Photodesorption and Photoadsorption of Oxygen on Zinc Oxide

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Photodesorption of oxygen was first observed by Terenin[1] with oxygen-zinc oxide when irradiated by iron spark. The phenomenon was re-investigated by us with lights having wavelengths near fundamental absorption of the adsorbent on both degassed and oxidized zinc oxide samples. It was found that while Terenin's finding was confirmed at room temperature and below on the degassed sample, the photoresponse turned out to be

1) A. N. Terenin, *Problems of Kinetics and Catalysis*, **8**, 17 (1955) USSR; *Chem. Abst.*, **50**, 1452 (1956).

an irreversible adsorption on the oxidized sample. In this communication we show such a reversal of the photoresponse and suggest that weakly chemisorbed oxygen molecules play a role in this phenomenon.

A 0.28 g. portion of zinc oxide sample with a surface of 6.2 m^2 per g.[2], placed in a Pyrex vessel of *ca.* 40 cm^3 volume, was degassed at 300°C for several hr. A small amount of oxygen was then admitted to the oxide kept at a desired temperature, equilibrium pressure being kept always below 10^{-3} mm Hg. Irradiation was made by a Matsuda mercury lamp SHL-100, passed through a Matsuda solid filter and a quartz cell containing cupric sulfate solution to remove light of long wavelengths. The pressure change of oxygen due to irradiation was recorded by a Pirani gauge having a sensitivity 5×10^{-7} mm Hg/div. for O_2. The oxidized zinc oxide was prepared by heating in 0.1 mm Hg oxygen at 300°C for about one hour, cooling down to room temperature and being degassed for about thirty minutes. The photoeffect with this sample was investigated similarly as above.

As shown in Fig. 1a and 1b, photoexcited desorption of oxygen took place with the degassed sample at room temperature in a reversible fashion, whereas an irreversible photoadsorption was found to occur on the oxidized sample. Photoeffect of this kind was most effective by the irradiation of light at wavelengths less than 4500 Å. With rise of temperature of the adsorption vessel, the photoeffect became faint and disappeared above 200°C. At −195°C photodesorption occurred with the degassed sample but this may partly be ascribed to thermal[3] or non-electronic response since nitrogen was likewise able to desorb upon irradiation.

The oxygen-zinc oxide system has been the subject of many investigations. Therefore it would be relevant to review some results relating to the interaction of oxygen with zinc oxide. i) Let us quote first the p-T relation of the oxygen-degassed zinc oxide system obtained when the temperature of the adsorption vessel was raised from room temperature to 300°C at a constant rate. Maximum appeared in the plot of p against T at 150—200°C. At first sight this might indicate that the adsorption of oxygen is *physical* below 150°C or that the photodesorption has actually taken place in the *molecular* layer. ii) Exchange reaction of oxygen, $^{18}O_2+{}^{16}O_2=2{}^{18}O^{16}O$, was investigated by Winter et al.[4] over a zinc oxide sample at temperatures where the exchange of oxygen with the surface is negligible. Accordingly the exchange reaction is not perceptible below 119°C. This finding provides the view that oxygen adsorption may occur without dissociation at least around room temperature. iii) The shape of the conductivity-temperature curve[5] due to Stöckmann with zinc oxide kept in an atmospheric air much resembles

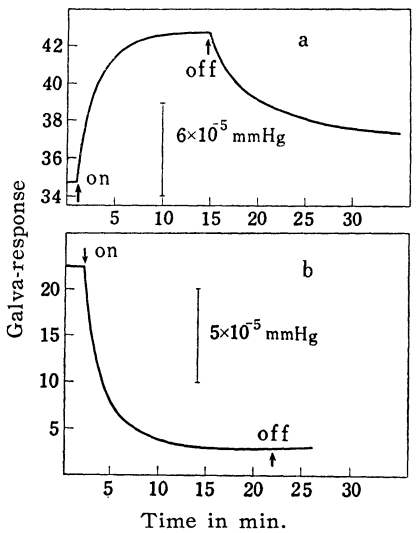

Fig. 1. Typical example for the photodesorption of oxygen (a) with a degassed zinc oxide sample and the photoadsorption (b) on an oxidized zinc oxide at room temperature.

our p-T relation; it deviates from the generally accepted linearity of $\log\sigma$ against $1/T$ of zinc oxide alone apparently near 200°C. On the other hand, according to Melnick[6] the photoconductivity of zinc oxide is entirely due to the desorption of chemically adsorbed oxygen *atoms*.

These facts now point toward the indication that weakly chemisorbed oxygen molecules are present having a kind of electronic interaction with the surface of zinc oxide. Probably molecular oxygen ion, O_2^-, is best fitted for such an adsorbed oxygen intermediate, and photodesorption or -adsorption may occur by combining with positive hole or electron of zinc oxide created upon irradiation.

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3) A. J. Rosenberg and C. S. Martel, Jr., *J. Phys. Chem.*, **61**, 512 (1957).
4) E. R. S. Winter, *J. Chem. Soc.*, **1954**, 1522.
5) F. Stöckmann, *Z. Physik*, **127**, 563 (1950).
6) A. D. Melnick, *J. Chem. Phys.*, **26**, 1136 (1957).