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PHYSICAL CHEMISTRY OF SURFACE PHENOMENA

Density of Silanol Groups on the Surface of Silica Precipitated from a Hydrothermal Solution

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Abstract—The physicochemical properties of amorphous silica precipitated from a hydrothermal solution were studied. Low-temperature nitrogen adsorption in conjunction with the BET method was used to determine the specific surface area of this silica. Based on thermogravimetry data, the total content of water was estimated. A comparison of the thermogravimetry data with the Zhuravlev physicochemical constants made it possible to determine the temperature dependences of the concentration of surface and internal silanols over a temperature range of from 200 to 1200°C. A new type of amorphous silica with enhanced internal water content was revealed. The distinctions between the mechanisms of the removal of surface and internal water were established.

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In the present work, we report the results of studying the physicochemical characteristics of silica precipitated from a high-temperature hydrothermal solution [1–3]. Using the Zhuravlev model [4], we determined the content of sorbed water and the distribution of silanol OH groups between the surface and the bulk of the silica sample. The formation of a colloid dispersion of silica in a hydrothermal solution occurs via a sequence of physicochemical processes. The initial concentration of silica depends on the temperature at which the chemical equilibrium between the water and the alumosilicate minerals of the rocks of the high-temperature hydrothermal deposit [1–3]. At 250–350°C, the overall content c_t of silica in water nearly coincides with the solubility of quartz (500–700 mg/kg), with the silica being present in the solution mainly in the form of H_4SiO_4 molecules (orthosilicic acid).

After ascending filtration in strata or after appearing at the surface in supplying wells of a hydrothermal power station, the solution becomes supersaturated with respect to the solubility c_e of amorphous silica [3] due to a decrease in the pressure and temperature and an increase in the silica concentration due to evaporation. The total concentration c_t of silica in the solution is typically 700–1500 mg/kg [3]. The supersaturation of the solution, which is equal to the difference between the concentration of orthosilicic acid c_s and the solubility c_e , $(c_s - c_e)$, is the driving force of the polycondensation of orthosilicic acid, a process that involves the formation of siloxane bonds and partial dehydration [5]:

$$\begin{array}{cccc}
OH & OH & OH & OH \\
OH-Si-OH + OH-Si-OH \longrightarrow OH-Si-O-Si-OH + H_2O \\
OH & OH & OH & OH \end{array}$$
(1)

or

$$Si_{m}O_{m-1}(OH)_{2m+2} + Si_{n}O_{n-1}(OH)_{2n+2}$$

$$\longrightarrow Si_{m+n}O_{m+n-1}OH_{2n+2m+2} + H_{2}O.$$
(2)

As a result of nucleation and polycondensation, hydrated colloid silica particles $nSiO_2 \cdot mH_2O$ are formed. The dissociation of surface silanol groups SiOH with the abstraction of H⁺ imparts a negative charge to the surface. Electrostatic repulsion prevents particles from coagulating, thereby making colloid silica stable in the hydrothermal solution.

Studying the physicochemical characteristics of colloid silica in a hydrothermal solution after its precipitation from the solution is important for developing models of the formation of hydrothermal minerals [6, 7], including ores, and for creating technologies of extraction and utilization of silica, technologies that can enhance the efficiency of geothermal power plants and combined heat and power plants [8].

The silica samples were obtained by freezing-out of dispersed solutions from wells of the Mutnovskii geothermal field. As solution droplets were frozen on a snow surface, colloid silica particles concentrated



Fig. 1. Scheme of the formation of the structure of a silica surface (\equiv Si–OH silanol groups): (a) condensation polymerization and (b) rehydroxylation.

between ice crystals; as a result, the distances between them decreased, a factor favorable for their coagulation. After being heated to 105°C, the gellike mass formed from the mixture of snow and deposited silica transformed into a fine power. The deposited silica was removed from the surface of the plate and dried using hydrothermal heat. The density of the gellike silica collected from the surface of the snow was 2.0 g/cm³. After drying at 110°C for 12–16 h, the material transformed into a fine powder with a density of from 0.22 to 0.24 g/cm³.



Fig. 2. Types of silanol groups and siloxane bridges at the surface of an amorphous silica and internal OH groups: vicinal (Q), germinal (Q^2), and isolated (Q^3) silanols; Q^4 denotes surface siloxanes.

Amorphous silicas with various degrees of hydroxylation are widely used in science and technology [4]. Generally, surface silanol groups (\equiv Si–OH) are formed via two thermodynamically favorable processes [4]. First, such groups are formed during synthesis, for example, the polycondensation polymerization of Si(OH)₄ (Fig. 1a), when a supersaturated solution of orthosilicic acid transforms into polysilicic acids, with the subsequent formation of SiO₂ sols and gels containing surface OH groups. When dried, the final product, xerogel, retains surface silanols, at least partially. Second, silanols can be produced by rehydroxylation of thermally dehydroxylated silica during its treatment with water of an aqueous solution (Fig. 1b).

The types of groups at the surface and in the bulk of silica are displayed in Fig. 2 [4, 9]: free single (isolated) surface silanols (\equiv SiOH; type Q³); free germinal (isolated) surface groups (=Si(OH)₂, silanediols; type Q²); vicinal bridge silanols (i.e., single silanols, single germinal silanols, or combinations thereof bound with one another by hydrogen bonds; \equiv Si–O–Si \equiv , siloxane bridges with the O atom at the surface (type Q⁴); and internal silanols (located in the skeleton and/or in ultramicropores of SiO₂). Thus, amorphous silicas, both treated over a wide temperature range and untreated, contain only two types of OH groups, single and germinal, which, in turn, can be subdivided into isolated, free, and H-bonded vicinal ones [4, 9].

The properties of disperse amorphous silica, as an adsorbent, are determined by its porous structure and the chemical activity of the surface, with the latter being dependent on the concentration of OH groups (i.e., the total concentration of all silanols and the concentrations of their varieties), on the temperature and energy distribution of the silanols, and on whether siloxane (SiOSi) bridges are present. At the same time, \equiv Si–OH groups can be located at the surface (surface silanols) or in the bulk of amorphous silica particles

| Substance | m _i | Substance | m _i | Substance | m _i | Substance | m _i |
|------------------|----------------|--------------------------------|----------------|-------------------|----------------|-------------------------------|----------------|
| SiO ₂ | 81.13 | Al ₂ O ₃ | 0.41 | FeO | 0.09 | K ₂ O | 0.29 |
| TiO ₂ | 0.02 | Fe ₂ O ₃ | 0.07 | Na ₂ O | 0.60 | P ₂ O ₅ | 0.06 |

Table 1. Chemical composition m_i (wt %) of silica sample AK1b of finely dispersed silica precipitated by freezing-out

Note: The mass losses associated with drying at 110°C and calcination at 1000°C were 10.93 and 6.03 wt %; MnO, MgO and CaO were not detected.

and/or in ultramicropores in them (less than 1 nm in diameter), which are accessible for small molecule, for example, water (internal silanols). As discussed in detail in [4], OH groups at the surface of large transport pores readily participate in deuteroexchange with heavy water D_2O in the gaseous or liquid state at room temperature, but the water bound in the SiO₂ skeleton remains virtually intact, while the isotope exchange with the silanols located in ultramicropores occurs very slowly.

Internal silanols, i.e., OH groups covalently bound to internal atoms of silica particles (Fig. 2), i.e., OH groups not involved in surface processes, are typical of amorphous silicas. Internal silanol groups (\equiv Si–OH) are not considered when it is necessary to calculate the surface concentration of OH groups (the silanol number α_{OH} , i.e., the number of OH groups per nm²) and to study the active behavior of only surface silanols, since such silanols play the main role in various processes at the surface.

Silanols in the skeleton and ultramicropores of silica can be formed by various mechanisms:

(1) Some silanols in silica obtained by condensation of low-molecular-weight polysilicic acids can remain in the network of the inorganic polymer (due to incomplete polycondensation) if suitable partners are absent during the synthesis. In addition, silicas prepared from sodium silicate can contain a certain amount of OH groups in the bulk, trapped during the aggregation of small particles and the subsequent aging of the SiO₂ gel.

(2) According to [5], when colloid particles are gradually grown in an alkaline solution $(pH \sim 9)$, sodium ions can be adsorbed on particles concurrently with SiO₂ deposition, a factor favorable for the trapping of silanols in the silica structure.

(3) Large spherical particles in pyrogenic silica (10-20 nm in diameter) are formed through the aggregation of primary elementary globules (1-2 nm in size) produced by hydrolysis at elevated temperatures (in flames). Since primary particles contain a certain amount of surface silanols, such OH groups may occur trapped in large globules of the final product.

(4) According to [10], the existence of internal silanols can be explained by the diffusion of H_2O molecules into the bulk of the solid SiO₂ structure (up to 15 nm in depth) at elevated temperatures.

(5) One of the most widespread methods that produces silanols in the skeleton and in ultramicropores of SiO_2 is hydrothermal treatment (HTT). Hydrothermal treatment of amorphous silica (at elevated temperatures of water and aqueous solutions brought in contact) involves complicated processes of dissolution and reprecipitation of silica and the diffusion of water in the solid phase, processes that lead to the formation of secondary (geometrically modified) silicas with a different pore structure, which is capable of retaining silanols or bound water inside particles and in ultramicropores.

(5a) Using HTT in an autoclave at the stage of SiO_2 hydrogels, the authors of [11] obtained a number of silica gels with a mesoporous structure and dense particle packing, but without ultramicropores.

(5b) Using HTT at the stage of SiO_2 xerogels, the authors of [12] obtained a number of silica gels with various porous structures of particles (globular, intermediate, and spongy). The silica gels contained silanols at the surface, inside particles, and in ultramicropores.

(5c) Using HTT of pyrogenic silicas (aerosils) in an autoclave, the authors of [12] obtained a number of silica gels with various porous structures, with silanols being located inside silica particles and at their surface.

(5d) In [13], various treatments and HTT (a prolonged boiling in water) of initial porous glasses yielded geometrically modified porous glasses with various porous structures. The modified glasses contained OH groups at the surface, inside particles, and in ultramicropores.

Note that internal silanols are expected to be present in various amorphous silicas that form precipitates at the walls of wells, pipelines, and hot-water-carrying units of geothermal heat and power plants in Russia, New Zealand, Japan, United States, the Philippines, Mexico, Iceland, Italy, etc.

Table 1 lists data on the chemical composition of silica sample AK1b, which were obtained in our experiments. The mass fraction of silicon dioxide in the sample (after subtracting the mass losses during drying at 105°C and calcining at 1000°C) was within 95.00–97.69 and even to 99.02 wt %; the total mass fraction of calcium, aluminum, and iron was below 0.6%.

The silica samples precipitated by freezing-out of hydrothermal solutions had an amorphous structure (Fig. 3a). The XRD patterns of the samples exhibited a well-pronounced halo with a maximum within 0.387–0.400 nm. After calcination at 1000°C, the amorphous silicas transformed into crystalline cristobalite (Fig. 3b).

The IR spectra of the precipitates were recorded on a Vector 22/N (Bruker) FTIR spectrometer within 250– 4250 cm⁻¹. The 250–1200-cm⁻¹ range featured three



Fig. 3. Data of an XRD analysis of the silica samples (a) before and (b) after calcination at 1000°C.

peaks (two moderate-intensity peaks at 500 and 750– 850 cm⁻¹ and a strong peak at 1096–1104 cm⁻¹), which corresponded to the vibrations of the Si–O–Si bonds of the SiO₄ tetrahedron (Fig. 4). The 1200–4000-cm⁻¹ range featured two moderate-intensity peaks at 1600– 1640 and 2344–2368 cm⁻¹ and an intense peak at 3440– 3480 cm⁻¹ (belonging to the vibrations of hydroxy groups). Note, however, that the 3750-cm⁻¹ band, typical of free =Si–OH groups, was undetectable, probably because of the screening by vicinal silanols and/or adsorbed water. The intensity of the IR bands and the



Fig. 4. IR spectrum of the silica sample.

positions of the two prime bands, at 1096–1104 and 3440–3480 cm⁻¹, are typical of various forms of amorphous silicas.

Figure 5 shows the results of a thermal analysis (on a Perkin Elmer Pyris Diamond TG/DTA instrument of silica sample AK1b) of silica sample AK1b. Table 2 lists the corresponding TGA data. The measurements were performed in air at a heating rare of 20 K/min.

The reflection coefficient of the surface within 400.0–760.0 nm was measured on an MSFU-K spectrophotometric microscope. The reflection coefficient (whiteness) of hydrothermal silica was within from 91–95 till 94–98%. It was found that the reflection coefficient increased with the wavelength (Table 3).

The surface area and volume of the pores in the silica samples was measured by low-temperature nitrogen adsorption on an ASAP-2010N porosimeter (Micrometrics, United States). The mechanism is based on measuring the adsorption–desorption of nitrogen at the liquid-nitrogen temperature [14]. Monitoring the mass of a disperse sample made it possible to determine the amount of nitrogen adsorbed at a given relative pressure of nitrogen p/p_0 (p and p_0 are, respectively, the current pressure and saturation vapor pressure of nitrogen at the temperature at which the experiment was performed) in the ampoule with the sample. The volume of adsorbed nitrogen V was first measured at increasing p/p_0 values (from 0.01 to 1.0), to plot the adsorption curve, and then at decreasing p/p_0 values (from 1.0 to



Fig. 5. Results of the thermal analysis of the silica sample in various modes: (1) TG, (2) DTA, and (3) DTG.

0.04), to plot the desorption curve. The $V(p/p_0)$ dependence for silica sample AK1b is displayed in Fig. 6.

The isotherms obtained belong to type IV of adsorption isotherms [14]. Such isotherms first run convex, pass through an inflection point (at $p/p_0 = 0.3-0.5$), become concave, and again convex near $p/p_0 = 1.0$ (Fig. 6). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) and Brunauer–Deming–Helsey (BDH) methods. The specific surface area was determined from measurements within $p/p_0 = 0.1.0$ by using the BET equation for polymolecular vapor adsorption [14].

Based on the classical theory of adsorption and desorption processes [14] and the dependence $V(p/p_0)$ we calculated the differential pore volume V_p and pore surface area s_p distributions over the diameter d_p within a particular range and the integral pore volume and the integral pore surface area for pores with diameters from 1.7 nm to a given value of d_p . The $dV_p/d\log d_p$ and $ds_p/d\log d_p$ distributions passed through a maximum at $d_p = 18.0$ and 11.7 nm, respectively.

The characteristics of pores in disperse hydrothermal silica as determined by the adsorption method are given below: T = 77.2 K, $p_0 = 747.17$, sample weight is 0.13 g, volume is 17.54 cm³, volume 2 is 54.32 cm³, $s_s =$ 263.53 m²/g, $s_{\text{BET}} = 274.64$ m²/g, $s_{\text{MP}} = 26.33$ m²/g, $s_{\text{AC}} = 260.25$ m²/g, $s_{\text{DC}} = 333.52$ m²/g, $V_{\text{S}} = 0.871$ cm³/g,



Fig. 6. Curves of (1) adsorption and (2) desorption from the silica sample.

 $V_{\rm MP} = 0.00827 \text{ cm}^3/\text{g}, V_{\rm AC} = 1.078 \text{ cm}^3/\text{g}, V_{\rm DC} = 1.088 \text{ m}^3/\text{g}, d_{\rm BET} = 12.692 \text{ nm}, d_{\rm A} = 16.575 \text{ nm}, \text{ and} d_{\rm D} = 13.058 \text{ nm}.$

Here, volumes 1 and 2 are the volumes of the ampoule at room and liquid-nitrogen temperatures (these quantities are measured by the instrument automatically and are then used in determining the coefficients of the equations); $s_{\rm S}$ is the specific pore surface area determined at $p/p_0 = 0.200$; s_{BET} is the total specific pore surface area determined by the BET method; s_{MP} is the specific surface area of pores with a diameter of ~1.7 nm; s_{AC} is the total specific pore surface area determined by the BDH method from the adsorption curve for pores with a diameter of from 1.7 to 300.0 nm; s_{DC} is the specific pore surface area determined by the BDH method from the desorption curve for pores with a diameter of from 1.7 to 300.0 nm; $V_{\rm S}$ is the total specific volume of pores with a diameter of less than 40.0 nm, which was measured at a relatively nitrogen pressure of $p/p_0 = 0.950$; $V_{\rm MP}$ is the specific volume of micropores with a diameter of ~1.7 nm; V_{AC} is the total specific pore volume determined by the BDH method from the adsorption curve for pores with a diameter of from 1.7 to 300.0 nm; d_{BET} is the mean pore diameter defined as $4V_{\rm S}/s_{\rm BET}$; $d_{\rm A}$ is the mean diameter $4V_{\rm AC}/s_{\rm AC}$; and $d_{\rm D}$ is the mean diameter $4V_{\rm DC}/s_{\rm DC}$.

Table 2. Mass of silica sample AK1b m (wt %) as a function of the temperature during thermogravimetric analysis

| t, °C | т | t, °C | т | t, °C | т | t, °C | m |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 22.6 | 100 | 300 | 92.10 | 600 | 90.09 | 900 | 89.27 |
| 100 | 94.65 | 400 | 91.30 | 700 | 89.76 | 1000 | 89.09 |
| 200 | 92.81 | 500 | 90.58 | 800 | 89.49 | 1100 | 88.61 |

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| Table 3. Dependence of the reflection coefficient k on the wavelength λ (nm) | | | | | | |
|---|--------|-----|---------|-----|---------|--|
| λ | K | λ | K | λ | K | |
| 480 | 0.9402 | 540 | 0.95394 | 600 | 0.97425 | |

0.96534

0.96592

560

580

Table 4. Dependences of the specific volume $V(g/cm^3)$ and surface area $s(m^2/g)$ on the mean pore diameter d_p for a hydrothermal silica sample as determined by adsorption analysis

620

640

| | - | | | | - |
|------------------|--------------------------|----------|--------------|-------|--------------|
| $d_{\rm p}$, nm | $d_{\rm p}^{\rm m}$, nm | V | V_{Σ} | S | S_{Σ} |
| 333.0-125.1 | 150.03 | 0.0238 | 0.0238 | 0.635 | 0.635 |
| 125.1-88.9 | 100.89 | 0.0333 | 0.0571 | 1.321 | 1.956 |
| 88.9-72.7 | 79.1 | 0.0284 | 0.0856 | 1.438 | 3.394 |
| 72.7-40.0 | 47.2 | 0.1539 | 0.2395 | 13.03 | 16.42 |
| 40.0-26.5 | 30.4 | 0.1669 | 0.4065 | 21.94 | 38.37 |
| 26.5-20.6 | 22.7 | 0.1303 | 0.5368 | 22.90 | 61.27 |
| 20.6-16.7 | 18.2 | 0.1182 | 0.6550 | 25.93 | 87.20 |
| 16.7–14.0 | 15.1 | 0.0960 | 0.7510 | 25.35 | 112.55 |
| 14.0-11.6 | 12.6 | 0.1005 | 0.8516 | 31.89 | 144.45 |
| 11.6-10.3 | 10.89 | 0.0550 | 0.9066 | 20.23 | 164.68 |
| 10.3-8.36 | 9.11 | 0.0764 | 0.9831 | 33.57 | 198.25 |
| 8.36-7.00 | 7.55 | 0.0425 | 1.0257 | 22.55 | 220.80 |
| 7.00-5.97 | 6.40 | 0.0243 | 1.0501 | 15.25 | 236.06 |
| 5.97-5.18 | 5.52 | 0.0141 | 1.0642 | 10.24 | 246.310 |
| 5.18-4.54 | 4.81 | 0.0079 | 1.0722 | 6.624 | 252.93 |
| 4.54-4.02 | 4.24 | 0.0039 | 1.0761 | 3.760 | 256.69 |
| 4.02-3.58 | 3.77 | 0.0011 | 1.0773 | 1.226 | 257.92 |
| 3.58-3.20 | 3.36 | 0.000061 | 1.0774 | 0.072 | 257.99 |
| 3.20-1.96 | 2.01 | 0.000059 | 1.0774 | 0.118 | 258.11 |
| 1.96-1.86 | 1.91 | 0.00046 | 1.0779 | 0.963 | 259.07 |
| 1.86-1.76 | 1.81 | 0.00053 | 1.0784 | 1.178 | 260.25 |
| | | | | | |

As can be seen from the above characteristics, the specific surface area of silica, porosity, and mean pore diameter for sample AK1b (prepared from a solution extracted from a Mutnovskii field well) are 300 m²/g, 1.1 g/cm³, and 12.7–16.6 nm, respectively. As can be seen, the hydrothermal silica samples are characterized by moderate values of the specific surface area and volume of pores in are moderate. The ratio of the surface area of micropores to the total surface area of pores and that of the volume of micropores to the total volume of pores were found to be 0.09–0.107 and 0.005–0.0085, respectively (Table 2).

Table 4 lists the distributions of the pore surface area and volume of pores over the pore diameter; as can be seen, these distributions are rather narrow. The differential distribution of the specific pore volume over the pore diameter passes through a maximum at $d_p = 33$ nm,

while the distribution of the specific pore surface area, while the distribution of the specific surface area over the pore diameter exhibits two maxima, at 13 and 9 nm. The volume of pores with diameters within 5.18–20.61, 5.18-26.47, and 5.18-40.0 nm constitutes 71.1, 79.8, and 88.3%, respectively, of the total pore volume. The surface area of pores with diameters within 5.18–26.47 and 5.18-40.0 nm constitutes, respectively, 60.9 and 76.4%. These characteristics of pores ensure a rather high reactivity of the deposited material and a rapid dissolution of it during technological processes.

λ

660

680

700

0.97911

0.97679

K

0.97182

0.97274

0.98265

Based on the specific surface area s_{BET} (m²/g) of silica and the mass loss associated with the removal of water and OH groups during thermogravimetric analysis $\Delta m_{\rm H,O}$ (wt %), one can determine the total concentration δ_{OH} (OH/nm²) of all silanol groups at the surface

500

520

0.9531

0.95029

| δ_{OH} | α_{OH} | γон | t, °C | δ_{OH} | α_{OH} | γон |
|------------------------|---|--|--|--|--|--|
| 8.29 | 4.90 | 3.39 | 600 | 2.23 | 1.52 | 0.71 |
| 6.71 | 3.56 | 3.15 | 700 | 1.49 | 1.30 | 0.19 |
| 4.92 | 2.33 | 2.59 | 800 | 0.89 | 0.70 | 0.19 |
| 3.33 | 1.84 | 1.49 | 900 | 0.40 | 0.40 | 0.0 |
| | δ _{OH} 8.29 6.71 4.92 3.33 | $\begin{array}{c c} \hline \delta_{OH} & \alpha_{OH} \\ \hline 8.29 & 4.90 \\ \hline 6.71 & 3.56 \\ \hline 4.92 & 2.33 \\ \hline 3.33 & 1.84 \\ \end{array}$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{ c c c c c c c c }\hline & & & & & & & & & & & & & & & & & & &$ |

 Table 5. Distribution of OH groups between the surface and the bulk of silica sample AK1b subjected to hydrothermal treatment

Note: *t* is the temperature of thermoevacuation of sample AK1b; δ_{OH} is the total water loss for sample AK1b measured by calcining it at elevated temperatures (thermogravimetric analysis) and expressed as the number of OH groups per unit area of SiO₂ surface; α_{OH} is the mean total concentration of silanols at the SiO₂ surface as a function of the pretreatment temperature, as determined by Zhurav-lev by using the deuteroexchange method (the Zhuravlev physicochemical constants at various temperatures, constants universal for amorphous silicas) [4]; γ_{OH} is the content of internal silanols (internal bound water) located in the skeleton and ultramicropores of sample AK1b, defined as the difference between $\delta_{OH} - \alpha_{OH}$ at a given temperature (Eq. (8)) (this quantity can also be expressed as the number of OH groups per unit area of SiO₂ surface (γ_{OH} , OH/nm²).

and in the bulk of silica per specific surface area of sample AK1b:

$$\delta_{\rm OH} = \Delta m_{\rm H_2O} \times 2 \times 6.02 \times 10^3 / 18 s_{\rm BET}.$$
 (3)

Assuming that the temperature at which the silanol groups are completely removed from the surface of AK1b equals 1000°C and using the data of Table 2, we calculated δ_{OH} (at the surface and in the bulk) per unit surface area of the sample at various temperatures (Table 5).

Various aspects of the dehydroxylation and dehydroxylation of the surface of amorphous silica have been considered in many studies, since the chemistry of such a surface, determined largely by the concentration, distribution, and reactivity of surface \equiv Si–OH groups, is of considerable theoretical and practical importance.

Figure 7 and Table 5 present the silanol number α_{OH} for the surface as a function of the thermoevacuation temperature t (°C), which was determined by the deuteroexchange method (the contributions from free isolated, free germinal, and vicinal OH groups were included). This dependence for various SiO2 samples makes it possible to determine the Zhuravlev physicochemical constants (the silanol number α_{OH} and the surface coverage of θ_{OH} on a SiO₂ surface at various fixed temperatures), which are widely used in studies on the subject. To determine the temperature dependence of α_{OH} , we used 100 samples of amorphous silicas with significantly different specific surface areas s_{Kr} determined by low-temperature krypton adsorption (from 9.5 to 945 m^2/g) and accessible pore diameters (from ~ 1.0 to 1000 nm or even higher).

Despite significant differences in the values of $s_{\rm Kr}$ and *d* (without the contribution from ultramicropores) for various SiO₂ samples, the values of $\alpha_{\rm OH}$ at a given pretreatment temperature are similar, as is the decrease of $\alpha_{\rm OH}$ with increasing temperature under similar conditions of heating. The value of $\alpha_{\rm OH}$ decreases rapidly as the temperature increases from 190 to 400°C (segment *AB* of the plot in Fig. 7) and, then, from 400 to ~780°C more slowly (segment *BC*). Table 6 lists the Zhuravlev physicochemical constants [4] (shown by the bold lines in Fig. 7), i.e., the set of the most probable values of α_{OH} or the concentrations of the silanols at the surface at fixed pretreatment temperatures. The corresponding coverages θ_{OH} of the surface by OH groups are also presented. These physicochemical constants, α_{OH} and θ_{OH} , are universal for amorphous silicas irrespective of their origin and structural characteristics (Table 6 and Fig. 7, segments *AB* and *BC*) if the SiO₂ surface in the initial state was completely hydroxylated (Fig. 7, point *A*) (whether silanols are present in the bulk and in ultramicropores is not taken into account).

The $\alpha_{OH} = f(t)$ and $\theta_{OH} = g(t)$ dependences exhibit two characteristic segments with markedly different slopes within range II in Fig. 7: the dependence can be described by a straight line (bold line) within subrange IIa (190–400°C),

$$\alpha_{\rm OH}$$
, OH/nm² = -0.0122t + 7.218 (4)



Fig. 7. Dependence of the silanol number α_{OH} of the pretreatment temperature for 16 various SiO₂ samples. The band limited the dashed lines show the range of experimental values. Range II consists of subranges IIa (segment *AB*, 190–400°C), IIb' (*BC*, 400–780°C), and IIb" (*DE*, 800– 1200°C); for details, see the text.

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Table 6. Surface concentration of silanols α_{OH} and OH group surface area coverage θ_{OH} as functions of the temperature of thermoevacuation of various amorphous silicas (the Zhuravlev physicochemical constants [4])

| t, °C | α_{OH} | θ_{OH} | | | | | |
|------------|---------------|---------------|--|--|--|--|--|
| Segment AB | | | | | | | |
| 190 | 4.90 | 1.00 | | | | | |
| 225 | 4.47 | 0.91 | | | | | |
| 250 | 4.17 | 0.85 | | | | | |
| 275 | 3.86 | 0.79 | | | | | |
| 300 | 3.56 | 0.73 | | | | | |
| 325 | 3.25 | 0.66 | | | | | |
| 350 | 2.95 | 0.60 | | | | | |
| 375 | 2.64 | 0.54 | | | | | |
| 400 | 2.33 | 0.48 | | | | | |
| | Segment BC | | | | | | |
| 425 | 2.18 | 0.44 | | | | | |
| 450 | 2.05 | 0.42 | | | | | |
| 475 | 1.94 | 0.40 | | | | | |
| 500 | 1.84 | 0.38 | | | | | |
| 525 | 1.75 | 0.36 | | | | | |
| 550 | 1.67 | 0.34 | | | | | |
| 575 | 1.59 | 0.32 | | | | | |
| 600 | 1.52 | 0.31 | | | | | |
| 625 | 1.46 | 0.30 | | | | | |
| 650 | 1.40 | 0.29 | | | | | |
| 675 | 1.35 | 0.28 | | | | | |
| 700 | 1.30 | 0.27 | | | | | |
| 725 | 1.25 | 0.26 | | | | | |
| 750 | 1.21 | 0.25 | | | | | |
| 775 | 1.17 | 0.24 | | | | | |
| Segment DE | | | | | | | |
| 800 | 0.70 | 0.14 | | | | | |
| 900 | 0.40 | 0.08 | | | | | |
| 1000 | 0.25 | 0.05 | | | | | |
| 1100 | 0.15 | 0.03 | | | | | |
| 1200 | 0.0 | 0.0 | | | | | |

Note: Segments *AB* and *BC* (Fig. 7) were approximated by a linear and a power equation, respectively.

(passes through point *A* (α_{OH} = 4.9, Table 6); the correlation coefficient equals $R^2 = 0.8768$) and by a power function within subrange IIb' (400–780°C) (α_{OH} = 2.33, Table 6),

 $\alpha_{\rm OH}$, (OH/nm²) = 1155.6 $t^{-1.0367}$ ($R^2 = 0.8516$). (5)

The condensation of silanols,

$$(\equiv Si-OH) + (\equiv Si-OH) \longrightarrow (\equiv Si-O-Si\equiv) + H_2O\uparrow, (6)$$

has been extensively studied extensively studied. This reaction is characteristic of subrange IIa, as well as subranges IIb' and IIb", although the values of the activation energy of desorption in these subranges differ from each other significantly [4]. At high surface coverages of silanols ($1 \ge \theta_{OH} > 0.5$; subrange IIa in Fig. 7 and Table 5), the following empirical equation is valid [4]:

$$E_{\rm D} = 31.4 - 12.3\theta_{\rm OH},\tag{7}$$

where E_D varies insignificantly, within 19–25 kcal/mol. In other words, the activation energy E_D is nearly independent of the concentration of silanols, being largely determined by perturbations arising at a surface containing H-bonded OH groups; such perturbations disappear as the vicinal silanols are removed at ~400°C (at $\theta_{OH} \sim 0.5$). Thus, when present in a high concentration (within subrange IIa (segment *AB* in Fig. 7)), neighboring vicinal OH groups interact with one another (lateral interactions).

At low OH-group surface coverages ($\theta_{OH} < 0.5$; subrange IIb'), free single and free germinal OH groups, as well as SiOSi bridges play the primary role (Figs. 2 and 7). In subranges IIb' and IIb", the activation energy $E_{\rm D}$ increases sharply, from 25 to 50 kcal/mol and higher, as α_{OH} decreases. If there are only free OH groups surrounded by SiOSi bridges, the latter can cover significant areas due to the high-temperature activation of SiO₂. Under such conditions, the main mechanism of the transfer of OH groups during the condensation of silanols (reaction (6)) may be stochastic migration of protons over the surface (the process of activated surface diffusion of OH groups). At the final stage, as two OH groups randomly come within ~0.3 nm (a typical length of a hydrogen bond) of each other, they interact to yield a water molecule. At low concentrations of OH groups (segments BC and DE in Fig. 7), the diffusion of protons over the SiO₂ surface limits the process of condensation as a whole (reaction (6)).

Segment DE (Fig. 7) corresponds to a situation where the surface contains no germinal silanols, and, hence, the reaction of condensation occurs only due to the interaction of sparsely distributed single OH groups. Within this high-temperature subrange (segment *DE* in Fig. 7), amorphous silica can completely or partially crystallize, as was demonstrated in the present work for amorphous sample AK1b (obtained by precipitation from a hydrothermal solution), which transformed into cristobalite at 1000°C (Figs. 3a, 3b). Since it is difficult to approximate segment *DE* in Fig. 7, we limited ourselves to calculating the mean values of α_{OH} (Table 6).

Thus, based on the above results, we found that, at180–200°C, the ultimate surface concentration of OH groups at a silica surface can be as high as 4.9 OH/nm²; the concentration of internal silanol OH group (internal water) per unit surface area of sample AK1b can be calculated by the formula

$$\gamma_{\rm OH}(T) = \delta_{\rm OH}(T) - \alpha_{\rm OH}(T). \tag{8}$$

The calculation results are listed in Table 5. These results show how the distribution of OH groups between the surface and bulk of silica sample AK1b depends on the temperature. The temperature dependences of δ_{OH} , α_{OH} , and γ_{OH} are displayed in Fig. 8. At 200°C, the contents of surface and internal silanol OH groups are comparable. Within 200–400°C, internal water is removed slowly, and, therefore, γ_{OH} decreases insignificantly with increasing temperature. Since the rate of the removal of internal water is relatively low, the content of internal OH groups coincides with that of surface OH groups at 375 and 425°C, being somewhat higher at the middle of this range, ~400°C (as can be seen from the crossing of the $\gamma(T)$ and $\alpha_{OH}(T)$ curves in Fig. 8.

Above 400°C, the rate of internal water removal increases; as a result, at 600°C, the concentration of internal OH groups is two times that of surface OH groups. The $\delta_{OH}(T)$ and $\alpha_{OH}(T)$ curves intersect at a temperature of ~900°C, a feature indicative of the existence of internal OH groups in silica AK1b at elevated temperatures. Hydroxy groups disappear completely at 900–1000°C, temperatures at which the concentration of surface OH groups is substantially lower than the initial one (4.6–4.9 nm⁻²). Within 400–800°C, the experimental values of γ_{OH} (nm⁻²), which correspond to the content of internal water in the silica sample, precipitated from a hydrothermal solution can be approximated by the formula

$$\ln \gamma_{\rm OH} = 0.943 - 0.0065(T^2 - 673^2). \tag{9}$$

The results obtained suggest that the mechanisms of the removal of internal and surface water differ significantly. Within 200–400°C, $\alpha_{OH}(T)$ decreases rapidly with increasing T; at temperatures above 400° C, this decrease slows down due to the disappearance of surface vicinal silanol groups. By contrast, γ_{OH} decreases slowly within 200–400°C, while the rate of the removal of internal OH groups increases as the temperature rises from 400 to 600°C. In our opinion, this distinction can be explained by two factors: (1) in this case, the internal condensation of silanol groups (reaction (6)) occurs in the bulk rather than on the surface and (2) internal water is removed by the transport of water molecules (through the solid material or ultramicropores) from the bulk to the surface. The diffusion rate increases with the temperature, giving rise to an increase in the slope of the $\gamma_{OH}(T)$ curve within 400–600°C.

A comparison of the thermogravimetry data for the silica sample precipitated from the hydrothermal solution, presented as the temperature dependence of $\delta_{OH}(T)$ with the Zhuravlev physicochemical constant $\alpha_{OH}(T)$ showed that this sample contained at 200°C a significant amount of internal OH groups, comparable to that of surface OH groups. Thus, we revealed a new type of amorphous silica, silica with a considerable amount of internal silanols. Samples of such silica were



Fig. 8. Temperature dependences of (1) δ_{OH} , (2) α_{OH} , and (3) γ_{OH} (Table 5).

prepared by coagulation and precipitation of colloid silica particles from a hydrothermal solution or collected from the walls of ducts through which a hydrothermal solution flowed.

In our opinion, the presence of a significant amount of internal water in silica deposited from a hydrothermal solution can be explained by (1) the mechanism of the formation of colloid particle during the polycondensation of orthosilicic acid, (2) the action of the aqueous solution at elevated temperatures and pressures (the effect of which is similar to hydrothermal treatment, accompanied by the dissolution and reprecipitation of silica), and (3) water diffusion.

A comparison of the $\alpha_{OH}(T)$ and $\gamma_{OH}(T)$ dependence for silica precipitated from a hydrothermal solution led us to conclude that the mechanism of the removal of internal and surface water differ drastically: within 200–400°C, internal water is removed slowly, with the rate of this process increasing at 400–600°C. This distinction can be explained by the fact that internal water is removed via the condensation of silanol group in the bulk of the particles and/or in ultramicropores while the transport of the condensation products to the surface of the particles occurs by the diffusion of molecules, the rate of which increases with the temperature.

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