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Abstract

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THE EFFECT OF ILLUMINATION ON THE ADSORPTION CAPACITY OF CERTAIN OXIDES

By the present time there is already a considerable number of works devoted to the study of the effect of illumination on the adsorption capacity of solids (see reviews ([1,2])); however, the range of objects studied is comparatively narrow. For oxides this phenomenon has been studied mainly on zinc oxide ([3–6]), silicon dioxide ([7]), and titanium dioxide ([8–10]). In the present work, which is exploratory in character, the task was set of broadening the range of objects (oxides) on which photosorption processes can be observed. In all, more than 30 different oxides were investigated; for each of them the effect of illumination on the adsorption capacity with respect to oxygen, hydrogen, and methane was monitored. For the experiments, either ready-made industrial preparations were used, or preparations made by the methods given in ([11]).

The work was carried out on an apparatus described earlier ([12]) for photosorption studies, which made it possible to obtain in the working vessel (reactor) a stable vacuum no worse than $5 \cdot 10^{-7}$ torr. In order to reduce the possibility of contamination of the samples by vapors of organic compounds, the working vessel was separated from the rest of the vacuum apparatus by a grease-free metal valve, heated during conditioning, and by a trap cooled with liquid air. Powdered samples weighing 30–50 mg were poured into a flat cuvette made of uvio glass, provided with sealed-in contacts of gold-plated molybdenum. Illumination of the samples was carried out with an SVD-120 mercury lamp with a mirror condenser. To reduce the thermal effect of the light, the cuvette with the sample was placed during illumination in a quartz beaker with distilled water at room temperature.

The pressure in the working vessel was measured with a Pirani gauge having a sensitivity of about $1 \cdot 10^{-5}$ torr and was automatically recorded by a self-recording microvoltmeter. Simultaneously with the manometric measurements, the conductivity and photoconductivity of the samples were measured. No definite connection of photosorption phenomena with photoconductivity phenomena was established.

Treatment of the samples before the experiments consisted of heating in air at 400–450° for several hours, evacuation and vacuum conditioning at the same temperature until gas evolution ceased, followed by additional heating of the sample in oxygen (approximately 10^{-1} torr, 1.5–2 h) for final purification from adsorbed organic impurities. Intermediate treatment of the samples between experiments, necessary for restoring their initial state, consisted of brief (3–6 min) heating in vacuum or in oxygen at a pressure of the order of 10^{-2} torr.

Illumination of the samples in order to detect changes in adsorption capacity under the action of light was carried out after dark adsorption equilibrium had been established at a pressure of the gas under study of the order of 10^{-2} torr. In those cases where equilibrium was established too slowly, illumination was carried out after the rate of dark adsorption to a value that did not hinder the observation of photosorption phenomena.

In the course of the work it became clear that a change in the adsorption capacity of oxides under illumination occurs for almost all the objects studied and is, perhaps, even more widespread than the phenomenon of photoconductivity. The experimental results are presented in Table 1 by plus and minus signs; it indicates the presence or absence of a manometrically measurable increase in adsorption capacity for the corresponding gases under illumination, i.e., the presence or absence of photosorption, which at room temperature is irreversible.

Table 1

Activity of various oxides with respect to photosorption of oxygen, hydrogen, and methane

Oxides	O_2	H_2	CH_4	Oxides	O_2	H_2	CH_4
Li_2O	+	+	+	TiO_2	$+^{4}$	$+^{2}$	$+^{2}$
Cu_2O	−	−		ZrO_2	+	+	+
BeO	+	+	+	ThO_2	+	$+^{5}$	+
MgO	+	+	+				
CaO	+	+	+	SiO_2	$+^{6}$	$-^{6}$	−
SrO	+	+	+	GeO_2	+	+	+
BaO	+	+	+	SnO_2	+	+	+
ZnO	$+^{1}$	$+^{2}$	$+^{2}$	PbO			
CdO	−	−	−		+	−	+
Sc_2O_3	+	+	+		+	−	−
Y_2O_3	+	+	+	V_2O_5	−	−	+
La_2O_3	+	+	+	Nb_2O_5	−	−	+
CeO_2	+	+	+	Bi_2O_3	+	−	−
Pr_6O_{11}	−	−	−	Cr_2O_3	−	−	−
Ho_2O_3	+	+	+	MoO_3	−	−	+
Er_2O_3	+	+	+	WO_3	−	−	−

Oxides	O_2	H_2	CH_4	Oxides	O_2	H_2	CH_4
Yb_2O_3	+	+	+	NiO[7]	−		
Lu_2O_3	+	+	+				
γ-Al_2O_3[3]	+	+	−				
Ga_2O_3	+	+	+				
In_2O_3	+	+	+				

[1] Photosorption of oxygen on zinc oxide had previously been observed in works (4-7). [2] Data are borrowed from works (9, 10). [3] Results obtained with the participation of V. A. Kotel' nikov. [4] Priority in the discovery of oxygen photosorption on titanium dioxide apparently belongs to the authors of work (8). [5] Photosorption of hydrogen on thorium dioxide was observed earlier in work (13) and was explained by mercury-vapor-sensitized photodissociation of hydrogen with subsequent strong chemisorption. In our case this explanation is completely excluded, since the phenomenon was observed in the absence of mercury vapor in the working vessel and in the spectral region (filter $\lambda > 330$ nm) where mercury-vapor-sensitized photodissociation of hydrogen is energetically impossible. [6] The results of work (7) are confirmed. [7] According to data of V. A. Kotel' nikov (14).

In some cases (for example, in the systems O_2/Cu_2O, O_2/CdO, H_2/CdO, O_2/Pr_6O_{11}, CH_4/γ-Al_2O_3), under illumination a more or less reversible increase in pressure (desorption) is observed; however, no convincing data were obtained that would indicate the nonthermal nature of the desorption observed under illumination under the specified conditions.

Regarding the results presented in Table 1, several remarks should be made:

1) For BaO, photosorption effects were observed only on a sample heated in vacuum, and disappeared after heating in oxygen (0.1 torr) at 300–350°. A new heating in vacuum at 450°, accompanied by

with the release of a considerable amount of oxygen, led to the restoration of photosorption activity. This result can be associated with the formation and decomposition of barium peroxide, which apparently does not possess photosorption activity. It should be emphasized, however, that for most other oxides an entirely different tendency is characteristic—the tendency toward an increase in photosorption activity (especially with respect to hydrogen and methane) as the samples are saturated with oxygen at a temperature of about 400°.

2) For most of the oxides studied, photosorption effects can be observed only in the wavelength region shorter than 330 nm. Only for certain oxides (ZnO, In_2O_3, TiO_2, ThO_2, SnO_2, PbO) were photosorption effects observed in the longer-wavelength region of the spectrum.

3) On γ-Al_2O_3, in contrast to all other oxides, abundant dark adsorption of

methane is observed. The action of light leads to an increase in pressure in the system, which apparently has a purely thermal character.

4) For lead oxide of both modifications, the changes in pressure observed under illumination are relatively small (in comparison with other adsorbents). One can speak with certainty only of oxygen photosorption. The magnitude of the methane photosorption effect on the yellow modification of PbO only slightly exceeds the possible experimental errors. For MoO_3, V_2O_5, and Nb_2O_5, methane photosorption is also insignificant, but quite measurable.

5) The absence of data on the magnitudes of the specific surface areas of the adsorbents and on the depth of penetration of active light into the bulk of the powder sample does not yet permit any quantitative comparison of the photosorption activity of different oxides.

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