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Abstract

Full Text

PHYSICAL CHEMISTRY

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ON THE POSSIBILITY OF CHANGING THE TEXTURE OF SILICIC ACID XEROGELS IN THE PROCESS OF VAPOR SORPTION

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In studying the interaction of an intermicellar liquid with the skeleton of silicic acid lyogels and its influence on the texture of xerogels ([1]), we were compelled in a number of cases, in order to establish the "native," very labile texture of the xerogels obtained, to abandon the generally accepted procedure for preparing samples for adsorption measurements—namely, high-temperature and high-vacuum activation of adsorbents, alternating with repeated "washings" of their surface by vapors of the substance whose adsorption was to be measured. Instead, we carried out prolonged evacuation at room temperature or at a not too high temperature (up to 220°) and pressures down to 10^{-3} mm Hg, and did not at all apply "washing" of the gels under study with adsorbate vapor.

Fig. 1. Isotherm of ad(de)sorption of methanol vapors at 20° on silica xerogel obtained from a propanol lyogel (black points here and below—desorption).

With this preparation of the adsorbents, in all the numerous experiments on vapor sorption (chiefly methanol) an unusual change in the sorption characteristics of the xerogels was observed which, apparently, differs both from irreversible poisoning of the silica-gel surface as a result of methoxylation of its surface ([2–6]), and from a fully reversible change in the linear dimensions of the sorbent or in its mechanical properties during methanol sorption ([7,8]).

The phenomenon observed by us consists in the fact that, when recording the isotherm of sorption of methanol vapors on silicic acid xerogels prepared for the experiment under the indicated mild conditions, the desorption branch of the isotherm at $P/P_S < 0.5$–0.6 was always located considerably below the adsorption branch. This divergence of the branches of the isotherm was especially

pronounced in samples obtained from alcogels in which the intermicellar liquid consisted of normal and isopropyl alcohols of the fatty series.

Analysis of the experimental conditions showed that this phenomenon cannot be explained by procedural errors or apparatus errors, and additional experiments were carried out to determine the cause of such behavior of the adsorbents.

Figure 1 gives the isotherm of ad(de)sorption of methanol vapors at 20° on silica gel obtained by drying a propanol alcogel; the sample was evacuated at $\sim 10^{-3}$ mm Hg and 200° without "washing." From this isotherm, each point of which is supplied with its number in the sequence in which they were recorded during the measurements, it is seen that if desorption is begun before $P/P_S \approx 0.5$, then the desorption points (Nos. 6–10) fall on the primary adsorption branch. But if this isotherm is brought to $P/P_S = 1$, then the desorption branch passes considerably below the adsorp-

···tional, whence it is clear that capillary condensation of methanol in the pores of the xerogel plays an essential role in the observed phenomenon.

The consecutive performance of several complete ad(de)sorption cycles ($0 \leq P/P_s \leq 1$) on one and the same sample (Fig. 2a) shows that during the first three cycles the desorption branches of the isotherms at $P/P_s \leq 0.5$–0.6 lie below the adsorption branches, which are superimposed on the preceding desorption branches; beginning with the fourth cycle, a reproducible reversible isotherm is observed in the indicated interval of P/P_s. The values of the specific surface area S of the xerogel, calculated from these isotherms by A. V. Kiselev' s simplified formula, gradually decrease, reaching a constant value in the fourth cycle (Fig. 2b). At the same time the total sorption capacity V_s of the gel decreases by only 0.02–0.04 cm^3/g ($\sim 5\%$), while the hysteresis loop at $P/P_s > 0.6$ shifts toward higher P/P_s.

It is known ([9]) that impregnation of an aerosilica gel with water followed by drying contracts the framework of the aerogel so that all large pores disappear, forming a typical finely porous silica gel with a small V_s and with the same value of S as in the initial aerogel. In our case something different occurs: V_s decreases very little, whereas S decreases quite substantially.

The results obtained could be explained by methoxylation of the surface of the xerogels during methanol sorption ([2–4]); however, the authors ([2–4]) indicate that, in contrast to our results, the methanol desorption isotherms obtained by them on the silicas studied either practically coincide with the adsorption curves or lie above the latter, especially at small P/P_s. Furthermore, from this point of view it is not entirely clear why capillary condensation of methanol is necessary for the phenomenon we observed. Finally, accepting methoxylation of the gel surface as the principal cause of the effect under consideration is difficult to reconcile with the results of the following experiment.

Fig. 2, a–Successive isotherms of ad(de)sorption of methanol on silica gel (I, II, III, IV); **b**–change in the value of the specific surface area as a function

Fig. 2

Figure 2: Fig. 2

Fig. 3. Adsorption–desorption isotherms of methanol vapor on the initial xerogel (1) and after its treatment with distilled water (2)

Figure 3: Fig. 3. Adsorption–desorption isotherms of methanol vapor on the initial xerogel (1) and after its treatment with distilled water (2)

of the number of ad(de)sorption cycles (1—from adsorption branches, 2—from desorption branches of the isotherms)

The initial silica xerogel, obtained from propanol lyogel, was treated with distilled water at room temperature for 24 h, with the water in the gel pores replaced and pumped out three times, after which the methanol ad(de)sorption isotherm on it was measured (Fig. 3). Comparison of this isotherm with the isotherm for the initial gel shows that the most probable cause of the phenomenon described should be regarded as a change in the texture of the gel during the ad(de)sorption cycle.

It seems to us that the results obtained in this work can be explained if one assumes that the silica gels obtained and studied by us consist of particles that are not compact formations but are permeated by very fine pores accessible to molecules of water and (to a lesser extent) methanol. During preparation of the samples under mild conditions such a structure of the particles is preserved, while during the consecutive performance of ad(de)sorption cycles, under the action of capillary forces, compaction (aging) of the initial loose particles occurs. As a result, S decreases, and the gaps between the contracting particles increase somewhat with a slight decrease in V_s, which is also observed experimentally.

Are there any grounds for assuming the presence of ultraporosity in ···

the particles themselves that make up the skeleton of the gels? Apparently there are, since in recent years experimental facts have been accumulating that may serve as indirect support for this hypothesis. In papers (10–12) there are substantial experimental data and conclusions in favor of the presence of OH groups inside gel particles. In paper (13) it was found that the last residues (~0.2%) of water in a calcined aluminosilicate catalyst are much less active catalytically than the same amount of water redeposited on a completely dehydrated catalyst; this fact can be understood if one assumes that the last residues of structural water during dehydration are removed from inside the elementary gel particles.

Fig. 3. Adsorption–desorption isotherms of methanol vapor on the initial xerogel (1) and after its treatment with distilled water (2)

The concept of the looseness of xerogel particles can explain the particle roughness adopted by the authors of work (14), as well as the possibility of "creeping" of water molecules under the modifying layer on the surface of silica gel (15).

This hypothesis is also consistent with the methanol chemosorption observed in (4) (0.5 mmol/g, i.e. ~0.02 cm^3/g) and water (1.2 mmol/g, i.e. also ~0.02 cm^3/g), which may represent intraparticle absorption of the adsorbate, and with the decrease in V_s by 0.02-0.04 cm^3/g found in our work over four adsorption-desorption cycles, during which compaction of the gel particles may occur. Finally, in some works, in order to explain the results obtained, the authors were forced to assume the presence of very fine ultrapores in particles of dehydrated $Al(OH)_3$ (16), quartz (17), and in silica-gel particles (18).

In conclusion, let us note that the results obtained in this work do not rule out the possibility of methoxylation of the silanol surface of silica gels, but, at least in the case of the samples studied here, the more important role is apparently played by the change in the texture of xerogels during vapor sorption. It also follows from this that the true values of the surface area of xerogels when methanol is used as the adsorbate can be obtained only from the primary adsorption branch of the isotherm and when the sample is prepared under mild conditions without "washing."

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