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V. M. CHERTOV, D. B. DZHAMBAEVA, A. S. PLACHINDA, I. E. NEIMARK

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Abstract

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SURFACE AND INTRAGLOBULAR SILANOL GROUPS OF SILICA GELS OBTAINED BY THE HYDROTHERMAL METHOD

(Presented by Academician M. M. Dubinin, 27 X 1964)

Hydrothermal methods for the synthesis of adsorbents, catalysts, supports and, in particular, silica gels with various adsorption-structural properties have recently been acquiring ever greater importance (1–3). In this connection, the study of the chemical structure of the surface of silica gels obtained by hydrothermal treatment is of considerable practical and theoretical interest.

The present article gives the results of an investigation of the concentration of silanol groups on the surface and inside the globules of silicaxerogels obtained from hydrogels subjected to hydrothermal treatment (3). Silicahydrogels were kept in an autoclave for 9-16 hr at temperatures of 90-350°. Longer treatment of the hydrogel and higher treatment temperatures correspond to xerogels with smaller values of specific surface area (2,3). The total amount of structural water in the xerogels, i.e., the amount of surface and intraglobular

$$> \mathrm{Si}-\mathrm{OH}$$

groups (4,5), was determined from the loss in weight upon calcination of the samples at 1100-1300° for 6-12 hr. The amount of surface silanol groups was determined by chemical methods: by the ion-exchange reaction of the H^+ ions of the surface hydroxyls for Ca^{2+}, and by the reaction of

$$> \mathrm{Si}-\mathrm{OH}$$

groups with lithium aluminum hydride $LiAlH_4$. From the difference between the total amount of structural water and the amount of surface hydroxyls, the concentration of intraglobular $\mathrm{Si}-\mathrm{OH}$ groups was found (4,5).

$$> \mathrm{Si}-\mathrm{OH}$$

groups (4,5).

The determination of surface hydroxyls by ion exchange is based on the equivalent ion-exchange replacement of the hydrogen of hydroxyls by Ca^{2+} in a solution of $Ca(OH)_2$, according to the reaction

$$2 > Si - OH + Ca(OH)_2 \rightleftharpoons (> Si - O)_2Ca + 2H_2O \quad (7).$$

A weighed portion of xerogel of 0.3-2.0 g of the 0.07-0.15 mm fraction was shaken with 300-100 ml of 0.027 N $Ca(OH)_2$ solution. At definite time intervals the concentration of hydroxide was determined in the solution. On the kinetic curve of absorption of Ca^{2+} by the xerogel, after the section with a steep rise corresponding to rapid ion-exchange absorption of Ca^{2+} ([6,7]), there follows a section close to linear, with a small slope, which corresponds to slow interaction of the hydroxide with the xerogel skeleton ([7]). By extrapolating the linear section of the curve to the ordinate axis, the value of the ion-exchange absorption of Ca^{2+} was found and, consequently, the amount of surface hydroxyl groups.

In determining surface $>$ Si—OH groups with $LiAlH_4$, an excess of a solution of lithium aluminum hydride in diethyl ether was added at 0° to a weighed portion of xerogel of the 0.07-0.15 mm fraction, and the amount of evolved H_2 was determined from the increase in pressure in the system (8—10).

The texture characteristics and the results of determining the structural water of the xerogels are given in Table 1. It follows from the data in the table that

Table 1.

Texture characteristics and content of structural water in silica xerogels*

Sample	Characteristics of silica gels: specific surface area S, m^2/g	Characteristics of silica gels: total pore volume V_{Σ}, cm^3/g	Total amount of structural water, μequiv OH per 1 g	Amount of surface silanol groups: by the ion-exchange reaction with $Ca(OH)_2$, μequiv OH per 1 g	Amount of surface silanol groups: by the ion-exchange reaction with $Ca(OH)_2$, μequiv OH per 1 m^2	Amount of surface silanol groups: by reaction with $LiAlH_4$, μequiv OH per 1 g	Amount of surface silanol groups: by reaction with $LiAlH_4$, μequiv OH per 1 m^2	Amount of intraglobular > Si–OH groups, μequiv OH per 1 g
Initial**	864	0.36	9.52	–	–	–	–	–
Initial**	425; 287	0.75; 1.04	5.24; 3.82	4.25; 2.93	10.0; 10.2	–	–	0.99; 0.90
12	634	0.90	7.34	–	–	6.40	10.1	0.94
13	368	1.01	4.56	3.54	9.6	3.27	8.9	1.02
14	166	1.19	2.74	1.67	10.1	1.61	9.7	1.07
15	91	1.42	1.98	0.91	10.0	0.90	9.9	1.07
16	73	2.12	1.70	0.64	8.8	0.62	8.5	1.06
17	36	2.51	1.32	0.35	9.7	0.29	8.1	0.97
18	21	2.42	1.14	0.19	9.0	0.20	9.5	0.95

* All data are referred to 1 g of anhydrous SiO_2. To remove adsorbed water, the xerogels were dried at 140–160° for 6–10 h. The specific surface area was calculated by the BET method from the adsorption isotherms of CH_3OH vapor, taking $\omega_{CH_3OH} = 25$ Å^2, which corresponds to $\omega_{N_2} = 16.2$ Å^2 (11).

** Here and below, “initial” denotes xerogels obtained from hydrogels that had not been subjected to hydrothermal treatment. For the initial sample with surface area 864 m^2/g, the hydrogel of which was used to obtain xerogels 12–18, the amount of surface silanol groups could not be determined by the methods used. Therefore these data are given in the table for two more wide-pore xerogels obtained from other hydrogels, likewise not subjected to hydrothermal treatment.

for all xerogels, irrespective of the magnitude of their specific surface area, i.e., of the temperature and duration of hydrothermal treatment of the hydrogel, the concentration of surface silanol groups remains practically constant and is equal to the concentration of > Si–OH groups in the initial samples.*

Consequently, De Boer' s assumption and conclusion (14, 15) concerning an increase in the degree of hydration of the surface of silica gel during hydrothermal treatment are not confirmed.

The concentration of intraglobular silanol groups in all xerogels obtained from hydrogels that had undergone hydrothermal treatment, in contrast to hydrothermally treated aerosil and silica xerogel (12, 13), remains practically constant and does not change in comparison with the initial samples.** This indicates that only part of their hydroxyl groups is involved in the recondensation reaction of silicic acids that have passed into solution during hydrothermal treatment, and that the fraction of uncondensed hydroxyls is the same as the fraction of $>$ Si—OH groups not involved because of steric hindrance

* The same result was obtained in the study of aerosil and silica gel subjected to hydrothermal treatment in an autoclave (12, 13).

** It is interesting to note that the amount of bulk hydroxyls in hydrothermally treated silica xerogel calculated from the data of work (13) is approximately 1.0 µequiv OH per 1 g. This figure is in good agreement with the values we found for hydrothermal samples.

in the reaction of spontaneous polycondensation of silicic acid during the preparation of silica gel under ordinary conditions. Thus, as a result of the hydrothermal treatment of silicahydrogel, the concentrations of surface and bulk silanol groups and, consequently, the chemical nature of the surface of the xerogels do not change.

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

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