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MASS-SPECTROMETRIC STUDY OF PHOTOSORPTION PROCESSES IN THE OXYGEN–ZINC OXIDE SYSTEM

In a number of works ([1,2]), photosorption processes in the O_2/ZnO system, which is of interest from the standpoint of photocatalytic oxidation reactions and photoelectric surface processes in semiconductors, were studied by a manometric method. In work ([2]), the connection between photosorption processes in this system and the effect of illumination on the reaction of homomolecular oxygen exchange was also investigated. The simultaneous existence of two opposite effects—photosorption and photodesorption—is considered theoretically possible ([2,3,4]). Since the manometric method records the total effect, in the present work an attempt has been made to separate the opposite photosorption effects with the aid of the oxygen isotope O^{18} and mass-spectrometric analysis of the isotopic composition of the oxygen above the sample.

The experimental setup consists of a standard MI-1305 mass spectrometer and a photosorption attachment shown in Fig. 1. A thin layer of zinc oxide was deposited on the walls of a cuvette (1) made of fused quartz of optical quality. The high purity ([5]) of the oxygen leaking in was ensured by its diffusion through the walls of a silver capillary (2), heated by a spiral (3). The cuvette was evacuated by a glass mercury diffusion pump to a pressure of $2 \cdot 10^{-7}$ torr. The shutoff (4, 5) and needle (6) valves, made entirely of stainless steel and allowing heating to 350°, were connected to the cuvette through kovar–glass–quartz transition seals. The inlet valve (6) was mounted directly on the flange of the ion source of the mass spectrometer. A Pirani-type manometer (7) makes it possible to use the cuvette with the valves closed in a manometric mode. The volume of the cuvette was about 50 cm^3; the illuminated (geometric) surface of the zinc oxide layer was of the order of 120 cm^2. The layer was illuminated by a PRK-2 mercury quartz lamp, which could be placed both inside the cavity and outside the cuvette. In most experiments the lamp was placed outside, at a distance of 15 cm from the axis of the cuvette, which made it possible to use light filters to isolate particular spectral regions and considerably simplified the problem of thermostating the sample. A cylindrical jacket (8) of fused quartz

Fig. 1. Schematic diagram of the photosorption attachment

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of optical quality was filled with flowing distilled water and served as a thermal light filter.

Zinc oxide powder of grade M-1 was applied to the walls of the photosorption cuvette from a suspension in distilled water and dried in air. After sealing the cuvette to the apparatus and evacuation to a pressure of $2 \cdot 10^{-6}$, the diffusion pump was cut off by valve (4), and oxygen, the purity of which was monitored by the mass spectrometer, was admitted into the cuvette to a pressure of 100 torr. Standard conditioning began with a 10-hour heating of the layer in the admitted oxygen at 450–500°, with the evolved products frozen out by trap (9) and with the admitted portion of oxygen replaced every 30 min. Then valve (5) was closed and the sample was conditioned in a stream of oxygen leaking in through the silver capillary

at a pressure in the cuvette of 0.1–0.3 torr, with the oxygen being pumped out through the mass spectrometer. The conditioning was usually completed after 70 h, when the impurities CO and CO_2, formed as a result of oxidation of organic contaminants, disappeared from the oxygen leaving the cuvette with the zinc oxide powder heated to 450°. The heating of the sample was then turned off, and at a temperature of 250–300° the oxygen was pumped out of the cuvette. After the cuvette had cooled to room temperature, the heating of the silver capillary was selected so that the dynamic pressure in the cuvette during pumping by the mass spectrometer was $1 \cdot 10^{-3}$ torr. Under these conditions the ion current at the oxygen peak was of the order of 10^{-10} A. The noise level of the mass spectrometer was of the order of $2 \cdot 10^{-15}$ A. The uncontrolled instability of the ion current during the experiment did not exceed 1% of the measured value. This determined the minimum change in pressure in the cuvette detectable by the mass spectrometer. The sensitivity to impurities was no worse than 0.5%.

Fig. 1. Schematic diagram of the photosorption attachment

Results

In all experiments on the photosorption of oxygen, stringent requirements are imposed on the cleanliness of the sample surface, since the presence of traces of adsorbed organic vapors can lead to absorption of oxygen consumed in the oxidation of organic molecules. Such an effect was observed by us when illuminating the surface of an insufficiently conditioned sample, namely one heated in high-purity oxygen at an oxygen pressure of 100 torr to 450° for 5 h. Simultaneously with the drop in the oxygen pressure above the sample, CO and CO_2 were released into the volume, apparently products of photooxidation of organic contaminants. After the standard conditioning described above had been carried out on the same sample, illumination of the sample produced only irreversible

Fig. 2. Kinetics of the change in ion currents

Figure 2: Fig. 2. Kinetics of the change in ion currents

photosorption of oxygen, and no release of CO, CO_2, or H_2O into the volume was observed. Upon subsequent heating in the dark to 450°, only oxygen was released from such a sample; impurities CO, CO_2, and H_2O were not detected.

Fig. 2. Kinetics of the change in ion currents: 1 –$m/e = 32$, 2 –$m/e = 34$, 3 –calculated change in the ion current $m/e = 32$ caused by photosorption, 4 –total change of the peaks $m/e = 32$ and 34, 5 –calculated change in the ion current $m/e = 32$ caused by photodesorption of O_2^{32}, 6 –total change in the ion current as a result of photosorption processes

To separate photosorption and photodesorption processes, experiments were carried out with oxygen enriched with the isotope O^{18} to 18%. After standard conditioning in ordinary oxygen and pumping it out at 250-300° above a sample cooled to room temperature, a flow of the enriched mixture was established. The result of one of the experiments

is presented in Fig. 2. Curve 1 gives the dependence, on illumination time, of the ionic current of O_2^{16} molecules in the mass spectrometer; curve 2 gives the same for $O^{16}O^{18}$ molecules. Thus, curve 1 indicates the phenomenon of photodesorption of oxygen molecules initially adsorbed on the specimen, while curve 2 indicates photosorption of $O^{16}O^{18}$ molecules present in the subsequent oxygen flow. Since the isotopic composition of the oxygen molecule cannot be significant for photon effects, from a comparison of curves 1 and 2 it may be concluded that curve 1 is the result of two competing processes–photosorption and photodesorption of oxygen molecules. The concentration of O_2^{18} molecules in the gas phase was less than 3.5%; therefore a possible change in the ionic current of $O^{16}O^{18}$ molecules due to the reaction $O_2^{16} + O_2^{18} \rightleftharpoons O^{16}O^{18}$ could be neglected. Thus, the course of curve 2 reflects the kinetics of photosorption of oxygen of the isotopic composition that was present in the gas phase at the moment of illumination. Then, from the known percentage concentration of $O^{16}O^{18}$ molecules at the initial moment and curve 2, one can construct an analogous dependence for the photosorption of O_2^{16}, shown by curve 3. Addition of curves 2 and 3 gives the total amount of photosorbed oxygen (neglecting photosorption of O_2^{18} molecules). The difference between curves 1 and 3 (curve 5) should represent photodesorption of O_2^{16} oxygen adsorbed on the specimen by the beginning of illumination. The dependence of the sum of the ionic currents over all oxygen masses is shown by curve 6. It is seen that the total change in ionic current over all masses (curve 6), representing photosorption, amounts to 10-15% of the change for each of the opposite processes (curves 3 and 4). From curve 6 one can construct the kinetics of the pressure change in the cuvette. The kinetics thus obtained agrees with that observed in these experiments with a Pirani manometer.

A preliminary investigation of the spectral characteristic of the photosorption processes, carried out with the aid of light filters isolating mercury lines, showed that the competing processes of photosorption and photodesorption are not separated spectrally.

The photosorption processes observed under these conditions cannot be explained by heating of the specimen, for the reasons that they are not reproduced upon heating the specimen without illumination up to 200°, while the thermal conductivity of the specimen is sufficient to prevent macroscopic heating of the specimen by more than 1°. For grains having no thermal contact with the rest of the specimen mass, the heating does not exceed 10°, if it is assumed that all heat transfer is determined only by light absorption. Finally, removal of the water filter does not affect the observed effects.

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