HEAT OF ADSORPTION OF BENZENE AND HEXANE VAPORS ON CALCINED AND HYDRATED SILICAS

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Abstract

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In a number of works it has been shown that changes in the chemical composition of the surface of silica gels by carrying out surface chemical reactions—dehydration (^{1,2}), esterification (^{3,4}), halogenation ($^{5-7}$)—very sharply alter their adsorption properties with respect to substances adsorbed not only by universal dispersion interactions, but also by additional, stronger interactions, for example interactions of the acid–base type (^{1,8,9}). The influence of the degree of dehydration of the silica-gel surface on the adsorption of methanol and benzene vapors was studied, in particular, in (^{10}), where it was shown that thermal dehydration of silica gel leads to a decrease in the adsorption of these vapors in the initial part of the isotherm. In (^{9,11}) it was shown, on the other hand, that the adsorption of vapor of a saturated hydrocarbon (*n*-pentane) upon dehydration of silica gel by heating from 200 to 400° does not change.

In the present work the influence of the degree of hydration of the silica-gel surface on the magnitudes of the differential heat of adsorption of benzene and hexane vapors is investigated. Adsorption quantities were measured with an apparatus that was an improved version of that described in (^{11}). The heat of adsorption was measured in an automatic calorimeter with constant heat exchange, similar to that described in (^{12}). Benzene and hexane of high purity were obtained from E. A. Mikhailova, additionally distilled through a column, and introduced into the apparatus through columns with silica gel. Their vapor pressures at 20° were 75.25 and 121.7 mm Hg, respectively. All experiments were carried out at 20°.

As the initial adsorbent, silica was used that had been obtained by G. V. Vinogradov* in the form of "white soot" by burning organosilicon compounds in a muffle furnace and subsequently calcining the fine powder at 800–1000°. This method of obtaining silica excluded the possibility of formation on its surface of a dense layer of hydroxyl groups of silicic acid (in contrast to silica gels obtained from hydrogels (^{1,13})). The hydrated sample was obtained from this initial sample by keeping it under liquid water for 7 months and subsequently drying at 120°. Before measurements of the heats of adsorption, both these samples were evacuated in the calorimetric ampoule at 200°. The specific surfaces of both

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

samples after evacuation at 200° were determined by E. V. Khrapova from the adsorption of nitrogen vapors and were 185 m^2/g for the initial sample and 135 m^2/g for the hydrated sample. The reduction of the surface of highly dispersed silica upon prolonged treatment with water occurs, probably, analogously to that noted in (^{14}). The initial sample retained about 0.58% "structural water," i.e., contained 3.5 μmol OH per 1 m^2 of surface—

···ness. The hydrated sample retained 1.32% "structural water" in this process, i.e., it contained 10.8 μmol OH per 1 m^2. This value is close to the limiting amount of OH on the surface of hydrated quartz and silica gels: 12.8 μmol per 1 m^2, calculated in (15, 16).

Figure 1 gives the complete adsorption isotherms of benzene vapor on the original and hydrated silica samples. It is evident from the figure that the samples are porous; this porosity is due to some sintering during heating of the original sample to 1000° after its preparation. Figure 1 presents curves of the pore-volume distribution according to pore-neck diameters, calculated from the desorption branches of the obtained isotherms (without corrections for the thickness of the adsorption layer). Both samples belong to the fourth structural type, i.e., they are nonuniformly porous adsorbents (17) with a slight predominance of pores with neck diameters of about 60-70 Å. It is also evident from Fig. 1 that the total pore volume decreases somewhat upon hydration (14).

Fig. 1. Adsorption isotherm of benzene vapor on hydrated (1) and calcined (2) silica samples. Filled points—desorption. Above—curves of pore-volume distribution by size.

Fig. 2. Dependence of the differential heat of adsorption of benzene vapor Q_a on the adsorption value a for hydrated (1) and calcined (2) silica samples. L—heat of condensation. Filled points—desorption.

In the region of capillary condensation, the isotherms for both samples are very similar, but in the initial, purely adsorption region the isotherm for the hydrated sample, despite its smaller specific surface area, lies considerably higher. The increase in adsorption capacity with respect to benzene as a result of hydration of the silica surface is clearly seen from Fig. 2, which gives the dependences of the differential heats of adsorption of benzene on the original and hydrated samples on the magnitude of adsorption up to saturation. In the initial region the heats,

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as in the case of silica gels, fall sharply owing to the considerable heterogeneity of the silica surfaces (18). In the broad region of capillary condensation they differ little for the two samples and exceed the heat of condensation of the normal liquid by only 0.5-0.3 kcal/mol. Owing to the nonuniform porosity of these samples, capillary condensation near saturation in both cases ends only with weakly expressed maxima of the heats of adsorption, in contrast to uniformly porous silica gels (18). Measurement of the adsorption isotherms and of the differential heats of adsorption in the region of capillary condensation made it possible to calculate the values of adsorp-

tion films s' by the thermodynamic method $^{(17)}$. These values s' were, for the original sample, 172 m^2/g, and for the hydrated one 134 m^2/g, i.e.

Fig. 3 Fig. 4

Fig. 3. Dependence of the differential heat of adsorption of benzene $(1, 2)$ and hexane $(3, 4)$ on the absolute amount of adsorption a, for hydrated $(1, 3)$ and calcined $(2, 4)$ silica samples. Black points —desorption

Fig. 4. Adsorption isotherms a and differential heats of adsorption Q_a of benzene $(1, 2)$ and hexane $(3, 4)$ as a function of the relative pressure p/p_s, for hydrated $(1, 3)$ and calcined $(2, 4)$ silica samples. Black points —desorption

they are close to the corresponding values s, which indicates the accessibility of the surface of these samples for adsorption of the hydrocarbons taken.

Figure 3 gives the differential heats of adsorption of benzene and hexane on calcined and hydrated silica-gel samples as a function of the absolute amount of adsorption a (μ mole/m^2) in the region of monomolecular filling. The heat of adsorption of hexane vapor is only slightly sensitive to a sharp change in the degree of hydration of the surface of these samples. The heat of adsorption of benzene, however, is very sensitive to changes in surface hydration. It is seen from Fig. 3 that in the middle region of monolayer filling (near $\theta = 0.5$) the standard $^{(19)}$ heat of adsorption of benzene vapor, as a result of increasing the content of silicic-acid hydroxyls on the surface from 3.5 to 10.8 μ mole/m^2, increased by approximately 1.0 kcal/mole. Taking into account the area occupied by a flat-oriented benzene molecule on the surface of hydrated silica, $\omega_0 = 49$ Å^2 $^{(9)}$, and the area corresponding to one hydroxyl, we may ascribe this increase in the heat of adsorption of benzene by 1.0 kcal/mole to the energy of formation of π-complexes $^{(8,9)}$ between a benzene molecule and two or three hydroxyls of silicic acid. Clarification of the nature of the bonds in these π-complexes, and estimation of the relative role of polarization or of deeper chemical interactions, however, require further investigations and are connected with the general development of concepts concerning the hydrogen bond and similar bonds in molecular complexes of the donor–acceptor type.

The obtained values of the differential heats of adsorption of these hydrocarbons and their relation to surface hydration show that the principal interaction with the surface of silica gel consists of nonpolar van der Waals interactions, the energy of which, however, is smaller than in the case of adsorption on graphite (19), owing to the considerably sparser arrangement of force centers in the quartz lattice. The absence of a sharp influence

an increase in the concentration of hydroxyls on the silica surface on the heat of adsorption of hexane indicates a small contribution from the energy of ordinary induction interactions. In the case of benzene adsorption on a hydrated surface, however, the formation of π-complexes with silicic acid, while increasing the total heat of adsorption of benzene Q_a by only 10%, strongly increases the net heat of adsorption $Q_a - L$ (near $\theta = 0.5$, approximately by a factor of 2), which very strongly changes the shape of the adsorption isotherm for benzene vapors. This is clearly seen from Fig. 4, in which both the heat of adsorption and the absolute magnitude of the adsorption itself for hexane and benzene are expressed as functions of the relative pressure of their vapors p/p_s.

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