻² s⁻¹.

Diffuse-reflectance spectra were recorded on a Specord M-40 spectrophotometer using a reference sample of $BaSO_4$. The layer of a dispersed adsorbent (~ 5 mm thick) was placed in a plane quartz cell of a mobile vacuum setup providing the standard procedures of sample purification and recording the diffuse-reflectance spectra without depressurization. The setup construction also permited the precise fixation of the cell with respect to the entrance slit of the measuring unit.

The quantum yields were measured using an "ideal black body" type cell (Fig. 1) made of KU-1 high-grade quartz (≤ 1 mm thick; the outside diameter and height, 21 and 30 mm, respectively; the inner diameter and height, 12 and 22 mm, respectively). In this case, the thickness of the layer of the sample studied was ~ 3 mm. This layer thickness is sufficient [10] for the complete diffuse reflectance even on wide-zone highly dispersed oxides in the region of their transparency. The cell was equipped with an aluminum screen with a calibrated

hole, 2.5 mm in diameter, for introducing the luminous flux.

The thermostatic control system permitted the experiments to be conducted at 100–700 K. The specified temperature was maintained with an accuracy of 0.5 K. The low temperatures were maintained by purging liquid nitrogen vapors through the thermostat. The high temperatures were maintained by using a built-in electric heater.

The experimental setup as a whole ensures the sensitivity of measuring the quantum yield of photoadsorption better than 0.1%.

Between the runs, the sample was regenerated by heating for 1 h in oxygen at 20 Pa and 770 K with further cooling to room temperature and purging O_2. This technique allowed us to obtain a sample in the so-called oxidized state and ensured a good reproducibility of the experimental data. A more detailed description of the experimental setup and procedure is given in [7].

Upon regenerating, the gas studied was admitted into the reaction vessel and the temperature of the run was adjusted. Upon saturating dark adsorption, the initial working gas pressure in the reactor was ~1.5 Pa, which provided the independence of the initial photoadsorption rate from the pressure [2]. Thus, the measured quantum yield actually characterizes the efficiency of the generation of active adsorption sites formed upon localization of the photoinduced carriers on the potential sites.

RESULTS AND DISCUSSION

Figure 2 depicts the spectral dependences of the maximum quantum yield of hydrogen, methane, and oxygen photoadsorption. At room temperature, only donor gases can be photoadsorbed (curves *1* and *2*). The photoadsorption of oxygen at room temperature was detected only at $E_{hv} = 3.7$ eV (it was not, however, recorded in other numerous experiments conducted in our laboratory on the oxidized and thoroughly purified TiO_2 samples). However, the reliably measured photoadsorption of O_2 is observed as the temperature decreases (curve *3*).

The photoadsorption of O_2, H_2, and CH_4 occurs both in the region where the quanta energy is below the width of the band gap of TiO_2 and in the region of intrinsic absorption. In this case, the ϕ value nonmonotonically increases with the energy of exciting photons: there are local maxima on the spectral dependences of the quantum yield of photoadsorption near 3.0 eV for donor molecules and 3.7 eV for the three gases studied.

By and large, the shape of the $\phi(E_{hv})$ dependence for donor gases, the close numerical values of the quantum yields, and the existence of the band at 3.0 eV agree with the data obtained in [4]. However, the qualitative distinction of our results is that the pronounced structure is observed as a band with a maximum at 3.7 eV in the spectral dependences of the quantum yield of the
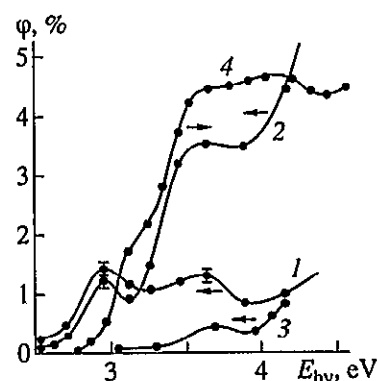

Fig. 2. The quantum yield of (*1*) hydrogen, (*2*) methane, and (*3*) oxygen photoadsorption and (*4*) the Kubelka–Munk function vs. the energy of exciting photons at temperatures, K: (*1* and *2*) 293 and (*3*) 250. The $F(R_\infty)$ function was calculated from the diffuse-reflectance spectra.

photoadsorption of the gases studied in the short-wave region.

It is known [11, 12] that the upper limit of the valent zone of TiO_2 is largely governed by the $2p$ states of the oxygen atom, and the lower limit is determined by the $3d$ states of the titanium atom. The minimum energy required for the formation of a hole in the valent zone and an electron in the conductivity zone due to the electron transfer is ~3.2 eV, which determines the width of the band gap for rutile. The exciton absorption bands, identified in the absorption spectra of single crystals [13, 14], are also observed at the edge of the intrinsic absorption band of titanium dioxide. Thus, it may be thought that the hypothesis [3, 4], relating the band at 3.0 eV in the photoadsorption spectrum to the exciton mechanism of light absorption, is confirmed by the data of [13, 14].

The peak at 3.7 eV may be attributed to the peculiarities of the interzone absorption. According to the theoretical calculations [12, 15–17], a maximum should exist exactly near 3.7 eV in the spectral dependences of the absorption coefficient, the value of which is determined by the character of the state density distribution in the valent and conductivity zones. The nonmonotonous character of the curve at this energy of quanta in the intrinsic absorption region is experimentally verified as well [18].

In this work, the experimental diffuse-reflectance spectra were also obtained. The spectral dependence of the Kubelka–Munk function [19, 20] (Fig. 2, curve *4*) was calculated that corresponds to the spectral dependence of the TiO_2 absorptivity assuming the constancy of the dispersion coefficient [10].

Thus, it is believed that the complex character of the spectral dependences of the quantum yield of photoadsorption in the intrinsic absorption band corresponds to the spectral dependence of the absorptivity. The changes in the absorptivity cause variations in the depth
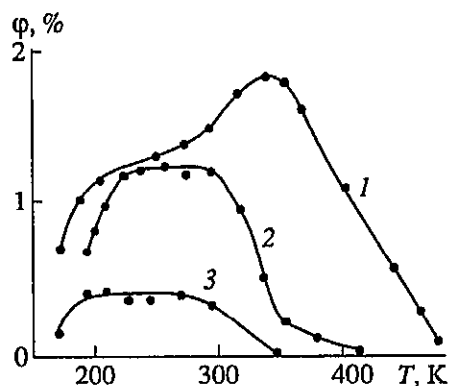
Fig. 3. Temperature dependences of the quantum yield of (*1*) hydrogen, (*2*) methane, and (*3*) oxygen photoadsorption at the energy of exciting photons, eV: (*1* and *2*) 3.0 and (*3*) 3.7.

at which the electron–hole pairs are generated. This changes the probability of the escape of carriers and their localization on the surface of a single crystal, as reflected by the dependences of $\varphi(E_{hv})$. The zone bend occurring near the surface favors the escape of positive holes to the surface, on the one hand, and hampers the approach of electrons to this place, on the other, thus favoring the photoadsorption of donor gases.

The temperature dependence of the quantum yield of hydrogen, oxygen, and methane photoadsorption on TiO_2 was examined in this work for the first time. Figure 3 presents the curves obtained at the energies of quanta corresponding to the maxima on the spectral dependences. The character of the temperature dependences obtained is similar to those obtained on other oxides [7, 21]: the photoadsorption effects are observed at temperatures below 450 K; with decreasing temperature, the quantum yield monotonically increases, then flattens out, and finally drops sharply.

The same temperature dependences are readily observed during the photoadsorption of O_2 and CH_4. In the case of H_2, they are distorted by a maximum at 340 K. We cannot yet explain the peculiar behavior of hydrogen.

The diminution of the quantum yield with decreasing temperature may be attributed to a drop in the free carrier concentration caused by the change in the probability of recombination and carrier scavenging on small traps. This decrease in φ may also be explained by blocking the photoadsorption sites by a large number of physically adsorbed molecules.

The decrease in the quantum yield at elevated temperatures may be associated with the thermal desorption of the photoadsorbed gas, as confirmed by the correlation between our findings and the thermal desorption data reported in [22].

Assuming that the decrease in the quantum yield of photoadsorption in the high-temperature region is described by the Arrhenius equation, we estimated the

activation energies of the photoadsorption processes on rutile. These values were as follows: for hydrogen, –36 and –16 kJ/mol ($T > 350$ K) at $E_{hv} = 3.0$ and 3.7 eV, respectively; for oxygen, –11 kJ/mol (300–350 K) at $E_{hv} = 3.7$ eV; and, for methane, –22 kJ/mol (330–400 K) at $E_{hv} = 3.0$ eV. The negative activation energies are typical of photoadsorption and indicate that the process is not elementary as a whole.

REFERENCES

1. Basov, L.L. and Solonitsyn, Yu.P., USSR Inventor's Certificate no. 387 730, *Byull. Izobret.*, 1973, no. 28.
2. Basov, L.L., Kotel'nikov, V.A., Lisachenko, A.A., *et al.*, *Usp. Fotoniki*, 1969, vol. 1, p. 78.
3. Basov, L.L., Kuz'min, G.N., Prudnikov, I.M., and Solonitsyn, Yu.P., *Usp. Fotoniki*, 1977, vol. 6, p. 82.
4. Solonitsyn, Yu.P., Kuz'min, G.N., Shurygin, A.L., and Yurkin, V.M., *Kinet. Katal.*, 1976, vol. 17, no. 5, p. 1267.
5. Cherkashin, A.E., Volodin, A.M., Koshcheev, S.V., *et al.*, *Usp. Fotoniki*, 1980, vol. 7, p. 86.
6. Basov, L.L., Dolgikh, Yu.K., Polzik, L.K., and Solonitsyn, Yu.P., *React. Kinet. Catal. Lett.*, 1982, vol. 21, no. 3, p. 277.
7. Kuz'min, G.N., Purevdorzh, D., and Shenderovich, I.G., *Kinet. Katal.*, 1995, vol. 36, no. 5, p. 790.
8. Basov, L.L. and Solonitsyn, Yu.P., *Kinet. Katal.*, 1965, vol. 6, no. 4, p. 752.
9. Lisachenko, A.A. and Vilesov, F.I., *Dokl. Akad. Nauk SSSR*, 1967, vol. 176, no. 5, p. 1103.
10. Kortum, G., Braun, V., and Herzog, G., *Usp. Fiz. Nauk*, 1965, vol. 85, no. 2, p. 365.
11. Companion, A.L. and Wyatt, R.E., *J. Phys. Chem. Solids*, 1963, vol. 24, no. 8, p. 1025.
12. Munnix, S. and Schmeits, M., *Phys. Rev. B: Condens. Matter*, 1984, vol. 30, no. 4, p. 2202.
13. Mathieu, H., Pascual, J., and Camassel, J., *Phys. Rev. B: Condens. Matter*, 1978, vol. 18, no. 12, p. 6920.
14. Agekyan, V.T., Berezhnaya, A.A., Lutsenko, V.V., *et al.*, *Fiz. Tved. Tela*, 1980, vol. 22, no. 1, p. 12.
15. Takeuchi, N. and Kanda, S., *J. Spectr. Soc. Jpn.*, 1970, vol. 19, no. 2, p. 141.
16. Hardman, P.J., Raikar, G.N., Muryn, C.A., *et al.*, *Phys. Rev. B: Condens. Matter*, 1994, vol. 49, no. 11, p. 7170.
17. Glassford, K.M. and Chelikowsky, J.R., *Phys. Rev. B: Condens. Matter*, 1992, vol. 45, no. 7, p. 3874.
18. Karakitsou, K. and Verykios, X., *J. Phys. Chem.*, 1993, vol. 97, no. 6, p. 1184.
19. Kubelka, P. and Munk, F., *Z. Techn. Phys.*, 1931, vol. 12, p. 593.
20. Kamat, P.V., *Chem. Rev. B: Condens. Matter*, 1993, vol. 93, no. 1, p. 267.
21. Kuz'min, G.N., Purevdorzh, D., and Shenderovich, I.G., Abstacts of Papers, *Int. Conf. on Radiation Heterogeneous Processes*, Kemerovo, 1995, part 1, p. 184.
22. Kuzmin, G.N., Knat'ko, M.V., and Kurganov, S.V., *React. Kinet. Catal. Lett.*, 1983, vol. 23, no. 3/4, p. 313.