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Abstract

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ADSORPTION OF WATER VAPOR ON SILICA GELS OF DIFFERENT DEGREES OF HYDRATION

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As is known, the adsorption of water vapor on silica gels has certain specific features. Thus, in works (^{1-4}) the irreversible adsorption of water vapor, associated with additional hydration of the silica-gel surface in the adsorption process, was studied in detail. In (^{2,5}) it was established that, as the surface of silica gels and porous glasses is dehydrated, the adsorption isotherm of water vapor changes from convex to concave, corresponding to a hydrophobic surface. Determinations of the specific surface area of silica gels from adsorption isotherms of water vapor usually give values considerably smaller than those calculated from adsorption isotherms of nitrogen vapor. The reason for this apparently lies in the assumptions that are made in estimating the "capacity of the monomolecular layer" (a_m), and also in the choice of the magnitude of the landing area of the water molecule in the monomolecular layer (_0) (10.6 Å(^2) (^{7}), 14.8 Å(^2) (^{8})). According to the data of (^{9}), the values of (_0) for water vary for different silica gels from 11.2 to 29.1 Å(^2). However, in all these works the authors did not analyze the chemical composition of the surface of those silica gels and porous glasses on which the measurements were carried out. In this connection it seemed of interest to carry out systematic studies of the adsorption of water vapor on silica gels as a function of the degree of hydration of their surface.

In the present work the same silica-gel samples were used as in (^{3,10}), i.e., silica gel K-2, obtained by hydrolysis of SiCl(_4), and thoroughly purified samples of technical silica gels KSK-1 and KSK-2. In addition, measurements were carried out on samples of silica gel K-2 calcined in air for 24 hr at temperatures of 500, 700, and 900°. The initial samples, as in (^{3,12}), were treated at 300°.

Table 1

Adsorption characteristics of the silica gels used

Silica-gel sample	Calcination temperature, °C	Specific surface, m^2/g	Limiting pore diameter, Å	Structural water, μm/m^2	Irrevers. sorption of water after pumping, μm/m^2 at 20°	Irrevers. sorption of water after pumping, μm/m^2 at 250°
KSK-1	300	275	65	4.78	0.38	0.0
KSK-2	300	400	60	4.12	0.32	0.0
K-2	300	695	44	3.20	0.29	0.0
K-2	500	620	–	1.74	1.93	1.49
K-2	700	550	–	0.98	1.60	1.00
K-2	900	178	–	0.87	2.61	1.93

The specific surfaces of all the samples investigated were determined by the BET method from adsorption isotherms of nitrogen vapor. The content of structural water in these samples had been determined earlier (^{6}). The data obtained are given in Table 1. The adsorption measurements were carried out on an adsorption apparatus with quartz spring balances. Before the measurements the samples were pumped off at a temperature of 250°.

Figure 1 presents the isotherms of adsorption of water vapor on the initial silica gels and the curves of pore-volume distribution by their effective diameters calculated from the desorption branches, taking into account the thickness of the adsorbed film. We did not carry out analogous measurements for the calcined samples, since on calcination of silica gel only the pore volume changes, while their diameter remains practically unchanged (11). Figure 2A shows the initial portions of the primary adsorption of water vapor on all silica-gel samples, calculated per 1 m^2 of surface. As follows from Fig. 2A, the isotherms for the three initial samples treated at 300° are arranged in such a way that adsorption at identical (p/p_s) decreases with decreasing degree of surface hydration, in agreement with the observed decrease in the heat of wetting by water of these same samples (6). The states obtained during adsorption of water on thermally dehydrated surfaces are not equilibrium states, since in this case a process of surface hydration may proceed. However, this process in the monomolecular region at small (p/p_s) proceeds very slowly (5). Therefore, if the small change in surface hydration during the establishment of adsorption equilibrium is neglected, the isotherms shown in Fig. 2A for samples of silica gel K-2 calcined at high temperatures may be regarded, in the adsorption sense, as equilibrium ones. Comparing these isotherms with the preceding ones, it may be seen that, as the surface is dehydrated, they change their form and become concave, and also that the adsorption capacity of the silica gel decreases.

Fig. 1. Isotherms of adsorption of water vapor at 15° on silica gels KSK-1 *(1)*, KSK-2 *(2)*, K-2 *(3)*, and desorption curves calculated from them for the

Fig. 1

Figure 1: Fig. 1

Fig. 2. Initial portions of the isotherms of primary adsorption (A) and desorption (B, V) on silica gels KSK-1 (1), KSK-2 (2), and K-2 (3), calcined at 300°, and on K-2 silica gel calcined at 500° (4), 700° (5), and 900° (6). Black points—desorption.

Figure 2: Fig. 2. Initial portions of the isotherms of primary adsorption (A) and desorption (B, V) on silica gels KSK-1 (1), KSK-2 (2), and K-2 (3), calcined at 300°, and on K-2 silica gel calcined at 500° (4), 700° (5), and 900° (6). Black points—desorption.

distribution of pore volume according to the values of their effective diameters. Black points—desorption.

After holding the samples at (p/p__s = 1) for 48 hours, desorption isotherms were measured; these are presented for the initial samples in Fig. 2B and for the thermally dehydrated samples in Fig. 2V. In all cases we observed irreversible sorption of water*. The values of irreversible sorption obtained after prolonged evacuation of the initial silica-gel samples at 20° are very small, as follows from the table. Subsequent adsorption measurements on such surfaces give fully reproducible results, coinciding with the desorption curve, in agreement with the data ([4], [5]). However, if the initial samples are evacuated at a temperature of 250°, irreversible adsorption is absent, and subsequent adsorption measurements coincide with the corresponding iso—

* For convenience of comparison, the desorption isotherms are reduced to zero, i.e., the values of irreversible sorption of water have been subtracted from all ordinates.

treatments shown in Fig. 2A. Thus, for the initial samples the data we obtained show that the degree of hydration of the surface proves to be different both after identical thermal treatment of these samples ((^6)) and after holding them in saturated water vapor. The content of structural water in the initial silica gels indicated in Table 1 approximately corresponds to the maximum possible for each of the samples ((^{6,17})).

Irreversible adsorption of water for thermally dehydrated samples of K-2 silica gel is large and remains significant also after evacuation at (250^{ }). According to the data given in Table 1, the degree of hydration of the surface in this case increases in comparison with the initial value, but still remains below the degree of hydration of the initial sample treated

Fig. 2. Initial portions of the isotherms of primary adsorption (A) and desorption (B, V) on silica gels KSK-1 (1), KSK-2 (2), and K-2 (3), calcined at (300^{ }), and on K-2 silica gel calcined at (500^{ }) (4), (700^{ }) (5), and

(900^{ }) (6). Black points—desorption.

at (300^{ }). It follows from this that even at (p/p__s = 1), the silica-gel surface is not completely hydrated and its properties are not restored, in contrast to the conclusions of ((^5)). This is also confirmed by the data given in ((^{6,16})). The very slow process of surface hydration in the region of low relative pressures is apparently explained by the fact that, up to a monomolecular layer, the adsorbed water molecules are arranged rather loosely and adsorption practically does not proceed on a considerable part of the surface capable of hydration.

Examination of the isotherms shown in Fig. 2 indicates that, at the same values of (p/p__s), the adsorption values calculated per unit surface area are not identical for all the silica gels studied. A more hydrated surface corresponds to larger adsorption values, and vice versa. Thus, in the adsorption of water vapor on different silica gels, one cannot expect coincidence of the so-called "absolute" isotherms ((^{12})), as occurs, for example, in the case of nonpolar nitrogen molecules ((^{10})). This circumstance cannot be explained by the disturbing action of pores ((^{13})). In work ((^{14})) it was shown that, in nitrogen adsorption, a noticeable influence of pores leading to distortion of the initial part of the isotherm appears only on passing to the most finely porous silica gels.

The silica gels used in the present work were uniformly large-pore samples ((^{15})), for which the adsorption isotherms of nitrogen vapor, referred to unit surface area, coincide ((^{10})). In the adsorption of water—a substance with smaller molecular dimensions—the influence of the porous structure of the adsorbent will apparently be still smaller than in the case of nitrogen. Therefore, the unequal adsorption capacity per unit surface of all the silica gels studied is due not to structural factors, but to differences in the chemical nature of their surfaces.

Since the adsorption values referred to unit surface area at each value of (p/p__s) decrease as the surface of the samples is dehydrated, the fraction of surface corresponding to one adsorbed molecule, (= 1/aN) (where (a) is the adsorption value referred to unit surface area, and (N) is Avogadro' s number), increases; this indicates a looser arrangement of water molecules on the surface of dehydrated samples. To estimate the area (__0) occupied by a molecule in a monomolecular layer, it is necessary to know the value of the "capacity of the monomolecular layer," (a__m). In the case of the desorption branches of the isotherms, determination of (a__m) from point (B) gives, for the original samples of silica gels K-2, KSK-2, and KSK-1, values of (__0) respectively equal to 55, 50, and 39 Å(^2), decreasing with increasing content of structural water on the surface. Determination of (a__m) by the BET equation ((^{9,11})) leads to values considerably higher than those determined from point (B). Despite the fact that on the isotherm plotted in BET coordinates an approximately linear segment can be distinguished, this equation is hardly applicable to the case of water adsorption on silica gel because of the heterogeneity of the latter' s surface ((^{6})). In any case, an estimate of the area per water molecule, even for the most hydrated

KSK-1 sample, shows that in the interval (p/p_s) from 0.1 to 0.3 it changes from 39 to 22.5 Å(^2), remaining far above the values for (_0) accepted in the literature (10.6 and 14.8 Å(^2)). The corresponding values of (a_m) already lie in the region of polymolecular adsorption and capillary condensation.

It should be noted that a number of assumptions expressed in the literature concerning the mechanism of adsorption of water vapor on silica gel and the hydration of its surface ((^{2,4,5,17-20})), based both on adsorption data and on studies of infrared spectra of the surface layer, contradict one another ((^{20})). To clarify these questions, further study of adsorption is necessary in parallel with spectroscopic investigations.

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