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Figure 1: Adsorption isotherms of benzene vapor on KSK-2 silica gel calcined at various temperatures in vacuum. Black dots indicate desorption. The isotherm on KSK-2, 200° is taken from (8). At upper right are pore-volume distribution curves calculated from these isotherms.

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Abstract

Full Text

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PHYSICAL CHEMISTRY

L. D. BELYAKOVA and A. V. KISELEV

THE EFFECT OF DEHYDRATION OF THE SURFACE OF SILICA GEL ON THE ADSORPTION OF BENZENE AND HEXANE VAPORS

(Presented by Academician M. M. Dubinin, 10 VIII 1957)

The study of the dehydration of the surfaces of adsorbents that are protonic acids is of great interest in connection with the fact that the presence of hydroxyl groups on the surface increases the adsorption energy

Fig. 1. Adsorption isotherms of benzene vapor on KSK-2 silica gel calcined at various temperatures in vacuum. Black dots—desorption. The isotherm on KSK-2, 200° is taken from (8). At upper right—pore-volume distribution curves calculated from these isotherms

of substances possessing an electron-donor function ([1,2]). This applies not only to adsorbates capable of entering into hydrogen bonding, but also to unsaturated and aromatic hydrocarbons, which in some cases are capable of forming molecular π-complexes with protonic acids. Thus, calcination of silica gel in air, leading to dehydration of its surface, reduces the adsorption of vapors not only of methanol but also of benzene ([3]). With increasing hydration of the surface of silica obtained by burning organosilicon compounds, there is an increase in the adsorption and heat of adsorption of benzene vapors, whereas for hexane these quantities remain practically unchanged ([4]).

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Fig. 2. Change in the surface concentration of hydroxyl groups α_{OH} (1), specific surface area s (2), and total pore volume v_s (3) as a function of the calcination temperature of silica gel KSK-2 in vacuum

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In the present work, the dependence of the adsorption of benzene and hexane vapors on the concentration of hydroxyl groups on the surface of coarse-macroporous silica gel KSK-2*, modified by thermal dehydration in vacuum. For this purpose the sample (about 3 g) was placed in a quartz sleeve of a vacuum apparatus and calcined at temperatures of 200, 400, 500, 650, 850, 950, and 1020°. At 200 and 400° pumping was carried out for about 100 h; at higher temperatures, from 25 to 60 h. The criterion for the end of pumping was the practical cessation of water evolution at the given temperature**. The evolved water was absorbed by magnesium perchlorate, weighed on quartz spring balances (7). The accuracy of the determination was $5 \cdot 10^{-6}$ g of water per 1 g of silica gel. After dehydration at each of the indicated temperatures, the adsorption isotherms of nitrogen vapor at $-195°$ (to determine the specific surface area of the sample) and the adsorption isotherms of benzene and hexane vapors at 20° were studied. These two hydrocarbons, with the same number of carbon atoms in the molecule, are adsorbed differently by acidic adsorbents, and comparison of their behavior makes it possible to judge the state of the adsorbent surface. The adsorption and desorption isotherms of benzene vapors were measured up to the relative pressure $p/p_s = 1$. The adsorption isotherms of hexane vapors were measured up to $p/p_s \approx 0.4$.

Fig. 2. Change in the surface concentration of hydroxyl groups α_{OH} (1), specific surface area s (2), and total pore volume v_s (3) as a function of the calcination temperature of silica gel KSK-2 in vacuum

Figure 1 presents the adsorption and desorption isotherms of benzene vapors. It is evident from this figure that the adsorption of benzene vapors in the region of monomolecular filling decreases strongly as the calcination temperature of the silica gel is increased, and even the form of the isotherm changes: from convex it becomes concave. Figure 2 gives the dependences of the specific surface area s, pore volume v_s, and concentration of hydroxyl groups α_{OH} on the surface of the silica gel on the temperature of its calcination in vacuum. When the silica gel was heated to 850°, the surface area of the sample s and the pore volume v_s decreased by 9%; when heated to 950°, by 20%. However, from the pore-volume distribution curves with respect to effective diameters (Fig. 1) it is seen that the pore size did not change in this case. Only heating at an even higher temperature led to a noticeable narrowing of the pores. Thus, after calcination at 1020° the mean pore diameter decreased from 100 Å to 62 Å, and, as is seen from the distribution curves, narrower pores now occupied a considerable

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Fig. 3. Absolute adsorption isotherms of benzene and hexane vapors

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fraction of the pore volume. Thus, upon calcination of macroporous silica gels in vacuum (9, 10), their structure does not undergo substantial change, and upon heating approximately to 900° the surface changes only slightly***. From Fig. 2 it is seen that the concentration of hydroxyl groups on the surface of the silica gel as a result of calcination to 950° decreased by more than a factor of 10****. The total amount of gases evolved from 400° to 1020° was about 4 μ-mol/g, i.e., considerably less than in (13).

Thus, by studying the adsorption of hydrocarbons on wide-pore

* This silica-gel sample was studied in works (5, 6).

** During the last 12 h of pumping, approximately $3 \cdot 10^{-4}$ g of water per 1 g of silica gel was evolved.

*** Calcination in air (11) and in water vapor (10) leads to a noticeable decrease in the surface area at a lower temperature.

**** The slight rise of the curve at 1020° is probably connected with the fact that part of the "structural water" of the silica gel is located inside the primary particles of its framework and is released at high temperatures. It cannot be attributed to the surface; however, its amount is small, as is also indicated by deuterium-exchange experiments (12).

samples calcined at temperatures from 200 to 950°, we were dealing with silica gel of the **same pore structure but different degrees of surface hydration**, which made it possible to follow the dependence of adsorption of benzene and hexane vapors only on the concentration of hydroxyl groups on the surface of the silica gel.

Fig. 3. Absolute adsorption isotherms of benzene vapors (left) and hexane vapors (right) on the surface of silica gel KSK-2 after calcination in vacuum at 200° (1), 400° (2), 500° (3), 650° (4), 850° (5), 950° (6), and 1020° (7). 8—data for quartz.

In Fig. 3, on the left, the absolute adsorption isotherms of benzene vapors in the monomolecular region are shown, obtained by recalculating the experimental isotherms of Fig. 1 per unit surface area, as determined from adsorption of nitrogen vapors. On the same figure, at the right, curves are given for the absolute adsorption isotherms of hexane vapors.

The adsorption isotherm of hexane vapors on the hydrated surface of silica gel is almost linear and, in character, is close to the adsorption isotherm of hexane vapors on liquid water (14). Whereas the adsorption of hexane vapors changed practically not at all when the hydration of the surface was changed by a factor of

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10, the adsorption of benzene vapors decreased by a factor of 3.5 (at $p/p_s = 0.1$, curves for KSK-2-200° and for KSK-2-950°).

In the case of adsorption of hexane on silica gel, van der Waals interaction takes place, in which not only atoms of the surface of the adsorbent participate, but also atoms located inside the particles of its framework; therefore, changes in the electrical and magnetic properties of surface groups upon dehydration cannot substantially alter the adsorption energy of saturated hydrocarbons. In the case of benzene adsorption, van der Waals forces also make a large contribution; however, the adsorption energy of benzene in purely van der Waals adsorption (15) is less than the adsorption energy of hexane. In contrast to adsorption on graphite (15), adsorption of benzene vapors on the hydrated surface of silica gel, as is seen from Fig. 3, considerably exceeds adsorption of hexane vapors, and the heat of adsorption of benzene vapors on the hydrated surface of silica is greater than that of hexane (8). This shows that, in the case of adsorption of benzene on the hydrated surface of silica, in addition to van der Waals interaction, an additional interaction of the π-complex type takes place (1,2,8,16,17). In contrast to hexane, adsorption of benzene vapors decreases sharply with a decrease in the concentration of OH groups on the surface of silica gel, because the possibility of such additional interaction between the benzene molecule and the OH groups of the surface is reduced. When hydroxyl groups are removed from the surface, the additional specific interaction characteristic of benzene adsorption on the hydrated surface of silica gel is eliminated. Whereas on the hydrated surface the absolute magnitude of adsorption of benzene vapors at the relative pressure $p/p_s = 0.1$ exceeds the adsorption of hexane by more than a factor of 2.5 (Fig. 3), on the dehydrated surface the absolute magnitudes of adsorption of benzene and hexane vapors are very close, since the dehydrated surface retains molecules of both benzene and hexane only through van der Waals interactions. Since

the polarizability of hexane is greater than that of benzene, the adsorption of hexane vapors on the dehydrated surface of silica gel, as on the surface of graphitized carbon black [15], is even somewhat greater than the adsorption of benzene vapors. Thus, at $p/p_s = 0.1$, the adsorption of hexane on silica gel KSK-2, 950°, is 1.7 times greater than that of benzene.*

Figure 4 gives the dependence of the absolute adsorption at $p/p_s = 0.1$ and of the constant C of the BET equation for benzene and hexane on the area per one OH group, ω_{OH}.** From this figure it is seen that the main decrease in the adsorption and adsorption energy of benzene vapors occurs over a comparatively narrow interval of change in α_{OH}, approximately from 3.5 to 5.5 μ-mol/m^2, which corresponds to a change in ω_{OH} from 30 to 45 Å^2. Since a benzene molecule adsorbed on the surface of silica gel in a dense monolayer occupies about 49 Å^2 (8,16), the sharp decrease in benzene adsorption is apparently associated with the fact that in this region the benzene molecule loses the possibility of interacting simultaneously with several surface hydroxyls.

Fig. 4. Dependence of the absolute magnitude of adsorption at $p/p_s = 0.1$ and of the constant C of the BET equation for benzene (1) and hexane (2) on the

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Figure 4

Figure 4: Figure 4

area per one hydroxyl, ω_{OH}. The designations of the points are the same as in Fig. 3. The vertical dashed line marks the value $\omega_{C_6H_6}$.

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LITERATURE CITED

1. A. V. Kiselev, DAN, **106**, 1046 (1956).
2. A. V. Kiselev, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, pp. 90, 199.
3. A. V. Kiselev, K. G. Krasilnikov, L. N. Soboleva, DAN, **94**, 85 (1954).
4. A. A. Isirikyan, A. V. Kiselev, DAN, **115**, 343 (1957).
5. A. A. Isirikyan, A. V. Kiselev, DAN, **110**, 1009 (1956).
6. L. D. Belyakova, O. M. Dzhigit, A. V. Kiselev, ZhFKh, **31**, 1577 (1957).
7. M. A. Kaliko, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 155.
8. A. A. Isirikyan, A. V. Kiselev, ZhFKh, **31**, 2127 (1957).
9. R. A. van Nordstrand, N. E. Kretger, H. E. Ries, J. Phys. Coll. Chem., **55**, 621 (1951).
10. G. Ries, in: *Catalysis. Catalysts of Organic Reactions*, IL, 1955, p. 37.
11. G. K. Boreskov, M. S. Borisova et al., DAN, **62**, 649 (1948).
12. R. G. Haldeman, P. H. Emmett, J. Am. Chem. Soc., **78**, 2117 (1956).
13. W. Stöber, Koll. Zs., **145**, 17 (1956).
14. D. C. Jones, R. H. Ottewill, J. Chem. Soc., 1955, 4076.

15. N. N. Avgul' , G. I. Berezin, A. V. Kiselev, I. A. Lygina, Izv. AN SSSR, OKhN, 1956, 1304.

16. A. V. Kiselev, Usp. Khim., **25**, 705 (1956).

17. A. N. Terenin, in: *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 206.

18. Yu. A. El' tekov, Dissertation, Moscow State University, Faculty of Chemistry, 1956.

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* From Fig. 3 it is seen that the adsorption of hexane vapors on silica gel calcined at 650° and above coincides with the adsorption on quartz (18). The adsorption isotherm of benzene vapors on the sample calcined at 1020° lies above the isotherms on the samples calcined at 850° and 950° (Fig. 3), owing to the increase in adsorption potential in fine pores (16), which constitute a large part of the pore volume of the sample calcined at 1020°.

** The BET equation is well obeyed for the adsorption isotherms of benzene vapors on silica gel calcined at 200°, 400°, 500°; for samples calcined at 650° and 850°, the range of applicability of the BET equation narrows. The adsorption isotherms of hexane vapors in all cases are described less well by this equation (16), but the sequence of the values of the constant C is not in doubt.

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

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