L. F. KIRICHENKO, V. M. CHERTOV, Z. Z. VYSOTSKII, D. N. STRAZHESKO

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Abstract

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L. F. KIRICHENKO, V. M. CHERTOV, Z. Z. VYSOTSKII, D. N. STRAZHESKO

STUDY OF THE SORPTION OF CATIONS FROM ACID SOLUTIONS ON SILICA GELS OBTAINED BY THE HYDROTHERMAL METHOD

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In works (1-4) it was shown for the first time, by a direct radiometric method, that ion-exchange uptake of cations on siliceous sorbents from acid aqueous solutions is a quite real phenomenon, apparently due to features of the structure of the surface of such adsorbents, and not to the presence in them of impurities (strong mineral acids, aluminum), as has often been assumed in the literature. At the same time, the question of the nature of the strongly acidic adsorption centers responsible for the uptake of cations from acid media on the surface of silicas still remains open. Experimental investigation of this question is substantially complicated by the fact that, in the pH range 2-4, the ion-exchange capacity of silica gels with respect to such weakly polarizing ions as Na^+ or Ca^{2+} is only 2–5 μg-eq/g.

In the present work we have studied the exchange uptake of monovalent ions of sodium, rubidium, cesium, thallium, of divalent ions—calcium, strontium, and barium, and also of the trivalent yttrium ion from acid aqueous solutions of their nitrate salts on silica gels obtained by hydrothermal treatment of silicic-acid hydrogels. The ion-exchange behavior of such adsorbents in the acid region has not been studied. In addition, one of the main tasks of this study was, on the basis of new experimental data, to obtain a more concrete idea of the nature of the surface regions of silica gel that determine cation exchange in the acid region. Hydrothermal silica gels are, in this sense, a very convenient object, since the conditions of their preparation (5, 6) predetermine the possibility of profound changes in the texture of these gels and in the crystallochemical structure of their surface.

The procedure for obtaining the hydrothermal silica gels studied by us was analogous to that described earlier (7), and their textural characteristics were determined as follows: the specific surface area S was calculated by the BET equation from isotherms of sorption of methanol vapor at 20° (the landing area of a methanol molecule was taken as 25 $\mathring{A}^2$); the total pore volume V_Σ was calculated as the difference between the apparent and true specific volumes; the mean pore diameter was found from the formula $D = 4V_{\Sigma}/S$, and the mean diameter of the elementary particles of the xerogel skeleton from the formula $d = 6/\gamma S$, where γ is the true density of silica gel (2.2 g/cm^3).

As is seen from the data of Table 1, raising the temperature and increasing the duration of autoclaving of the original hydrogel leads to a significant change in the textural characteristics of the final xerogels: the specific surface area decreases from 580 to 25 m^2/g, the mean diameter of the elementary particles increases from 50 to 1050 Å, and the mean pore diameter expands to 3550 Å, with a simultaneous substantial increase in the total ···

the pore volume of the samples. Thus, at our disposal there was a set of silica gels with textural properties varying within rather broad limits. For each of these gels, the adsorption of cations from acidic solutions of their nitric-acid salts was determined.

The sorption of cations was measured by a direct method—by the radioactivity of a weighed portion of gel containing the adsorbed labeled ions (the nitrates of the above-listed cations were labeled, respectively, with the radioactive isotopes Na^{22}, Rb^{86}, Cs^{134}, Tl^{204}, Ca^{45}, Sr^{90}, Ba^{133}, and Y^{91}). In calculating the adsorption values, corrections were introduced for background, isotope decay, and, in those cases where it was necessary, for attenuation of the radiation in the adsorbent layer; the measurements were carried out with a Geiger-Müller counter.

The conditions for preparing the samples for the adsorption experiment and for treating them after adsorption were the same as in work (^{4}), with the sole difference that the nonexchange electrolyte was washed out of the gel pores with demineralized water and the number of washings in all cases was three.

In Fig. 1 the absorption curves of monovalent cations Na$^+$, Rb$^+$, Cs$^+$, and Tl$^+$ by hydrothermal silica gels are presented as a function of the magnitude of their surface area (the adsorption here and below is referred to unit surface area). In Fig. 2 analogous data are given for divalent ions Ca^{2+}, Sr^{2+}, and Ba^{2+}, and in Fig. 3 the sorption curves are compared for the monovalent ion Na$^+$, the divalent Ca^{2+}, and the trivalent Y^{3+} (all curves were obtained in the pH range from 4.3 to 4.7). As is evident from Figs. 1-3, in all cases without exception one and the same picture is observed: the specific uptake of cations in the acidic region by hydrothermal silica gels increases regularly as the severity of the hydrothermal treatment is intensified and as the corresponding specific surface area of the samples decreases, the average particle diameter increases, etc.

Fig. 1. Adsorption of monovalent cations on hydrothermal silica gels with different specific surface areas:
a –Na$^+$ (pH 4.3), *b* –Rb$^+$ (pH 4.6), *v* –Cs$^+$ (pH 4.7), *g* –Tl$^+$ (pH 4.7)

In view of the fact that different conditions of hydrothermal treatment lead to

Fig. 2 and Fig. 3: adsorption curves

Figure 1: Fig. 2 and Fig. 3: adsorption curves

appreciable differences in the texture of the final xerogels, it is necessary to analyze the possibility that such structural changes influence cation uptake. In work ([8]) the conclusion was drawn that, for finely porous and medium-porous silica gels, especially in the case of sorption on them of strongly hydrated multicharged cations of small radius (for example, Al^{3+}), part of the volume of the narrowest pores of the gels proves inaccessible to such ions. However, the hydrothermal silica gels we studied had wider pores, and the series of ions given in work ([8]), in order of the difficulty of their entry into narrow pores, bears no relation to the relative adsorbability of various cations measured on our samples. Thus, the texture of the samples studied, apparently, does not exert any appreciable influence on the ion-exchange uptake of cations in the acidic region, which is governed by the structural features of the surface of hydrothermal silica gels.

Table 1

Conditions of preparation and textural characteristics of hydrothermal silica gels

Sample designation	Hydrogel treatment conditions in an autoclave: temperature, °C	Hydrogel treatment conditions in an autoclave: duration, h	Specific surface area, m^2/g	Average diameter of elementary particles, Å	Average pore diameter, Å	Total pore volume, cm^3/g
C-11 (control)	–	–	580	50	50	0.74
C-12	90	10	465	60	75	0.90
C-13	130	11	280	100	140	0.97
C-14	170	10	180	150	230	1.05
C-15	250	10	75	380	780	1.40
C-16	300	20	25	1050	3550	2.31

Fig. 2. Adsorption of divalent cations on hydrothermal silica gels with different specific surface areas:
a –Ca^{2+} (pH 4.7),

b –Sr^{2+} (pH 4.5),
c –Ba^{2+} (pH 4.7)

Fig. 3. Adsorption of cations of different valence on hydrothermal silica gels:
a –Na^{+} (pH 4.3),
b –Ca^{2+} (pH 4.7),
c –Y^{3+} (pH 4.3)

Comparison of the uptake curves of ions of different valence, Na^{+}, Ca^{2+}, and Y^{3+} (Fig. 3), shows that their sorption is equivalent in character; hence it follows that the exchange centers on the surface of hydrothermal silica gels must apparently be the same for all these ions. If, in addition, one takes into account that the siliceous framework of silica gel has the properties of a dielectric and, consequently, interaction of charges through the skeleton of elementary particles is hardly possible, it must be assumed that the adsorption centers under investigation must include 2–3 exchange-capable hydrogen atoms.

The conditions of hydrothermal treatment ([5–7]) are such that here, apparently, dissolution (decondensation) of the smaller particles is inevitable, with subsequent recondensation of molecularly dissolved silicic acids on larger elementary particles in the gel skeleton ([9]). In this process, the number of groups $\equiv Si{=}(OH)_2$ and $-Si{\equiv}(OH)_3$ on the surface of the growing particles may probably increase. Although in works ([10,11]) and

it has been concluded that the degree of hydration of a unit surface of ordinary and hydrothermal silica gels is approximately the same (it is expressed by several thousand micromoles of OH groups per 1 g of gels); an increase, during hydrothermal treatment, in the number of strongly acidic groups, measured in micromoles per 1 g of adsorbent, is quite possible, since the accuracy of determining the degree of hydration is at present still insufficient for detecting such changes.

Thus, the growth of exchange absorption of cations in the acidic region on hydrothermal silica gels as their specific surface decreases can be associated with a corresponding increase in the number of groups $= Si = (OH)_2$ and $-Si \equiv (OH)_3$ on the surface of these adsorbents. It should be noted that in work [12] the presence of groups $= Si = (OH)_2$ on the surface of silica gels was also assumed, and it was indicated that an increase in the number of hydroxyl groups at one and the same silicon atom should promote easier protonation of the hydrogen atoms of these groups.

In conclusion, let us dwell on one further circumstance which, probably, may play a certain role in strengthening the acidic properties of hydrothermal silica gels. The detailed mechanism of hydrothermal synthesis has not yet been clarified, but there is no doubt that further growth of large elementary particles proceeds through decondensation of smaller ones, and the transfer of the silicic acid molecules split off to the surface of the growing particles takes place in the presence of a large excess of water. Under these conditions, apparently, the possibility is not excluded of the formation of hydrates of the type $Si(OH)_4 \cdot 2H_2O$, having (by analogy with $H_2[SiF_6]$) the structure $H_2[Si(OH)_6]$, in which the central silicon atom exhibits sixfold coordination with respect to oxygen (cf. [13]). Transfer of silicic acid in the form of such molecules, with their subsequent condensation on the surface of the growing particles, may lead to the formation of surface groups $= Si = (OH)_2$ and $-Si \equiv (OH)_3$, with preservation of the octahedral coordination of the silicon atoms and a corresponding enhancement of the acidic properties of the hydroxyls.

Institute of Physical Chemistry named after L. V. PisarzhevskyAcademy of Sciences of the Ukrainian SSR

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