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STUDY OF THE ADSORPTION OF BENZENE VAPORS ON PALLADIUM FILMS

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For the study of catalytic and adsorption phenomena, metal films sublimed in vacuum are often used; these are distinguished by the high purity of their surface. It has been shown ([1]) that palladium films obtained by sublimation in high vacuum possess catalytic activity with respect to the hydrogen redistribution reaction in cyclohexadiene-1,3. In studying the kinetics of this reaction, it became necessary to investigate the adsorption of one of its products—benzene—on palladium films.

To measure adsorption, the flow method was used, which had been developed in detail by N. N. Kavtaradze ([2]). Palladium films were prepared by subliming the metal from a wire heated by an electric current onto the walls of the adsorption vessel at a residual pressure of $5 \cdot 10^{-7}$ mm Hg, after careful removal of sorbed gases from the heated walls of the vessel and the wire. The film thickness was determined from the loss in weight of the palladium wire; in the calculation it was assumed that the density of the film was equal to the density of massive palladium. The visible surface of the palladium film was 100 cm^2. Benzene vapors entered the adsorption vessel from a flask of volume 10 l, in which the pressure was equal to 3 mm Hg, through a capillary 5 cm long and 0.1 mm in diameter. Krypton, by whose adsorption the surface of the palladium films was determined, was supplied through the same capillary from another cylinder of volume 10 l. The pressure in the adsorption vessel was measured after 2–3 minutes with a Pirani manometer, which was thermostated at 20° and had been calibrated in advance for krypton and benzene vapor by means of a McLeod manometer. In those cases where the temperature of the adsorption vessel differed from that of the Pirani manometer, corrections for thermal effusion were introduced into the treatment of the results by the method of N. N. Kavtaradze ([4]). Special experiments showed that, at the flow rates used, adsorption equilibrium is established extremely rapidly. Thus, the kinetics of adsorption did not complicate the obtaining of isotherms. The adsorbed amount was calcu-

Fig. 1

Figure 1: Fig. 1

lated from the difference in flow rates measured before and after depositing the palladium film on the walls of the adsorption vessel.

The adsorption of benzene vapors on the glass parts of the apparatus proved to be considerable and was determined by an independent method suggested by N. N. Kavtaradze. An ampoule was sealed near the capillary and was cooled with liquid nitrogen. The weight of benzene condensed in the ampoule after several hours of vapor flow through the capillary agreed well with that calculated by the Knudsen formula:

$$\frac{dN}{dt} = \frac{1}{2}\sqrt{\frac{\beta}{2\pi MRT}}\,\frac{1}{l}(p_1 - p_2), \qquad \beta = 16\frac{a^3}{3},$$

where M is the molecular weight, a is the radius of the capillary, l is the length of the capillary, p_1 is the pressure of benzene vapor in the ten-liter flask, and p_2 is the pressure in the adsorption vessel. Comparing the amount of benzene that entered the adsorp-

tion vessel, with the amount of benzene in the vapor phase, it is easy to calculate its adsorption on the glass at different pressures.

Adsorption isotherms of benzene vapor were obtained at temperatures of 20 and 79°, since it was precisely in this temperature interval that the kinetics of the disproportionation reaction of hydrogen in cyclohexadiene was studied. Figure 1 gives the adsorption isotherms of benzene vapor on four palladium films at a temperature of 20° (curves 1–4) and the adsorption isotherm of benzene vapor at a temperature of 79° (curve 5). Repeated fillings in each of the experiments showed that part of the adsorbed benzene is readily removed from the surface, but the greater part remains on the palladium film even after many hours of pumping down to $1 \cdot 10^{-5}$ mm Hg at the temperature of the experiment. Desorption occurs only when the film temperature is raised to 250°. When the temperature is lowered to 20°, not all of the previously adsorbed amount of benzene is adsorbed again. This is probably due to a reduction in the total surface area of the palladium film upon heating, which is confirmed by the results of surface-area determination with krypton (see below). For all the palladium films studied, the fraction of benzene firmly adsorbed on the surface at 20° is approximately 75–80% of the total amount of adsorbed substance in the pressure range $1 \cdot 10^{-2}$–$2.6 \cdot 10^{-2}$ mm Hg.

Fig. 1. Isotherms of total adsorption of benzene vapor on palladium films at 20° (1, 2, 3, 4) and at 79° (5)

It turned out (Fig. 2) that at pressures below $5 \cdot 10^{-3}$ mm Hg the amount of firmly adsorbed substance depends on the pressure. At higher pressures this

Fig. 2

Figure 2: Fig. 2

dependence is less pronounced. For films Nos. 1–4 at 20°, the curves for the dependence of adsorption on pressure have a stepwise character. Apparently, it may be assumed that the surface on which firm adsorption of benzene occurs is not homogeneous, but consists of sites of two or three kinds. Film 2 was subjected to preliminary sintering at 100°, and film 3 at 300°. Comparison of the corresponding curves shows that the character of the surface heterogeneity depends little on thermal treatment. Films Nos. 1 and 4 were prepared under identical conditions; however, the number of sites with different adsorption potentials is not the same for them. Eischens, Francis, and Pliskin[4], in studying the effect of coverage of the palladium surface on the infrared spectra of chemisorbed carbon monoxide, came to the conclusion that several types of surface sites with different adsorption potentials exist, and that for each site a relative homogeneity of the surface is observed. This agrees with our data, despite the fact that the methods of preparing the palladium adsorbents differed sharply.

Fig. 2. Firm adsorption of benzene on palladium films at 20° (1, 2, 4) and at 79° (5)

In the coordinates of the BET equation, for all films except film 1, broken lines are obtained, consisting of two rectilinear sections. From the slope of the initial straight line, the amount of firmly adsorbi-

sorbed benzene molecules N'; from the slope of the second straight line—the total number of adsorbed benzene molecules N''. The results of the calculations are given in Table 1. In the coordinates of the Langmuir equation, $\frac{p}{N'}-p$, where N is the

Table 1

Number of benzene molecules adsorbed on palladium films at 20 and 79°

No.	T, °C	Preliminary treatment	Film weight, g	BET $N' \cdot 10^{-16}$	$N'' \cdot 10^{-16}$
1	20	Without sintering	0.0054		17.3
2	20	Sintering at 100°	0.0042	8.8	13.9
3	20	» » 300°	0.0059	11.05	19.25

No.	T, °C	Preliminary treatment	Film weight, g	BET $N' \cdot 10^{-16}$	$N'' \cdot 10^{-16}$
4	20	Without sintering	0.0077	15.4	29.3
5	79	» »	0.0025		11.5

number of adsorbed molecules at pressure p, the isotherms of total adsorption likewise consist of two rectilinear segments, from whose slopes the same values of N' and N'' are obtained as from the BET equation. From the data of Table 1 it is evident that the surface accessible to firm adsorption of benzene is only slightly reduced as a result of sintering palladium films at 300 and at 100°. The isotherm of total adsorption of benzene vapor at 79° obeys the BET and Langmuir equations and has no break in the coordinates of the indicated equations, as also for film No. 1.

To determine the surface area of sublimed palladium films and its dependence on sintering, krypton adsorption at −195° was studied. In calculating the surface area by the BET equation, the value of the saturated-vapor pressure for solid krypton was used as p_s (5). It turned out that the heterogeneity of the palladium surface is manifested in this case as well, since in the coordinates $\frac{p}{N(p_s-p)}$ and $\frac{p}{p_s}$ two straight lines with different slopes are obtained. Table 2 gives the surface areas of the film

Table 2

Values of the total surface areas of Pd films in cm^2

σ_{Kr}, Å^2	By krypton: before sintering S_{act}	By krypton: before sintering S_{full}	By krypton: after sintering at 300° S_{act}	By krypton: after sintering at 300° S_{full}	By benzene: No.	By benzene: preliminary treatment	By benzene: S_{act}	By benzene: S_{full}
14.7	447	909	320	718	1	Without sintering		700
22 (5)	667	1340	480	1075	2	Sintering 300°	346	547
					3	Sintering 100°	446	761

Fig. 3. Isotherms of reversible adsorption of benzene. 1-4 —at 20°. 1-4 —palladium films not subjected to heat treatment, 2, 3 —palladium films after preliminary heat treatment; 5 —at 79°

Figure 3: Fig. 3. Isotherms of reversible adsorption of benzene. 1-4 —at 20°. 1-4 —palladium films not subjected to heat treatment, 2, 3 —palladium films after preliminary heat treatment; 5 —at 79°

σ_{Kr}, Å^2	By krypton: before sintering S_{act}	By krypton: before sintering S_{full}	By krypton: after sintering at 300° S_{act}	By krypton: after sintering at 300° S_{full}	By benzene: No.	By benzene: preliminary treatment	By benzene: S_{act}	By benzene: S_{full}
					4	Without sintering	622	1160

before and after sintering at 300°; for comparison, the surface areas of four films from Table 1 are given, calculated from benzene adsorption on the assumption that the area occupied by one benzene molecule in flat orientation is equal to 40.3 Å^2 (6). The data presented indicate good qualitative agreement in the surface-area values determined from krypton and from benzene, regardless of the choice of the area of Kr (5). This becomes especially clear if one takes into account the nonreproducibility of the surface of films obtained even under identical sublimation conditions. The specific surface area of the films is of the order of 15 m^2/g; this value is close to the specific surface areas of metallic films obtained by Beek (7). Geometric-

surface of the adsorption vessel is equal to 100 cm^2. It follows from Table 2 that the surface of the palladium film before heat treatment is approximately 13 times greater than the geometric surface, and after heat treatment, 10 times greater. The coincidence of the surfaces for benzene and krypton shows that palladium films are wide-pore adsorbents.

The isotherms of reversible adsorption of benzene vapors are presented in Fig. 3. For films Nos. 1 and 4, which were not subjected to heat treatment, the shape of the isotherms differs sharply from the isotherms for films Nos. 2 and 3, which were heat-treated.

Fig. 3. Isotherms of reversible adsorption of benzene. 1-4 —at 20°. 1-4 —palladium films not subjected to heat treatment, 2, 3 —palladium films after

preliminary heat treatment; 5 —at 79°.

In the same figure the isotherm 5 of reversible adsorption at 79° is shown. The adsorption isotherms obtained on heat-treated films are concave and cannot be described by the Langmuir or BET equation. The isotherms obtained on films Nos. 1 and 4 have a convex shape, but also do not obey the BET and Langmuir equations. The convex shape of the isotherms for films Nos. 1 and 4 apparently indicates the predominance of the interaction of the adsorbate with the surface over intermolecular interaction in the monolayer. The isotherms of reversible adsorption of benzene obtained on heat-treated palladium films (Nos. 2 and 3) can be described by the equation of A. V. Kiselev ([8]):

$$\frac{\theta}{p(1-\theta)} = k_1 + k_1 k_n \theta,$$

which takes into account the interaction of molecules in the adsorption layer. Here k_1 is a constant characterizing the interaction of adsorbed molecules with the surface, and k_n is a constant taking into account the interaction of molecules with one another. The isotherm obtained on film No. 3 in the coordinates

$$\frac{\theta}{p(1-\theta)} - \theta$$

gives a straight line, from which it was found: $k_1 = 6.1$ mm^{-1}, $k_n = 7.5$ mm^{-1}. For film No. 2, sintered at a lower temperature, in the same coordinates a broken line with two rectilinear sections was obtained. For the first of them $k_1 = 9.4$ mm^{-1}, $k_n = 0.8$ mm^{-1}; for the second, $k_1 = 4.9$ mm^{-1}, $k_n = 7.5$ mm^{-1}. These results show that for the indicated films the intermolecular interaction in the monolayer is of considerable importance: for film No. 3 $k_n > k_1$. In this case a "stepwise" nonuniformity in adsorption potential is also observed. Indeed, k_1 for film No. 2 decreases approximately by a factor of two on going from low coverages to higher ones, while the role of intermolecular interaction increases almost 10-fold in the region with the smaller adsorption potential.

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