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

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Abstract – The dependence of the quantum yield of oxygen and methane photoadsorption on the energy of incident photons (1.7 - 4.9 eV) and the temperature (100 - 700 K) was investigated further with the use of a manometric technique and a sample of ZnO possessing the properties of the black body, in the interior of which exciting light was introduced. A band of photoadsorption activity with respect to O_2 and CH_4 with a maximum at 3.25 eV was first observed, and the dependence $K_0(T)$ was found for methane. As the temperature decreases, K_0 increases for both gases, and this dependence has a stepwise character up to 150 K for O_2 and 250 K for CH_4. As the temperature decreases further, the corresponding K_0 value drops sharply.

INTRODUCTION

Studies of the photoadsorption of gases on metal oxides conducted by various authors [1 - 7] showed that the quantum yield defined as a ratio of the number of photoadsorbed molecules to the number of absorbed photons is a characteristic value that allows for a comparison between the efficiencies of this process in different heterogeneous systems.

A study of the photoadsorption effects by the manometric method has to be performed with dispersed samples, because the sensitivity of instruments employed for measuring even very low gas pressures is insufficient to work with single crystals. However, when such adsorbents are exposed to light outside the region of their intrinsic absorption, the losses of light due to the diffuse reflectance on the samples are difficult to control. Therefore, Basov and Solonitsyn [8] proposed a technique for measuring the quantum yield of photoadsorption: the examined dispersed sample is placed as a thick opaque layer between the walls of a glass cell made in the form of a narrow-necked Dewar flask in the interior space of which a light flux is introduced. Because of this, the question of what part of the incident light is absorbed by the sample can be unambiguously solved: because the losses of light for scattering or transmition through the thick layer of the sample are eliminated, the total light entering the cell will be absorbed by the adsorbent.

Using this technique, the photoadsorption of oxygen, hydrogen, and methane on a number of oxides was studied. The values of quantum yields that characterized the most active, initial state of the adsorbents were determined [2]. Because the kinetics of photoadsorption for various gas–solid systems is, in general terms, similar (the rate increases at the initial stage,

then the maximum rate of adsorption is reached, and, finally, the rate of the process gradually decays to zero), it is convenient in practice to find the value of the quantum yield as a ratio of the maximum rate of the photoadsorption of gas molecules at the surface to the rate of the absorption of light quanta

$$K = \frac{dQ/dt}{dN/dt},$$

where Q is the number of adsorbed gas molecules and N is the number of light quanta absorbed by the sample within the time interval t.

In these measurements, the value of the rate can be determined either analytically by the equation approximating photoadsorption or graphically from the barogram of the process. That is, the problem reduces to determining two reliably measured experimental quantities: the number of photons delivered to the cell and the number of adsorbed molecules. The latter value can be estimated by measuring the change in the gas pressure at a given value of the working volume.

It is evident that the experimentally determined value of K_0 is the average over the entire surface of the sample. However, as shown in [2], the measured quantum yield is independent of the value of the actually irradiated surface area and its illuminance if the intensity of the light flux introduced into the interior space of the cell does not exceed a certain value (for ZnO, about 10^{13} photon cm^{-2} s^{-1}).

Up to now, the photoadsorption properties of type M-1 zinc oxide have been the most thoroughly studied [1, 2]. In particular, the spectral dependences of the quantum yield of oxygen and methane photoadsorption were determined at room temperature in the energy range of exciting quanta 2.0 - 3.4 eV. These measurements were performed using the discrete radiation of a mercury

lamp, which eliminated the possibility of observing the fine structure of the spectrum. The temperature dependence of the photoadsorption effect was studied only for O_2 in the temperature range 200 - 500 K [9].

This work continues the experiments with the same sample of zinc oxide with the aim of examining the spectral dependences of the quantum yield of oxygen and methane photoadsorption in a wider energy range of exciting quanta with the use of a light source of continuous radiation and to study the temperature dependence of the quantum yield of O_2 photoadsorption in a wider temperature range. The problem of studying the temperature dependence of the quantum yield of CH_4 photoadsorption was first posed as well.

EXPERIMENTAL

The setup designed for conducting these experiments included a high-vacuum unit, an optical unit, and a system of the thermostatic control of a sample. The vacuum setup was made of stainless steel with the use of greaseless parts and an oil-free evacuation system, which enabled the thorough purification of a sample from biographic organic impurities. The optical unit permitted measurements to be conducted over the spectral range 1.7 - 4.9 eV, and the width of the derived spectral range was 0.1 eV at $E_{hv} = 3.0$ eV. A DKsSh-120 lamp was used as a light source. The cryostat temperature was set and maintained in the course of the experiment to an accuracy of 0.5 K by purging liquid nitrogen vapor through the cryostat or by heating with a built-in electric heater, which ensured the experiments to be conducted in the temperature range 100 - 700 K. A dispersed sample was placed in a quartz cell, 25 mm in height and 20 mm in outside diameter; the layer of the powder between the walls of the cell was 3 mm thick, and the diameter of the inlet calibrated hole was 2.5 mm.

A sample was pretreated according to the following procedure. Powdered ZnO was preheated in air at a temperature of 770 K for a few hours and then placed in the cell. Thereafter, the sample was treated in oxygen for a length of time (tens of hours) at a pressure of about 100 Pa and a temperature of 770 K with evacuation and replacement of O_2 from time to time. The sample was considered to be sufficiently purified if the amount of gas evolved on heating in the course of thermal desorption performed after oxygen photoadsorption was equal to the amount of photoadsorbed oxygen, and there were no products frozen out at a temperature of liquid nitrogen. As was previously shown by mass spectrometry [10, 11], this procedure of sample pretreatment actually ensured the degree of purification that was sufficient to obtain the reproducible results.

The regeneration of a sample between experiments included heating in oxygen at a pressure of 20 Pa and a temperature of 770 K for about 1 h; then the ZnO was cooled down to the experimental temperature. After such a treatment, oxygen was evacuated, and a working

portion of the test gas was admitted. This order was chosen because of the necessity of reducing the dark adsorption of the analyzed gas and its temperature dependence to a minimum.

In photoadsorption experiments, the initial working pressures of O_2 and CH_4 in the volume of the reactor after the saturation of dark adsorption were 1.7 and 1.3 Pa, respectively. According to [12], this ensured the independence of the initial rate of photoadsorption from the pressure.

In our experiments, the maximum rate of photoadsorption was determined by the graphical differentiation of the barograms.

RESULTS AND DISCUSSION

Figure 1 demonstrates the spectral dependences of the quantum yields of oxygen and methane photoadsorption obtained in our experiments. At room temperature, the dependence of the quantum yield of O_2 photoadsorption (curve *1*) is bell-shaped with a maximum at 2.85 eV. At a lower temperature (190 K, curve *2*), the bell is broadened from the side of high-energy quanta, and the quantum yield becomes independent of the energy of exciting photons at $E_{hv} > 3.4$ eV. The spectral dependence $K_0(E_{hv})$ for methane at room temperature takes a more complicated form (curve *3*). It exhibits a slightly pronounced maximum at about 2.5 eV and an extremely intense (100%) peak at 3.25 eV, and a new rise in photoadsorption activity begins at $E_{hv} > 3.7$ eV.

As the energy of exciting quanta increases, especially in the region of intrinsic absorption, the rapid saturation of photoadsorption is observed for both gases. This increases the error in determining the process rate and, hence, increases the error of determination of the quantum yield. Nevertheless, one can definitely infer that the quantum yield of methane photoadsorption increases as the photon energy rises, whereas the yield in the case of oxygen either remains unchanged (at low temperatures) or falls down.

At certain temperatures, the experiments were also performed in which the sample was irradiated with light quanta of various energy without regenerating the sample between experiments. In this case, the spectrum was scanned from the long-wave region to the short-wave region in order to eliminate photosensitized photoadsorption, which can proceed [13, 14] after the preliminary ultraviolet irradiation of the adsorbent. Such an experimental procedure revealed a few well-resolved maxima in the spectral dependence $K_0(E_{hv})$. Thus, for oxygen photoadsorption, three peaks was observed with maxima at 2.2 and 2.85 eV and a maximum at 3.25 eV appearing at lower temperatures. In the case of methane photoadsorption, there are two such peaks with maxima at about 2.5 and 3.25 eV.

The results of these experiments indicate that there are three bands in the dependence $K_0(E_{hv})$ for oxygen photoadsorption. Furthermore, these data permit us to
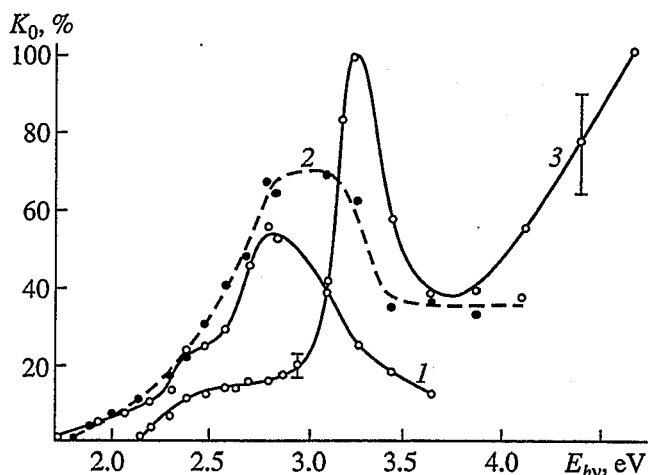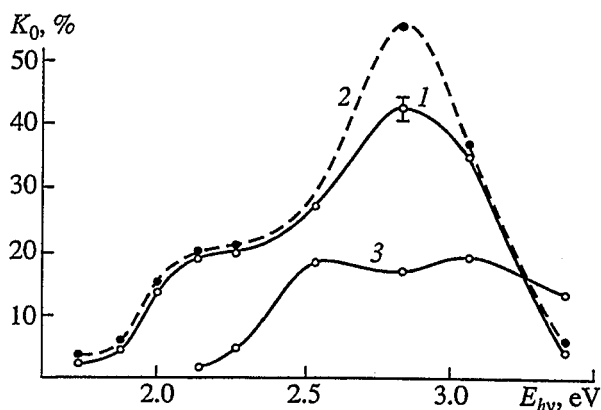
K_0, %

Fig. 1. Dependence of the quantum yield of (*1* and *2*) oxygen and (*3*) methane photoadsorption on zinc oxide on the energy of exciting photons at different temperatures, K: (*1*) 300, (*2*) 190, and (*3*) 300.

K_0, %

Fig. 2. Dependence of the quantum yield of (*1* and 2) oxygen and (*3*) methane photoadsorption on zinc oxide on the energy of exciting photons at different temperatures, K (according to [2, 9]): (*1*) 300, (2) 207, and (*3*) 300.
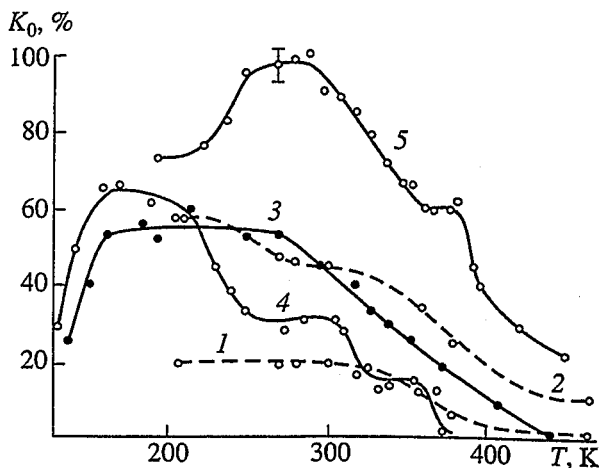
K_0, %

Fig. 3. Temperature dependence of the quantum yield of (*1 - 4*) oxygen and (*5*) methane photoadsorption on zinc oxide for different energies of exciting photons E_{hv}, eV: (*1*) 2.15, (2) 2.84, (*3*) 2.7, (*4*) 3.25, and (*5*) 3.25. Curves *1* and *2* are taken from [9].

explain the broadening of the peak at 2.85 eV with lowering temperature (Fig. 1, curve 2) by the sharp enhancement of the band at 3.25 eV. The fact that the band intensity at 3.25 eV actually increases (twice) as the temperature decreases from room temperature to 190 K can clearly be seen from curve *4* in Fig. 3.

Comparing our results with the results of [2, 9] presented in Fig. 2, one can note that, in both cases, the bands with maxima at 2.2 and 2.85 eV for oxygen and 2.5 and about 3.2 eV for methane are present in the spectral dependences of the quantum yields of photoadsorption. The fact that the band at 3.25 eV was not observed in the spectral dependences of the quantum yield of oxygen photoadsorption presented in the cited work can be explained by the use of a discrete light source in the previous work, because of which the region of E_{hv} from 3.05 to 3.4 eV could not be explored in detail.

We attach no particular significance to the differences in the quantum yields because these differences are not of crucial importance within the scope of this work. It is a different matter that they can be explained both by specific features pertinent to the procedure of determining the maximum rates of photoadsorption and by many other factors, including, for example, some differences in the pretreatment of samples and the resulting difference in the state of their surface.

Figure 3 demonstrates the temperature dependence of the quantum yield for oxygen and methane photoadsorption at the energies of exciting photons corresponding to the maxima in the dependences $K_0(E_{hv})$.

The character of the temperature dependences of the quantum yield is qualitatively similar for both gases and for all studied quantum energies: the measured photoadsorption effects are observed at temperatures below 450 K; as the temperature further decreases, the quantum yield of photoadsorption increases stepwise, reaching a flat maximum, where the quantum yield does not vary with temperature; then K_0 sharply decreases (starting with a temperature of 250 K for methane and with 150 K for oxygen). The drop in K_0 at low temperatures is explained, in our opinion, by the sharp enhancement of dark adsorption. Unfortunately, we could not follow the course of this drop in the direction of low temperatures, because additional gas adsorption, which depends on slightest temperature fluctuations and manometric measurements, are hardly possible in the experiments on photoadsorption under such conditions.

It is interesting to note that the greater the number of steps in the curve $K_0(T)$, the greater the energy of the exciting photons. It should also be noted that the regions in which the quantum yield does not vary with temperature coincide for oxygen and methane at $E_{hv} = 3.25$ eV.

It follows from the experimental data that the temperature dependence of the quantum yield of photoadsorption is well-described by the equation $K_0 = K_{0i}\exp(-E_{ai}/kT)$, where K_{0i} is the quantum yield at the

ith step and E_{ai} is the activation energy of the process. On this basis, we found that $E_a = -(18 \pm 2)$ kJ/mol for methane photoadsorption in the temperature range 380 - 450 K at $E_{h\nu} = 3.25$ eV, and $E_a = -(6.6 \pm 0.7)$ kJ/mol in the temperature range 300 - 370 K. For oxygen photoadsorption under exposure to quanta of the same energy, we found $E_a = -(20 \pm 2)$ kJ/mol in the temperature range 310 - 340 K, and $E_a = -(7.2 \pm 0.3)$ kJ/mol in the temperature range 220 - 280 K. For oxygen photoadsorption at $E_{h\nu} = 2.7$ eV in the temperature range 280 - 420 K, we obtain $E_a = -(18 \pm 2)$ kJ/mol. These values are in good agreement with the results of [9].

On the basis of the available experimental data, it was proposed previously [2] to divide photoadsorbents conventionally into two groups. For example, titanium and tin oxides were assigned to the first group, considering that they are characterized by low photoadsorption activity beyond the long-wave region of intrinsic absorption, an increase in this activity upon shifting into the region of the band-to-band absorption of the adsorbent, and the dependence of the effect's magnitude on the height of the surface potential barrier. ZnO, MgO, BeO, and Al_2O_3 were assigned to the adsorbents of the second group on the basis that all of these oxides exhibit high photoadsorption activity upon irradiation far beyond the long-wave region of the intrinsic absorption band and low activity in the range of intrinsic absorption.

Observing the drop in the quantum yield of photoadsorption on ZnO upon shifting into the region of intrinsic absorption (Fig. 2), and considering this oxide to be inactive in this region, the authors of [2] did not examine photoadsorption under the action of high-energy photons.

However, the spectral dependences of the quantum yields of oxygen (at a low temperature) and methane (at room temperature) photoadsorption on ZnO obtained by the authors indicate that photoadsorption is sufficiently efficient not only outside the intrinsic absorption band of the oxide. Thus, at $E_{h\nu} > 3.4$ eV, the quantum yield of oxygen photoadsorption is constant and amounts to about 37%, and that of methane photoadsorption increases monotonically, reaching 100% (Fig. 1, curves 2 and 3).

It is believed that the interband absorption of zinc oxide is active with respect to photoadsorption. The mechanism of photoadsorption in this region is associated with the fact that the domain of free-carrier generation is flattened against the surface of the microcrystal, with an increase in the probability of escaping the free carriers to the surface, and with a high surface barrier on oxidized samples, as was suggested previously [2].

Thus, the spectrum of photoadsorption activity under irradiation by photons with energies below the band gap is superimposed on the photoadsorption effect associated with irradiation in the region of the fundamental absorption band of ZnO. Whereas the effects of photoadsorption on zinc oxide in both spectral regions are comparable in their magnitude, photoadsorption stimulated by irradiation in the region of intrinsic absorption distinctly predominates in the case of titanium dioxide, which is close to zinc oxide in its optical properties.

On the basis of the spectral and temperature dependences of the quantum yield of oxygen and methane photoadsorption on ZnO obtained in this work and the available literature data, it is difficult to draw any definite conclusions that directly concern the surface adsorption sites. More reasonable conclusions can be made only on the mechanisms of light absorption that are responsible for the formation of adsorption sites. In the region of intrinsic absorption, the mechanism of photoadsorption is apparently very close to the model proposed in [15]. In this model, the nonequilibrium charge carriers created by illumination and localized at biographic surface defects are considered to be the sites that participate in adsorption.

The spectrum of photoadsorption activity observed outside the region of zinc oxide intrinsic absorption can be associated either with absorption by defects or impurities or with excitonic or specific surface absorption. In particular, the band of photoadsorption activity at a photon energy of 3.25 eV is likely due to excitonic absorption [16, 17]. However, the possibility that this band is generated by the photodissociation of surface bridge bonds [4]

$$\underset{Zn\cdots Zn}{\overset{O}{\diagup\diagdown}} \quad \xrightarrow{h\nu} \quad \underset{Zn^{\pm}\cdots Zn}{\overset{O^-}{\diagdown}}$$
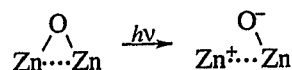
must not be ruled out.

In a number of works [3, 17], the absorption of quanta with an energy of 3.3 eV was associated with the photoexcitation of lithium centers; however, in our opinion, this conclusion makes sense only for samples obtained by the hydrothermal method, when lithium is brought into ZnO as an impurity.

Up to now, the maxima at photon energies of 2.2, 2.5, and 2.85 eV observed in the spectral dependences of the quantum yields of photoadsorption cannot be unambiguously assigned to specific sites as well. Thus, a signal, which reached a maximum value at $E_{h\nu} = 2.50 - 2.65$ eV, was observed in [18] in the EPR spectra after irradiating a sample of ZnO by light quanta with energies above 1.7 eV at lowered temperatures. The author assigned this signal to photoinduced F^+ centers and suggested that light quanta with energies 3.2 eV can lead to their further ionization. This hypothesis finds a theoretical corroboration: it is estimated that the depth of F^+ centers is by 2.7 - 3.2 eV below the bottom of the conduction band [19, 20]. However, in [21], the same EPR signal was associated with the photoionization of interstitial oxygen O_i^{2-} and its transition to the state O_i^- in the tetrahedral environment.

Absorption at 2.85 eV can also result from the photoexcitation of an electron localized at a V^- center [22].

In addition, photoadsorption activity in the region of 2 - 3 eV can be associated with the presence of an iron impurity in the sample under investigation [18].

Our results of studying the spectral and temperature dependences of the quantum yield of photoadsorption (Fig. 3), as well as the results of other authors who investigated the thermal desorption of photoadsorbed oxygen [23] and methane [24] also point to the diversity of photoadsorption sites and possible forms of adsorption species.

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