V. E. OSTROVSKII, N. V. KUL’KOVA

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Abstract

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V. E. OSTROVSKII, N. V. KUL’ KOVA

HEATS OF CHEMISORPTION OF OXYGEN ON SILVER AND THEIR CHANGE UPON INTRODUCTION OF SULFUR ONTO THE SURFACE

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The addition of sulfur to a silver catalyst causes significant changes in the rate of ethylene oxidation (^{1}-^{3}) and in the rate of oxygen adsorption (^{4}, ^{5}). These effects are observed at sulfur surface coverages as small as 0.01 and even lower. Similar data have been obtained with selenium and other electronegative elements (^{2}, ^{3}). These results indicate that each atom of the additive located on the surface changes the energetic properties of a large number of adsorption centers. The possibility of such effects was discussed theoretically by Opper (^{6}).

In the present work, the change in the heats of adsorption of oxygen on silver upon introduction of sulfur was investigated by direct calorimetric measurements. Until now there had been only indirect determinations of the heats of adsorption of oxygen on silver (^{7}-^{9}). To attain sufficiently high rates of oxygen adsorption, calorimetric measurements must be carried out at elevated temperatures. We used a calorimetric apparatus described earlier (^{10}), which made it possible to perform measurements at temperatures up to 170° (the maximum operating temperature of the oil used in the thermostat). The errors in determining differential heats of adsorption did not exceed 10% of the measured quantities (the uncertainty in measurements of thermal effects and amounts of adsorbed gas). The adsorbent was porous silver obtained by decomposition of Ag_2CO_3 under the conditions of the ethylene oxidation reaction (^{2}). About 13 g of Ag was loaded into the adsorption vessel. To determine the surface area of the silver, krypton adsorption was measured at the temperature of liquid nitrogen by the BET method, taking the saturated vapor pressure of krypton as $p_0 = 3.175$ mm Hg and the area of the Kr atom as 19.5 Å^2. The experiments were carried out on two silver samples: sample I with a specific surface area of 0.21 m^2/g and sample II with 0.20 m^2/g. The silver grains had a size of 1-2 mm. Pressure measurements were made with a mercury manometer, an LT-2 thermocouple manometric gauge calibrated with various gases, and an LM-2 ionization manometer. The catalyst was protected from mercury vapors by traps cooled with liquid nitrogen.

Fig. 1

Figure 1: Fig. 1

Before the calorimetric experiments, the adsorbent was evacuated to a pressure of about $2 \cdot 10^{-7}$ mm Hg at a temperature of 110° and was then treated with hydrogen at a temperature of 170° and a pressure of 25 mm Hg for 2 h. The water formed as a result of the interaction of adsorbed oxygen with hydrogen was frozen out in a trap cooled with liquid nitrogen. The adsorbent was then evacuated for 2 h at 140° and for 30 h at 120°. This treatment was carried out three times, after which measurements of the heats of oxygen adsorption at 110° were performed. Oxygen was admitted into the adsorption vessel in portions, each of which corresponded to 0.017-0.020 cm^3 O_2 per 1 m^2 of silver surface (here and below gas volumes are reduced to 0° and 760 mm Hg). The initial oxygen pressure before adsorption was equal to

0.15-0.18 mm Hg. The course of adsorption was followed from the change in pressure (by a thermocouple manometer). Portions of oxygen were admitted until the rate of heat evolution fell to $3 \cdot 10^{-5}$ cal/sec. At lower rates of heat evolution the measurements are insufficiently accurate. The first portions of oxygen were adsorbed practically completely; after adsorption of several portions the residual pressure became greater than $1.0 \cdot 10^{-3}$ mm Hg. After completion of the experiment on oxygen adsorption, the sample was treated with hydrogen, as described above, and then the heats of adsorption of oxygen on a surface partially covered with sulfur were determined. To deposit sulfur on silver, small portions of hydrogen sulfide were introduced into the adsorption vessel at a temperature of 110° by means of a dosing tap (0.0055 cm^3/m^2 in the experiment on sample I, and two portions of 0.0028 cm^3/m^2 each in the experiment on sample II). After several minutes a gas was formed that was not frozen out by liquid nitrogen—evidently hydrogen. Its pressure corresponded to the reaction

Fig. 1

$$H_2S + (\ ) = H_2 + (S), \tag{1}$$

where ( ) is a divalent adsorption center on the surface, and (S) is a chemisorbed sulfur atom. The hydrogen formed was pumped off for 5 min at 110° to a pressure of about $1 \cdot 10^{-5}$ mm Hg, and then the heats of adsorption of oxygen were measured as described above. The amount of heat evolved in the course of reaction (1) was insignificant (at the limit of sensitivity of the method). It follows from this that the heat effect of reaction (1) lies within the range 0-15 kcal/mole. This makes it possible to estimate the enthalpy change for the reaction $(\ ) + S_{gas} = (S)$. Using data on bond energies (^{12}), we obtain $\Delta H = -78 \pm 10$ kcal/mole.

Figure 1A presents the results of experiments on sample I. Curve Ia corresponds to the adsorption of oxygen on pure silver; curve Ib, to the adsorption of oxygen after sulfur had been deposited on the silver surface. The hatched region corresponds to the amount of hydrogen sulfide that had interacted with silver before oxygen adsorption. Figure 1B similarly presents the results of experiments on sample II in the absence of sulfur (curve IIa) and in the presence of sulfur (curve IIb). The initial heat of adsorption on pure silver is the same for both samples and is close to 120 kcal per 1 mole of O_2. With increasing degree of surface coverage, the heat of adsorption of oxygen decreases; from 0.04 to 0.17 cm^3 O_2 per 1 m^2 the dependence is nearly linear, which corresponds to a logarithmic adsorption isotherm ([11]). At higher coverages a more rapid decrease in Q is observed. The rate of oxygen adsorption then decreases sharply.

If the preliminary treatment of the surface with hydrogen is carried out not at 170°, as in the experiments described above, but at 110°, then, as follows from

of the results, which will be presented in another communication, only comparatively weakly bound oxygen is removed from the surface, up to coverages close to 0.16 cm^3 O_2 per 1 m^2 Ag. Therefore the heats of adsorption measured after treatment with hydrogen at 110° (10) on the specimen designated in this communication as specimen II pertain to coverages greater than 0.16 cm^3 O_2 per 1 m^2. It is not excluded that even after treatment with hydrogen at 170° the silver was not completely freed of oxygen.

The presence of sulfur atoms on the surface in an amount 10^2 times smaller than the maximum number of adsorbed oxygen atoms does not affect the initial heat of adsorption of oxygen, but increases the slope of the curve of differential heats of adsorption, so that the heat of adsorption of oxygen proves to be smaller than at the same fillings on a clean surface. The difference reaches 35 kcal/mole O_2 at 0.14 cm^3 O_2/m^2. An analogous effect was also observed on specimen II (Fig. 1B). If the possibility of oxidation of sulfur on the silver surface to $SO_4{}^{2-}$ is taken into account, the difference between the heat of adsorption of oxygen on pure silver and on silver in the presence of sulfur will be still somewhat greater. The heat effect of the reaction $(S) + 2O_2 = (SO_4)$ on the surface of silver may, in a first approximation, be taken as equal to the heat effect of the reaction $Ag_2S + 2O_2 = Ag_2SO_4$. Calculation shows that, upon complete oxidation of the sulfur adsorbed on silver, an additional 0.110 cal could be liberated, which amounts to 7% of the total amount of heat evolved during the adsorption of oxygen on silver in the presence of sulfur.

Several explanations are possible for the change in the character of the curve of differential heats of adsorption; in order to choose between them, it is essential to know what amount of oxygen corresponds to formation of a monolayer. On the densest faces of the silver crystal, namely the (111) faces, an Ag atom occupies an area of 7.2 Å^2; these faces apparently should be encountered most frequently. If it is assumed that one O atom corresponds to one Ag atom, then a monolayer of oxygen on silver contains 0.26 cm^3 O_2 per 1 m^2. On other faces the amount of oxygen corresponding to a monolayer will be smaller. Thus, the change in the slope of the curve of differential heats of adsorption occurs at surface coverages greater than half a monolayer. This can be explained by a change in the type of adsorption, for example by a transition from adsorption of O atoms to adsorption of O_2 molecules. In this connection we point to the existence of the compound AgO, which does not have the character of a peroxide (13), and of a surface compound of silver with oxygen, to which the structure of a superoxide was assigned (14).

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Physicochemical Institute
named after L. Ya. Karpov

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