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Change in the Electronic Work Function upon Adsorption of Oxygen on a Silver Catalyst

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It is known ([1–3]) that several forms of adsorbed oxygen exist on the surface of silver. One of the important characteristics of chemisorbed oxygen is the degree of polarity of its bond with the surface. This can be judged from the dependence of the change in the electronic work function on the coverage of the surface with oxygen. The data available in the literature are insufficient, since they contain only the maximum value of the increase in the work function upon adsorption of O_2 on silver: 0.6 V ([4]), 0.2 V ([5,6]), 0.6-0.7 V ([7]). The value 0.2 V was obtained with a gold reference electrode; it reflects not the change in the work function of silver upon adsorption of O_2, but the difference of such changes for silver and gold ([7]). In the present work data are given on the dependence of the work function of silver on the amount of adsorbed O_2.

The change in the work function of silver was taken to be equal to the change in the contact potential difference. The contact potential difference was measured by the vibrating-capacitor method. A glass cell described earlier ([7]) was used. A molybdenum disk sealed with a thin layer of glass served as the reference electrode ([8]). The cell also served simultaneously as the adsorption vessel. The amount of adsorbed oxygen was measured from the change in pressure in a known volume by means of a Pirani manometer with a platinum filament 10 μ in diameter, the readings of which were recorded with an EPP09 electronic potentiometer. Owing to the presence in the system of a bulb of large volume, adsorption could be carried out at approximately constant pressure ($2.5—2.8 \cdot 10^{-2}$ mm Hg). Simultaneous recording of the contact potential difference and of the change in pressure made it possible to obtain the dependences of the work function and the amount of adsorbed oxygen on time. By eliminating time from these dependences, the dependence of the change in work function on the amount of adsorbed O_2 was obtained. Another way of obtaining this dependence consisted in successively covering the silver surface with small portions of oxygen, which were admitted into the cell from the Pirani manometer. In such experiments the bulb was disconnected. Stepwise reduction was also used, i.e., successive removal of oxygen from the Ag surface by small portions of hydrogen admitted into the cell from the Pirani manometer.

Into the cell were loaded 2-3 g of powdered Ag. Before each experiment on

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

adsorption of O_2, the silver powder was kept in H_2 (30-40 mm Hg) for 2-3 hours at 250-275°, and then evacuated at the same temperature for 10-15 hours. A vacuum of $5 \cdot 10^{-7}$ mm Hg was attained. Before experiments on stepwise reduction, the silver powder was kept in O_2 (10 mm Hg) for about half an hour at 250-275°, and then evacuated for 3-5 minutes at the same temperature.

The catalyst was prepared by precipitating Ag_2CO_3 from a solution of chemically pure $AgNO_3$ with spectrally pure soda. Ag_2CO_3 was decomposed in an ethylene-air mixture at 218° and heated at 250-300° for 10 hours to stabilize the surface. The value of the specific surface area, determined from krypton adsorption, was after the measurements 0.13 m^2/g.

The increase in the work function in comparison with the work function of an Ag surface free of oxygen will be denoted by $\Delta\varphi$ and expressed in volts. The ratio of the amount of adsorbed O_2 to the surface area of the specimen will be denoted by v and expressed in cubic centimeters (N.T.P.)/m^2.

Measurements carried out by the method of successively covering the surface with small portions of O_2 showed that different values of $\Delta\varphi$ may correspond to one and the same amount of adsorbed O_2. This is illustrated by Fig. 1, which contains typical curves of the dependence of $\Delta\varphi$ on time t. The curves are given for the first two portions of O_2, i.e., for comparatively small surface coverages. After the stepwise increase of $\Delta\varphi$ (at the moment when a portion of O_2 is absorbed) to the value $\Delta\varphi_{\text{init}}$, there follows a slower change of $\Delta\varphi$ not associated with adsorption or desorption. At 23 and 100° an increase of $\Delta\varphi$ with time usually occurs; at 200 and 250° $\Delta\varphi$ decreases with time. The decrease of $\Delta\varphi$ at constant v is accelerated with increasing temperature; it slows down, and then ceases altogether, with increasing v. Figure 2 presents

Fig. 1. Dependence of the change in work function on time after complete absorption of a portion of oxygen. Positive values of $\Delta\varphi$ correspond to an increase in the work function.

Fig. 2. Dependence of the change in work function on the amount of adsorbed oxygen

the results of measurements of $\Delta\varphi$ during successive coverage of the surface by small portions of O_2. The vertical lines show the sizes of the portions. The points of curves 1 correspond to the values of $\Delta\varphi$ immediately after admission and absorption of a portion; the points of curves 2, to the values of $\Delta\varphi$ after

Fig. 3. Stepwise reduction of the silver surface. 1 —dependence of $\Delta\varphi$ on v, 2 —dependence of $\lg k$ on v

Figure 3: Fig. 3. Stepwise reduction of the silver surface. 1 —dependence of $\Delta\varphi$ on v, 2 —dependence of $\lg k$ on v

~ 10 min following admission of a portion, immediately before admission of the next portion. Curves 3 give the sum of the quantities $(\Delta\varphi_{\text{init}})_1 + (\Delta\varphi_{\text{init}})_2 + ... + (\Delta\varphi_{\text{init}})_n$, where n is the number of the portion (see Fig. 1). In the same figure, curves 4 show the results of continuous measurements at constant O_2 pressure; they were obtained by eliminating t from the dependences of $\Delta\varphi$ and v on t. At 200° curve 4 directly continues curve 3; at 100° curve 4 lies between curve 3 and the curves 1 and 2, which are close to one another. As is seen from Fig. 2, the slope of the curves $\Delta\varphi$–v decreases with increasing v; at 200° even a certain drop in the work function is observed in the region of large v.

Figure 3 gives the dependences $\Delta\varphi - v$, obtained by the method of stepwise reduction (curves 1). Curves 2 show the dependence of the specific rates of surface reduction on the degree of coverage with oxygen. The specific reduction rates K were calculated from the equation $k = \Delta \lg P/\Delta t$, where P is the hydrogen pressure and t is time. Fig. 4a refers to the sample whose preparation procedure was described above. Fig. 4b refers to a sample prepared from $AgNO_3$, obtained by dissolving silver wire of 99.999% Ag in nitric acid with an impurity content of no more than 0.001%. Curves 1 in Fig. 3 do not coincide with the curves obtained for oxygen adsorption. However, common to them is a considerable slope at low coverages and independence of the work function from v at high coverages. A definite correspondence is observed in the course of curves 1 and 2.

Fig. 3. Stepwise reduction of the silver surface. **1** —dependence of $\Delta\varphi$ on v, **2** —dependence of $\lg k$ on v

To discuss the results, let us determine the value of v corresponding to a monolayer. The most frequent planes should be the close-packed ones; in the case of silver these are the (111) planes, which contain $1.4 \cdot 10^{19}$ Ag atoms per 1 m^2. If each surface Ag atom attaches an O atom, then v is equal to 0.26 cm^3 O_2 (NTP)/m^2. The largest values of v in the experiments described were close to this value.

The changes in $\Delta\varphi$ with time at 100 and 200° (Fig. 1) have different directions; this indicates the existence of two processes leading to changes in $\Delta\varphi$. The increase in $\Delta\varphi$ with time observed at low temperatures (for example, at 100°) can be explained if it is assumed that O_2 is initially adsorbed in molecular form, and then, at small surface coverages, the molecules dissociate with the formation of adsorbed atoms. Since the Ag surface is inhomogeneous, dissociation occurs at different sites at different rates. This process is accompanied by an increase in $\Delta\varphi$. Obviously, $\Delta\varphi$ will increase only on the condition that $2\mu_O > \mu_{O_2}$,

where μ_O and μ_{O_2} are the dipole moments of the O atom and the O_2 molecule on the surface. At high temperatures (for example, 200°), the establishment of equilibrium between O_2 and O on the surface occurs practically instantaneously at all sites. On the other hand, the process of transfer of oxygen into the layer of Ag adjacent to the surface becomes appreciable; the name "deep adsorption" was proposed for it (9). Since this process leads to a decrease in the amount of oxygen on the surface, $\Delta\varphi$ decreases. It is also possible that O atoms located beneath the surface near it create a potential step, reducing

which lowers the work function. Another possible interpretation of the two forms of adsorbed oxygen is discussed below.

The difference between the curves $\Delta\varphi - v$ in Fig. 3 and Fig. 2 may be caused by nonuniform distribution of oxygen over the height of the layer.

The slope of the $\Delta\varphi - v$ curve in the region of small v makes it possible to determine the dipole moment M of the bond of an O atom with the silver surface from the equation

$$\frac{M}{D} = \frac{10^{18}}{2\pi\,300}\,\frac{d(\Delta\varphi)}{dN}, \tag{1}$$

where N is the number of O atoms per 1 cm^2 of surface. Curve 1 of Fig. 3b gives $M \cong 1.5D$.

An estimate of the mutual depolarization of the dipoles shows that it is too small to explain the observed decrease in the slope of the $\Delta\varphi - v$ curve with increasing v. This decrease in slope and the horizontal section of the curve may be ascribed to the transition from atomic adsorption to molecular adsorption, as well as to deep adsorption of oxygen. If it is assumed that the dipole moment of a chemisorbed oxygen atom is approximately equal to the dipole moment of a chemisorbed molecule, and that both the O atom and the O_2 molecule are bonded to two surface Ag atoms, then the adsorption process [10]

$$2\mathrm{Ag} \qquad \mathrm{Ag} + \overset{\mathrm{O}}{\underset{\mathrm{O}}{\diagup\diagdown}} = 2\mathrm{Ag}\ \ \mathrm{Ag} \qquad (2)$$
$$\qquad\qquad\qquad\qquad\qquad\quad \mathrm{O}-\mathrm{O}$$

will not be accompanied by a substantial change in $\Delta\varphi$. As long as the number of adsorbed O_2 molecules does not exceed one-half the number of Ag atoms on the surface, oxygen is adsorbed predominantly in the form of atoms, and an increase in its amount on the surface causes $\Delta\varphi$ to increase. A further increase in the amount of sorbed oxygen occurs predominantly as a result of process (2), which does not lead to an increase in $\Delta\varphi$, and of the process of deep adsorption, which likewise does not increase $\Delta\varphi$, or even decreases this quantity.

The change in the nature of the bond of O_2 with the surface may be attributed to a change in the valence of silver, similar to what was postulated for gold [11]. In this case the adsorption process, when the ratio of the number of O and Ag atoms on the surface exceeds 1/2, is described not by equation (2), but by the following:

$$2Ag_2O + O_2 = 4AgO, \tag{3}$$

The proposed representation is consistent with data on the nature of the higher oxide of silver, AgO [12].

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