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1965

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

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KINETICS OF OXYGEN ADSORPTION ON SILVER AT LOW PRESSURES

(Presented by Academician S. S. Medvedev, February 1, 1965)

Chemisorption of oxygen on silver has been investigated in a number of works ($^{1-7}$). The kinetics of this process was studied (^{5}) at pressures of 200-600 mm Hg.

In the present work the kinetics of oxygen chemisorption on powdered silver at low pressure was investigated. Simultaneously with the adsorption measurements, changes in the electron work function were determined (from the change in contact potential difference). The method for preparing the catalyst and the procedure for carrying out the experiments have been described previously (^{6}); the layout of the apparatus is shown in Fig. 1. The measurements were carried out at an approximately constant pressure of $2.5 \cdot 10^{-2}$ mm Hg. Figure 2 shows the dependences of the increase in work function $\Delta\varphi$ (V) and the amount of adsorbed oxygen v (cm^3 at 760 mm Hg and 0° per 1 m^2) on time t (sec). The portion of the $v, \ln t$ curve at values of v not exceeding a certain value v_1 is linear, i.e., it obeys the Elovich-Roginskii equation

Fig. 1. Schematic diagram of the apparatus: 1 —cell; 2 —Pirani manometer; 3 —mercury diffusion pump; 4 —trap; 5 —flask; 6 —vacuum valve

$$v = \frac{1}{b} \ln(abt + 1) \tag{1}$$

($abt \gg 1$). For $v > v_1$ the data can be represented by an equation of the Benham type,

$$v = v_1 + c(t - t_1)^{0.5}, \tag{2}$$

where c is a constant, and t is the time during which the amount of oxygen v_1 is adsorbed (Fig. 3).

From equation (1), the values of the initial adsorption rate a and the constant b, given in Table 1, were determined graphically. The values of a are close to the initial adsorption rates obtained by extrapolation in the coordinates $\lg \frac{\Delta v}{\Delta t}, v$. The values of a do not increase with temperature; hence it follows that the activation energy of adsorption E_0 on the free surface is close to zero. Table 1 gives the values of the ratio of a to the number of impacts M of O_2 molecules on the surface, which may be regarded as

steric factor. Theoretical calculation by the activated-complex method (8) shows that the steric factor for chemisorption of oxygen can reach $2 \cdot 10^{-5}$ (at room temperature), if the vibrational frequencies of the activated complex are very high. For a less "rigid" activated complex, the steric factor will lie between the value given and 1. Thus, the experimentally obtained values of a/M do not contradict the conclusion that $E_0 \simeq 0$.

Fig. 2
Fig. 2. 1—23°; 2—100°; 3—200°

Fig. 3
Fig. 3. 1—23°; 2—100°; 3—200°

Taking the cause of the decrease in the adsorption rate with increasing surface coverage by oxygen to be an increase in the activation energy, we determine E/v from the equation

$$E/v = RTb. \tag{3}$$

As is seen from the data of Table 1, the ratios E/v for 23, 100, and 200° approximately coincide. From this it may be concluded that the initial form of chemisorbed oxygen at these temperatures is the same. Measurements of contact potential differences (6) at 23 and 100° showed the presence of a comparatively slow process of dissociation of chemisorbed oxygen. Consequently, at these temperatures at least part of the oxygen is initially adsorbed in the form of molecules. The results obtained are most simply explained if it is assumed that at 23—200° oxygen is initially adsorbed in molecular form.

Table 1

$P_{O_2} = 2\ 5 \cdot 10^{-2}$ mm Hg

Temperature, °C	$v_1 \cdot 10^2$, cm^3/m^2	a, cm^3/m^2 · sec	b, m^2 · sec	a/M	E/v, kcal · m^2/(mol · cm^3)
23	9	6.2	156	$1.8 \cdot 10^{-3}$	91
100	10	4.0	100	$1.3 \cdot 10^{-3}$	74.6

Fig. 4

Figure 2: Fig. 4

Temperature, °C	$v_1 \cdot 10^2$, cm^3/m^2	a, cm^3/m^2 • sec	b, m^2 • sec	a/M	E/v, kcal • m^2/(mol • cm^3)
200	13.5	4.3	83	$1.6 \cdot 10^{-3}$	77

A number of authors (9-12) relate changes in the heats and activation energies of chemisorption to changes in the electron work function. In Fig. 4 the logarithm of the specific adsorption rate $dv/dt\,p$, where p is the oxygen pressure, is plotted as a function of $\Delta\varphi$ for several samples of silver catalysts. The data are given for the region where equation (1) is fulfilled and where, as is assumed, the dominant reason for the decrease in the adsorption rate with filling is the increase in activation energy. As a rule, with increasing $\Delta\varphi$ the adsorption rate decreases linearly. On the basis of the aforementioned

assumption, one can find the change in activation energy from the change in the specific adsorption rate by the equation

$$\Delta E = -RT\Delta \ln \left(\frac{1}{p} \frac{\Delta v}{\Delta t} \right). \tag{4}$$

Table 2 gives the ratios of ΔE to the corresponding changes $\Delta\varphi$ (expressed in identical units). The closeness of the values of ΔE and $\Delta(\Delta\varphi)$ makes it possible to suppose that the increase in the activation energy of adsorption is caused by the mutual influence of adsorbed particles. If an increase in the work function is the cause of the increase in the activation energy of adsorption, then

$$\Delta E/\Delta(\Delta\varphi) \leq 1.$$

From Table 2 it is seen that in most cases $\Delta E/\Delta(\Delta\varphi)$ is 0.7-0.8. However, in some cases, namely those in which the work-function values are affected by the presence of a deep-adsorption process [6], $\Delta E/\Delta(\Delta\varphi) > 1$. This fact speaks rather against a simple interpretation of the changes in E as being caused by changes in $\Delta\varphi$.

Fig. 4. 1—sample 1, 23°; 2—sample 1, 100°; 3—sample 1, 200°; 4—sample 2, 100°; 5—sample 3, 23°; 6—sample 3, 100°; 7—sample 4, 100°

In that region of surface coverages where the adsorption kinetics is described by equation (2), the use of equation (4) would be unjustified, since there is no reason to believe that the decrease in the adsorption rate with coverage is determined by an increase in the activation energy. On the contrary, it is apparently determined by a change in the number of free sites. The transition from kinetics (1) to kinetics (2) may be explained by the existence on the surface of two forms of adsorbed oxygen. In this case kinetics (2) describes the transition from chemisorbed atoms to chemisorbed molecules, or a change in the nature of adsorption due to a change in the valence of the surface silver atoms [6].

The kinetics of desorption was not investigated systematically by us; individual experiments show that the desorption rate decreases linearly with decreasing filling. During desorption of $11 \cdot 10^{-2}$ cm^3/m^3 O_2, the work function decreased by only 0.015 V. The region of surface coverage in which the linear dependence of the desorption rate on filling is observed corresponds to the region of applicability of equation (2).

Table 2

Sample-catalyst No.	Se concentration, at. %	$\Delta E/\Delta(\Delta\varphi)$, 23°	$\Delta E/\Delta(\Delta\varphi)$, 100°	$\Delta E/\Delta(\Delta\varphi)$, 200°
1	–	0.81	1.18	2.36
2*	–	–	0.80	1.44
3	$1 \cdot 10^{-3}$	0.73	0.78	0.71
4	$1 \cdot 10^{-2}$	0.78	0.81	0.80

* Sample without additive, prepared from $AgNO_3$ obtained by dissolving 99.999% Ag in especially pure HNO_3.

We consider it our pleasant duty to express our deep gratitude to Prof. M. I. Temkin for discussion of the results obtained.

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Received
28 I 1965

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