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The surface chemistry of amorphous silica. Zhuravlev model

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Abstract

A review article is presented of the research results obtained by the author on the properties of amorphous silica surface. It has been shown that in any description of the surface silica the hydroxylation of the surface is of critical importance. An analysis was made of the processes of dehydration (the removal of physically adsorbed water), dehydroxylation (the removal of silanol groups from the silica surface), and rehydroxylation (the restoration of the hydroxyl covering). For each of these processes a probable mechanism is suggested. The results of experimental and theoretical studies permitted to construct the original model (Zhuravlev model-1 and model-2) for describing the surface chemistry of amorphous silica. The main advantage of this physico-chemical model lies in the possibility to determine the concentration and the distribution of different types of silanol and siloxane groups and to characterize the energetic heterogeneity of the silica surface as a function of the pretreatment temperature of SiO_2 samples. The model makes it possible to determine the kind of the chemisorption of water (rapid, weakly activated or slow, strongly activated) under the restoration of the hydroxyl covering and also to assess of OH groups inside the SiO_2 skeleton. The magnitude of the silanol number, that is, the number of OH groups per unit surface area, α_{OH}, when the surface is hydroxylated to the maximum degree, is considered to be a physico-chemical constant. This constant has a numerical value: $\alpha_{OH,AVER} = 4.6$ (least-squares method) and $\alpha_{OH,AVER} = 4.9$ OH nm^{-2} (arithmetical mean) and is known in literature as the Kiselev–Zhuravlev constant. It has been established that adsorption and other surface properties per unit surface area of silica are identical (except for very fine pores). On the basis of data published in the literature, this model has been found to be useful in solving various applied and theoretical problems in the field of adsorption, catalysis, chromatography, chemical modification, etc. It has been shown that the Brunauer–Emmett–Teller (BET) method is the correct method and gives the opportunity to measure the real physical magnitude of the specific surface area, S_{Kr} (by using low temperature adsorption of krypton), for silicas and other oxide dispersed solids. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Amorphous silica; Surface characterization; Silanol and siloxane groups; Internal silanols; Physico-chemical model; Physico-chemical constant; BET method

1. Introduction

Research into the silica-water system is important both for elucidating the theoretical aspects of the problems involved and for practical applications [1]. In this connection an investigation of the so-called combined, structurally bound water [2–5] in dispersed amorphous silica is of interest.

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This term describes OH groups that are bound via the valence bond with Si atoms on the silica surface (hydroxyl coverage), and in some cases with Si atoms inside the particles of silica.

In the 1930s, studies of the condensation processes of silicic acids, carried out by Hofmann, Endell and Wilm [6], Rideal [7] and Kiselev [8], and slightly later by Carman [9], showed that hydroxyl (silanol) groups, ≡Si–OH, should be present on the surface of silicates and silicas. On the basis of measurements of the heat of wetting and a comparison of the adsorption data with the data from chemical analysis and the corresponding results reported in the literature, Kiselev suggested that the water evolved during calcination of silica gel, besides physically adsorbed water, is formed from OH groups that are chemically held on the silica surface. This suggestion led to an understanding of the dehydroxylation mechanism [8].

Yaroslavsky and Terenin [11–13], by using an infrared spectroscopy method, proved for the first time the existence of hydroxyl groups on the silica surface (porous glass). This fact was soon confirmed by Kurbatov and Neuymin [14]. Now numerous spectral and chemical data unambiguously confirm the presence of the OH groups on such SiO_2 surface.

Silanol groups are formed on the surface by two main processes [1,36]. First, such groups are formed in the course of silica synthesis, e.g. during the condensation polymerization of $Si(OH)_4$ (Fig. 1a). Here, the supersaturated solution of the acid becomes converted into its polymeric form, which then changes into spherical colloidal particles containing ≡Si–OH groups on the surface. Upon drying, the hydrogel yields xerogel, the final product, which retains some or all of the silanol groups on its surface. Secondly, surface OH groups can form as a result of rehydroxylation of dehydroxylated silica when it is treated with water or aqueous solutions. The surface silicon atoms tend to have a complete tetrahedral configuration, and in an aqueous medium their free valence becomes saturated with hydroxyl groups (Fig. 1b).

The surface properties of amorphous silica, which is considered to be an oxide adsorbent, in many cases depend on the presence of silanol groups. At a sufficient concentration these groups make such a surface hydrophilic. The OH groups act as the centers of molecular adsorption during their specific interaction with adsorbates capable of forming a hydrogen bond with the OH groups, or, more generally, of undergoing donor–acceptor interaction. The removal of the hydroxyl groups from the surface of silica leads to a de-

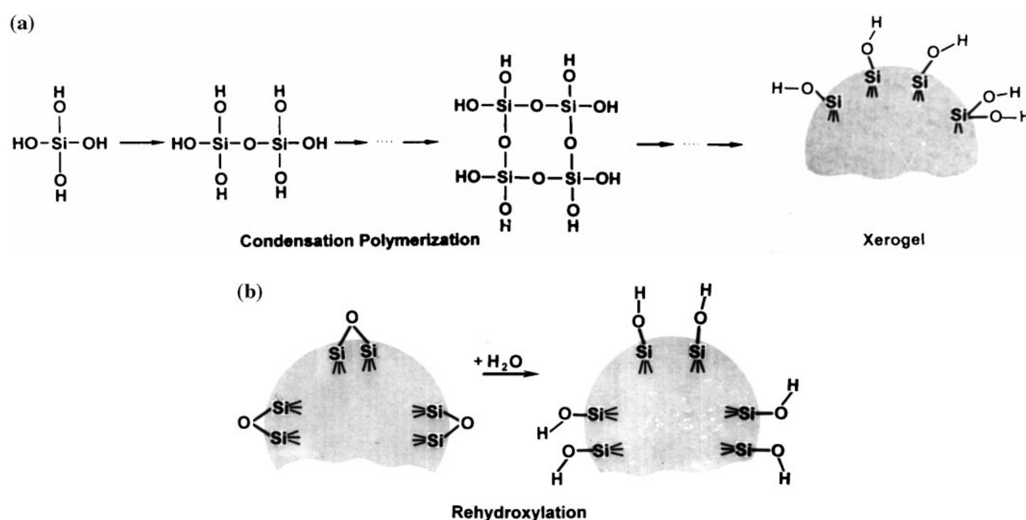


Fig. 1. The formation of silanol groups on the silica surface: (a) Condensation polymerization; (b) Rehydroxylation.

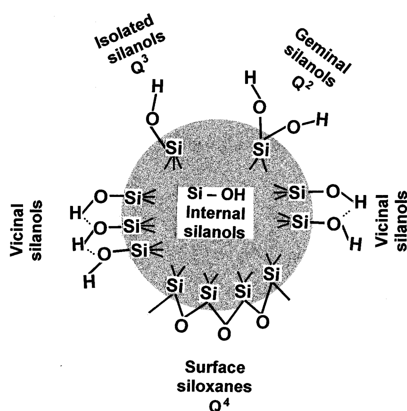


Fig. 2. Types of silanol groups and siloxane bridges on the surface of amorphous silica, and internal OH groups (see text). Q^n-terminology is used in NMR, where n indicates the number of bridging bonds (–O–Si) tied to the central Si atom: Q^4, surface siloxanes; Q^3, single silanols; Q^2, geminal silanols (silanediols).

crease in the adsorption, and the surface acquires more and more hydrophobic properties [1,36].

Surface OH groups are subdivided as following (Fig. 2): (i) isolated free (single silanols), $\equiv$SiOH; (ii) geminal free (geminal silanols or silanediols), $=Si(OH)_2$; (iii) vicinal, or bridged, or OH groups bound through the hydrogen bond (H-bonded single silanols, H-bonded geminals, and their H-bonded combinations). On the SiO_2 surface there also exist surface siloxane groups or $\equiv$Si–O–Si$\equiv$ bridges with oxygen atoms on the surface. At last, there is structurally bound water inside the silica skeleton and very fine ultramicropores, $d < 1$ nm (d is the pore diameter), i.e. internal silanol groups.

The last number of decades saw a rapid growth in those fields of science and technology that deal with production and utilization of various colloid and microheterogeneous forms of silica with developed surfaces, such as sols, gels, and powders. The properties of a pure silica, as an oxide adsorbent, are determined in the first place by: (i) the chemical activity of the surface — this activity depends on the concentration and the distribution of different types of OH groups, and on the presence of siloxane bridges; and (ii) the porous structure of the silica.

Various problems related to silica surface characteristics are encountered in different areas of science and technology: physics, chemistry and physical chemistry, agriculture, soil science, biology and medicine, electrical energetics, the oil processing industry, the metallurgical and mining industries, some fields of geology, etc. Traditional building and other materials based on silica, such as cement, concrete, firebrick, silicate glasses, rough and fine ceramics, and enamels, occupy a significant place in human life. Different types of silica are widely used as efficient adsorbents and selective absorbents, active phase carriers in catalysis, fillers for polymeric systems, adsorbents and supports for gas and liquid chromatography, thickeners for dispersion mediums, binding agents for molding materials, reinforcing fibres, and so forth. Chemical modification of the surface of dispersion silica has received a large amount of interest; this process allows researchers to regulate and change adsorption properties and technological characteristics of composite materials. Of late the use of SiO_2 is on the rise in the manufacture of modern high-quality materials (microelectronics, optics, fiber optics, liquid crystals, different composites including biocomposites, ordered nanostructured silica materials, monodispersed colloids, etc.).

In the past 50 years, many reviews have appeared on the subject of surface chemistry of silica. And we refer readers to these numerous monographs, reviews, and the most interesting and significant, in our opinion, articles [1,11–300].

In view of this, is there need for yet another review in this field? The author of the present review article has carried out numerous experimental studies on the subject in question, systemized such important characteristics as the concentration and the distribution of different types of silanol groups, established the energetic heterogeneity of the surface in a wide temperature range of the pretreatment, and investigated the characteristics of bound water inside SiO_2 particles. Besides, it was made careful study of the structure characteristics of many different silica samples. On the basis of these researches the author was able to construct an original physico-

chemical model [301–303], describing the surface properties of amorphous silica (referred in literature as the Zhuravlev model). Therefore, it would be pertinent to compare in this review article the results obtained by the author with those reported in literature.

In this model for the amorphous silica surface the determining factor is the presence of silanol groups and siloxane bridges. The concentration of these groups depends on the conditions of thermal treatment of the SiO_2 sample in vacuo (or on other types of pretreatment). It is necessary to take into account possible changes occurring simultaneously in the degree of surface coverage with adsorbed water molecules or with different surface groups and in the energetics of dehydration (the removal of physically adsorbed water), dehydroxylation (the removal of silanol groups) and rehydroxylation (the restoration of the hydroxylated covering) processes. Also it ought to follow some changes in structure of the surface and the skeleton of the silica matrix. These factors determine the starting conditions that are necessary for working out the model for the amorphous silica surface. To avoid the introduction of such complicating factors as the possible effect on the silica surface properties of any impurities, structural defects, other functional groups and active sites, etc. they are not considered at this stage.

2. Experimental section

The versions of the method of deuterium exchange (DE method) developed by the author [304–306,311,312,321,322,328] have been used for determining the concentration of the hydroxyl groups on the surface of dispersed oxide adsorbents. The advantage of this method is that, under certain conditions, deuterium exchange is limited to the surface and does not involve structurally bound water inside silica. According to this DE method an isotopic exchange takes place between a known quantity of heavy water D_2O and an unknown number of hydroxyl groups on the surface of the sample. The concentration of the original OH groups or the silanol number, that is, the number of OH groups per unit surface area, α_{OH} (OH nm^{-2}), is determined from the known ratio of the concentrations of the isotopes, [H]/[D], in the water vapor phase, after completion of the deuterium exchange, and from the known weight of the sample and its specific surface area:

$$\alpha_{OH} = \delta_{OH}^{(S)} \cdot N_A \cdot 10^{-21}/S \quad (1)$$

or

$$\alpha_{OH} = K \cdot \delta_{OH}^{(S)}/S \quad (1')$$

where $\delta_{OH}^{(S)}$ (mmol OH groups g^{-1} of SiO_2) is the concentration of OH groups on the surface of SiO_2 per unit mass of the sample as obtained from the DE data; S (m^2 g^{-1}), the specific surface area of the sample as determined by the BET method [10] by using low temperature adsorption of krypton (the area occupied by one Kr atom in a monolayer, $\omega_{m,Kr} = 0.215$ nm^2) [50]; N_A, the Avogadro number; and $K = 602.214$ is constant.

The determination of the isotopic composition of water vapor following the DE reaction was carried out by using mass spectrum measurements and other methods of the isotopic analysis. One of the variants of this DE method [311,322] made it possible to determine the silanol number and simultaneously to study the kinetics of water adsorption and isotopic exchange between D_2O and the surface OH groups. The minimal measured amount of water on the SiO_2 surface formed from $\sim 2 \cdot 10^{-4}$ to $\sim 2 \cdot 10^{-6}$ moles H_2O with a relative error of ± 1–5% (the different versions).

The DE method has some drawback: it cannot be used for determining separately the molecularly adsorbed water and different kinds of silanol groups. For such a determination we used the mass spectrometric thermal analysis in conjunction with the temperature-programmed desorption (the MTA-TPD method), the infrared spectroscopic method, and some others.

The process of the removal of physically adsorbed water and hydroxyl groups from the surface of the silica sample has been investigated using the MTA-TPD method. In general, the versions of the MTA-TPD method, worked out by the author [302,303,332], make it possible to obtain the following: thermal desorption curves

(or mass thermograms); the spectra of volatile components under the condition of linear heating of the sample (in the temperature range 25–1000°C); the energy of activation of thermal desorption; and other kinetic parameters. The kinetic parameters have been estimated by known methods [341–346]. A characteristic feature of the MTA-TPD method is a high sensitivity due to the design of a pyrolysis chamber. An open-type microcrucible for holding the SiO_2 sample is simultaneously as a thermojoint of the thermocouple and locates near the ion source of the mass spectrometer. The weight of the SiO_2 sample was less than 10 mg. The precision of determining of the sample temperature at any given moment of time and throughout the entire temperature range was ± 1.5°C.

In our work we used pure amorphous silica samples of different origins: silica gels, aerosils (pyrogenic silicas), aerosilogels and porous glasses. In all about 150 samples were investigated; for 100 of these determinations were made of the silanol number when the surface was hydroxylated to the maximum degree [301–303]. A large number of different samples had to be used in order to obtain a reliable physico-chemical constant (see below).

The following varieties (a–i) of amorphous silica were investigated (Table 5):

a. laboratory-made and industrial silica gels synthesized by the acidic method (26 samples);
b. laboratory-made silica gels obtained by the acidic method with the use of hydrothermal treatment at the hydrogel or xerogel stage (nine samples);
c. laboratory-made silica gel obtained by hydrolysis of tetraethoxysilane (one sample);
d. laboratory-made and industrial silica gels obtained by the Bard ion exchange method [339] from alkali and acid sols (14 samples);
e. laboratory-made aerosilogels obtained from an aqueous suspension of aerosils (20 samples);
f. laboratory-made porous glasses obtained by leaching sodium borosilicate glass (ten samples);
g. rehydroxylated industrial silica gels (12 samples);
h. rehydroxylated laboratory-made and industrial aerosilogels (five samples);
i. rehydroxylated laboratory-made porous glasses (three samples).

The skeleton structure of the silica samples was of a globular- [1,36] or sponge-form [320]. The samples differed strongly in the following characteristics: specific surface area, types of pore, distribution of pores according to their size, and the density of packing of the particles. The study of such structures proved to be an important stage in our work [301–303,305–311,317–320,323–327]. To determine the structure of different samples, besides the adsorption of Kr and N_2, we measured the total isotherms of adsorption and desorption — including capillary condensation, of water vapor, methanol and benzene, we used the method of apparent density, the mercury-porosimetric method, and the electron-microscopic and the kinetic methods. The silica samples had specific surface areas S_{Kr} varying from 9.5 to 945 $m^2\ g^{-1}$ [301–303].

When measuring α_{OH} one of the most important factor is the specific surface area, S_{Kr}, as determined by BET method based on low temperature adsorption of krypton [50]. This inert substance Kr was chosen because the adsorption of krypton on the silica surface as determined by the dispersion interaction is non-specific in nature, i.e. it is insensitive to changes in the degree of hydroxylation of the sample. Thus, the silanol number α_{OH} was determined on the surface of the pores, which were accessible to Kr atoms. According to the classification (IUPAC) by Dubinin [340] such pores include: macropores, $d > 200–400$ nm; mesopores, $3.0–3.2\ \text{nm} < d < 200–400$ nm; and supermicropores, $1.2–1.4\ \text{nm} < d < 3.0–3.2$ nm (d is the pore diameter). In those cases where the biporous SiO_2 samples contained very narrow pores (ultramicropores, $d < 1$ nm) together with wide pores (mesopores), the samples were considered to be wide-pores ones, and the very narrow pores were excluded from consideration when determining α_{OH}. The diameter of ultramicropores is comparable with that of water molecules, and therefore only water molecules can penetrate them. The OH groups in these very narrow pores were classified not as surface silanol groups but as bound water inside the silica particles.

Determinations were made of the structural characteristics of the silica samples both before thermal treatment and after treatment at temperatures from 180–200 up to 1000–1100°C.

To study surface dehydration and dehydroxylation of amorphous silica by the MTA-TPD method, without side undesirable effects, it was necessary to prepare a standard SiO_2 sample. This sample had to meet the following requirements:

1. the surface of the starting sample should be completely hydroxylated;
2. the diameter of the pores should be much greater than the size of the water molecule so that the effects of diffusive retardation and the readsorption inside pores are suppressed to a maximum extent;
3. there should be no structurally bound water inside the silica skeleton so that the side effect due to the evolution of water from the bulk of the sample at higher temperatures was absent at all;
4. the silica sample should be free of extraneous impurities on its surface and inside it; and
5. the structure of the SiO_2 skeleton should be stabilized.

The method of synthesizing such the standard sample has been reported [302,303,332]. It was found that the most suitable type of SiO_2 which meets the above-mentioned requirements was an aerosilogel, amorphous silica containing uniformly wide pores (mesopores) [142]. It was prepared from an aqueous suspension of very pure pyrogenic silica (aerosil, $S = 180$ m^2 g^{-1}). The stabilized structure of the silica skeleton was obtained by multiple heating (in the atmosphere or in the water vapor) at temperatures up to 940°C with following cooling of the sample each time. The distribution of the pores in terms of their diameter, d, lay within a narrow range with a maximum at 51 nm. The specific surface area of the sample was $S = 79$ m^2 g^{-1} as determined by the BET method from the low temperature adsorption of Kr, and this standard sample was named ‘S-79’.

The comparison of the results obtained by the author [301–303,332,334–338] with those reported in literature covers the following topics: (i) limiting temperature for removing physically adsorbed water from the hydroxylated surface of amorphous silica; (ii) completely hydroxylated state of the surface; (iii) structurally bound water inside the particles of amorphous silica; (iv) dehydroxylation and rehydroxylation of the silica surface; (v) energetic heterogeneity of the surface; and (vi) physico-chemical model of amorphous silica surface: main stages and distribution of various types of surface groups.

3. Results and discussion

3.1. Boundary temperature for removing physically adsorbed water from the hydroxylated surface of amorphous silica

To elucidate the nature of hydroxyl coverage and to quantitatively determine the concentration of OH groups on the silica surface it is necessary to distinguish these groups from the molecularly adsorbed water. Although many investigations have been carried out by different researchers using various methods for determining the value of the boundary temperature, T_B, for removing the physically adsorbed water, there is no agreement between the values obtained so far. The following examples of the results reported in literature show a wide discrepancy of T_B values.

Iler, after reviewing numerous reported results, concluded in his monograph [1], that on silica dried from water, the hydrogen-bounded water molecules came off at room temperature in vacuum or at 150°C in the atmosphere. The prevailing view is that drying in vacuum at low temperatures is the only way to remove the adsorbed water without disturbing the OH groups. Also, this is the conclusion reached by Gregg and Sing in their monograph [158].

De Boer et al. [37–39] found that silica dried in air at 120°C loses all physically adsorbed water but at 110°C still retains water if the air is humid. According to Okkerse [104] the removal of all physically adsorbed water at 120°C is possible only if the silica sample is free of micropores. When silica contains micropores the adsorbed water can be retained in the micropores at temperatures up to 180°C even though the surface of

wide pores begins to be free of OH groups. Bermudez [106] in his investigations using the NMR method has established that after exposure for 6 h at 110°C all water is removed from the silica surface including some silanol groups, as well as some internal water. Taylor, Hockey et al. used 115°C during subjecting silica to pretreatment either in air or in vacuum [73,82].

Young and Bursh investigated the interaction of water vapor with the surface of amorphous silica using different methods (thermal analysis, heat of immersion in water and others) [41,51]. On the basis of these results the authors concluded that the dexydroxylation of surface OH groups begins at 180°C.

The removal of physically adsorbed water from the silica surface has been studied by many researches using thermogravimetric, thermodesorption and other thermographic methods. As an example, in Fig. 3 is presented the TGA (thermogravimetric analysis) thermogram of a silica sample, obtained by Vansant, Van Der Voort and Vrancken [263]. This thermogram distinctly shows a sharp DTG (differential thermogravimetric analysis) peak, attributed to the loss of physically adsorbed water from the surface of the porous sample. The profiles of curves 1 and 2 (DTG and TGA, respectively) indicate that desorption of such physisorbed water is completed at $\sim 150°C$ and is followed by a broad region of weight loss, due to dehydroxylation process.

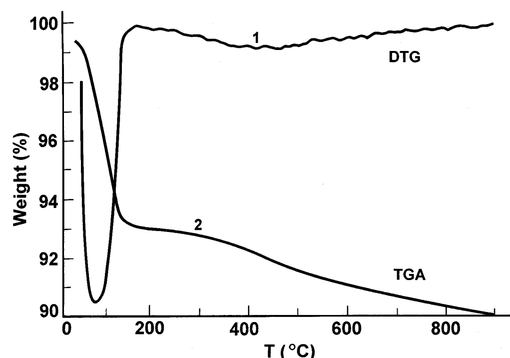
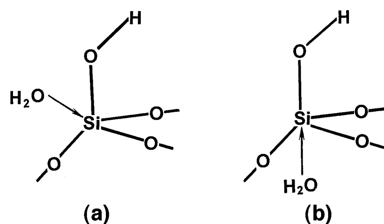


Fig. 3. Thermogravimetric analysis of a hydroxylated silica with physically adsorbed water on the surface (the mesoporous silica gel, $S = 400$ m^2 g^{-1}): (1) DTG curve, (2) TGA curve (From Vansant et al. [263]).



Scheme 1. Chuiko's scheme (a) and (b).

It is necessary to note, that in numerous thermographic investigations, fulfilled by different authors, an endothermic effect, i.e. a rather sharp DTA peak, in the range about 120–200°C is also directly related to the removal of physically adsorbed water from the SiO_2 surface.

A number of researchers gave the limiting temperature $T_B > 200°C$. Thus, Baverez and Bastick [66] on the basis of IR spectroscopic analysis found that $T_B \cong 240°C$. Fripiat and Uytterhoeven, using the same method, came to the conclusion [58] that physically adsorbed water is completely removed only at $\sim 300°C$.

Some Russian and Ukrainian researchers suggested a concept according to a part of Si atoms on the silica surface are coordinately unsaturated (so-called nonhydroxyl centers of the II-type). Thus, Kiselev et al. [83,102] assumed that these water molecules are completely removed in vacuum only at $\sim 400°C$. Chuiko et al. [150,188] considered that the adsorbed water molecule (with the coordinate bound) near the II-type site can be located either over the face of the silicon–oxygen tetrahedron (Scheme 1(a)) or under the Si atom of the silanol group (Scheme 1(b)). The centers of the II-type ensure a strong retention of the coordinately bound water molecules on the SiO_2 surface up to $\sim 650°C$, with the energy of the interaction of one H_2O molecule with such a center being up to ~ 62 kcal mol^{-1} (~ 260 kJ mol^{-1}) [150].

It could be continued an enumeration of similar examples, because many data are given in literature that show a broad scatter of T_B values.

In order to find the limiting temperature, T_B, we have carried out a series of investigations by employing the DE and MTA-TPD methods together with some others [301–

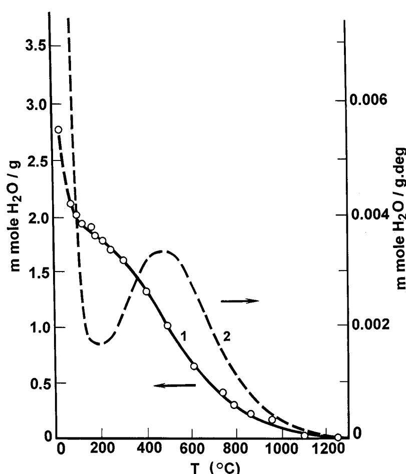


Fig. 4. (1) TGA curve, or total loss of water during thermal treatment of hydrated silica gel: each point on the curve was obtained by summing up the amount of water that came off in fixed temperature intervals and the amount of water measured by the DE method; (2) DTG curve, or rate of the water loss (for each 1°C increase in temperature), obtained by graphic differentiation of curve 1.

303,306,311,329,332]. In our complex thermographic investigations of several different silica samples, we have detected endothermic peak at ~ 150°C on a DTA curve [329], and this effect, as it noted before, is related to the removal of physically (molecularly) adsorbed water.

Using a method which combines thermogravimetric measurements, deuterium exchange, and mass spectral analysis, we have investigated [306] large-pore silica gel ($S = 320$ m^2 g^{-1}). In Fig. 4 are shown the total loss of water, i.e. the loss of physically adsorbed water, hydroxyl coverage, and structural water inside globules of the SiO_2 sample, as a function of temperature, or the TGA curve 1. The rate of the water loss (for each 1°C increase in temperature) is shown in the DTG curve 2. From the shape of curves 1 and 2, it can be seen that under step-wise heating conditions in a vacuum from room temperature to 150–200°C there came off mainly physically adsorbed water. At higher temperatures, there was desorption of the surface OH groups and the removal of structural water from the bulk of the SiO_2 sample also.

We have carried out studies of dehydration and dehydroxylation using the silica standard sample S-79 by the MTA-TPD method [302,303,332]. A series of curves representing the reduced mass thermograms of water obtained at the same rate of linear heating ($\beta = 5.8$ grad min^{-1}) are shown in Fig. 5. The intensity, I, of the spectral peak of water, $m/Z = 18$ (as determined according to the ordinate axis), characterizes the rate of formation or the rate of thermal desorption of water. Prior to measurements by the MTA-TPD method these samples S-79 were subjected to treatment in vacuum under different conditions of heating (Table 1). It is necessary to note that a mass spectral analysis of the escaping volatile products during the heating (25–1000°C) of the standard silica sample S-79 has shown that water is practically the only substance to be identified.

An examination of the ascending branches of curves 1–7 and curve 8 up to the maximum (point A in Fig. 5) shows the following.

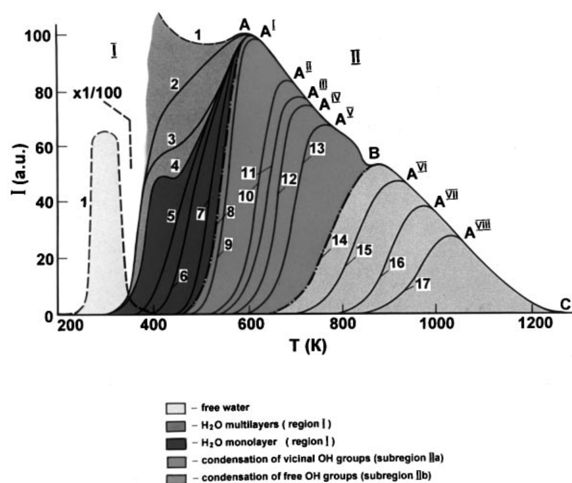


Fig. 5. Mass thermograms of water for the standard silica sample S-79 (rate of heating $\beta = 5.8$ grad min^{-1}); T, temperature (K); I, normalized intensity of the peak due to water ion $m/Z = 18$ (arbitrary units): yellow zone corresponding to the free water; light blue zone corresponding to the adsorbed H_2O multilayers, region I; dark blue zone corresponding to the adsorbed H_2O monolayer, region I; red zone corresponding to the condensation of vicinal OH groups, subregion IIa; crimson zone corresponding to the condensation of free OH groups, subregion IIb. Point A indicates the maximum of kinetic curves 1–8; points A^i, the maxima of curves 9–13 and 15–17 (i = I, II, III,…VIII); curves 8 and 14 are boundary curves (see Table 1 and text).

Table 1
Conditions for pretreatment in vacuum of standard samples S-79, conditions of studies by MTA-TPD method (at $\beta = 5.8$ deg min^{-1}) and temperature of mass thermogram maximum (K)

Thermogram no.	Conditions for pretreatment and conditions of studies by MTA-TPD method	Temperature (K)
1	Suspension of SiO_2 in an excess of water frozen at −196°C; evacuation in vacuum for 1 h at −196°C; gradual warming up from −196 to 0°C with the recording of mass thermogram; heating under linear condition from 0 to 1000°C with the recording of the thermogram	600
2	Loading of the wet sample; evacuation for 66 h at 25°C; heating under linear condition from 25 to 1000°C with the recording of the thermogram	600
3	Ditto, with evacuation for 87 h at 25°C	600
4	Ditto, with evacuation for 306 h at 25°C	600
5	Ditto, with evacuation for 14 h at 107°C	600
6	Ditto, with evacuation for 2 h at 136°C	600
7	Ditto, with evacuation for 1 h at 169°C	600
8	Dotted line (curve 8)-boundary curve (see text)	600
9	Loading of the wet sample; evacuation for 14 h at 203°C; heating under linear condition from 25 to 1000°C with the recording of the thermogram	621
10	Ditto, with evacuation for 12 h at 240°C	688
11	Ditto, with evacuation for 12 h at 276°C	711
12	Ditto, with evacuation for 14 h at 286°C	718
13	Ditto, with evacuation for 16 h at 335°C	769
14	Dotted line (curve 14)-boundary curve (see text)	875
15	Loading of the wet sample; evacuation for 13 h at 438°C; heating under linear condition from 25 to 1000°C with the recording of the thermogram	916
16	Ditto, with evacuation for 14 h at 495°C	972
17	Ditto, with evacuation for 14 h at 588°C	1037

Curve 1 reflects the behavior of the thermogram for an SiO_2 sample introduced into a pyrolyzer as a suspension with a large excess of liquid water. The experiment was carried out at a temperature range starting from −196°C (the sample was in a frozen state) and up to 1000°C. As can be seen, a very intense maximum appears in the range of 270–350 K. This effect is directly related to the evaporation of the excess of water in the liquid phase (free water — yellow colour in Fig. 5), which was in suspension, and is not related to the desorption of water. Upon further heating, thermogram 1 passes through a second maximum, which is weaker but clearly defined, at the characteristic point A.

Curves 2, 3 and 4 (ascending regions) correspond to samples which have been first subjected to treatment in vacuo at room temperature for 66, 87 and 306 h, respectively; curves 5, 6, 7 and 9 correspond to samples treated at 107, 136, 169 and 203°C, respectively. Curve 8 (as well as curve 14, which is considered below) was not registered experimentally; it was constructed by interpolation with account taken of the behavior of the ascending regions of the neighboring thermograms 7 and 9. An important conclusion can be drawn from the experiments: the maxima of all the kinetic curves 1–7 occurred at the same temperature T_A (600 K, point A in Fig. 5 and Table 1). It should be noted that for curves 1–7 the temperature of the prelimenary treatment of the corresponding samples of S-79 did not exceed 200°C. When the temperature of pretreatment was above 200°C, the maxima of the corresponding thermograms were shifted into the region of temperatures greater than T_A (to the right of point A). Such a shift was the greater, the higher the temperature of the preliminary treatment of SiO_2 (curves 9–17, Fig. 5 and Table 1). Curve 8 lies at the boundary since it is the last (on the right) which still passes through the stationary point A.

An analysis of region I to the left of the boundary curve 8 shows that the region represents

numerous ascending branches of the mass thermograms each of which passes through a common point A. It is reasonable to assume that region I corresponds to the state when, in addition to the surface coverage consisting of hydroxyl groups, the surface contains physically adsorbed water. The removal of such water (molecularly adsorbed water within the limits of multilayers and a monolayer, curves 1–8) at different initial degrees of coverage has no any effect on the position of the maximum (point A). This means that there coexist simultaneously two independent types of bound water on the SiO_2 surface: physically adsorbed water (region I to the left of the boundary curve 8 — light blue and dark blue colours) and chemisorbed water or hydroxyl coverage (region II to the right of the boundary curve 8 — red and crimson colours). Any change in the state of molecularly adsorbed water (which depends on the conditions of pretreatment of the S-79 sample in vacuo at temperatures $<200°C$, Table 1) in no way affects the hydroxyl coverage. Thus, the characteristic point A (at $T_A = 600$ K), which corresponds to the maximal rate of thermal desorption of water from the SiO_2 surface, is an indicator of the dehydroxylation process but not of the dehydration process.

In order to determine the kinetic parameters characteristic of dehydration (region I, Fig. 5)

Table 2
Dehydration: determination of the kinetic parameters[a]

Subtractive thermokinetic curve	Reaction order n	Activation energy of desorption E_D	
		kcal mol^{-1}	kJ mol^{-1}
(2–3)	0.85	6.2	25.9
(2–5)	1.25	7.3	30.6
(2–6)	1.34	7.3	30.7
(3–6)	0.97	6.4	26.9
(5–8)	0.85	8.9	37.1
(6–8)	0.84	9.4	39.3
(6–9)	0.91	10.4	44.2

[a] Note: (*i*–*j*)* The ordinate of such a curve at any point at a fixed temperature equals the difference between the ordinates of the corresponding ascending branches of reduced thermograms *i* and *j* (Fig. 5).

we resorted to graphic construction of the subtractive differential thermokinetic curves, which were then processed according to a known procedure [332,342,343]. The results, which are summarized in Table 2, show that the activation energy of desorption E_D increases from 6 to 10 kcal mol^{-1} (26–44 kJ mol^{-1}) as the extent of the silica surface covered with physically adsorbed water decreases to $\theta_{H_2O} \approx 0$. Data in column 2 of Table 2 show that the experimentally determined kinetic order of the thermal desorption reaction n is close to unity. This confirms that the water adsorbed on the surface, which is in a molecular form, is removed in region I (Figs. 11 and 12, see below).

On the basis of the ratios between the areas belonging to regions I and II we can conclude that under the experimental conditions employed the amount of physically adsorbed water (for samples, which were pretreated at temperatures more 25°C, Table 1), i.e. the area limited by ascending curves 4 and 8 (dark blue colour, Fig. 5), is less than a single monolayer of water on the silica surface.

Thus, the main mass of adsorbed water, including the region corresponding to polymolecular adsorption (between curves 1 and 4 — light blue colour), is removed in vacuum at room temperature. However, a small amount of physically adsorbed water, within the limits of a monolayer (between curves 4 and 8), remains on the hydroxylated surface of silica up to approximately 200°C.

The increase in the values of E_D with a decrease in the degree of surface coverage by adsorbed water in region I (Table 2 and Fig. 12, see below) is close to the observed changes in the values of pure differential heat of adsorption of water vapor ($Q_A - L$) (where Q_A is the differential heat of adsorption, and L is the heat of condensation) at a low degree of coverage by adsorbed water on the surface of silica, as shown by Dzhigit et al. [55]. As may be expected, the approximate equality between E_D and ($Q_A - L$) indicates that the direct process of physical adsorption of water vapor on the hydroxylated silica surface is non-

Table 3
Heating rate (β) and the temperature corresponding to the maximum (point A)

β (deg min^{-1})	5.8	12.3	25.0
T_A(K) (the average of several determination)	599.8	630.9	659.0

Table 4
Kinetic parameters determined for thermal desorption on the basis of the shape of the ascending branches of the boundary thermogram 8 and the thermogram 9 (between regions I and II in Fig. 5)[a]

Thermokinetic curve	Reaction order n	Activation energy of desorption E_D	
		kcal mol^{-1}	kJ mol^{-1}
8	2.00	16.5	69.1
8	(2.0)*	17.0	71.1
9	1.70	18.8	78.6
9	(2.0)*	19.2	80.6

[a] Note: * Parentheses indicate that $n = 2$ is taken as a known value.

activated, and $E_A \cong 0$ [70]. The rate of physical adsorption depends only on the rate at which the water molecules approach the surface of porous SiO_2 sample.

Mass thermograms 2–4 (ascending regions, Fig. 5, and Table 1) relate to samples which have undergone preliminary treatment in vacuo at room temperature, followed by increasingly prolonged periods of treatment. It can be seen that for the subregion between curves 2 and 5 the slope of the ascending sections of the thermograms decreases and there is a weak maximum (curves 3 and 4) at approximately 400–420 K. For the next subregion between curves 5 and 8, with an increase in the temperature of preliminary treatment from about 100 to 200°C (Table 1), the ascending sections become steeper while still passing through the common point A. On the basis of the shape of the thermograms of the subregions in region I, one can probably speak of the presence of two types of physically adsorbed water at a low degree of coverage. This accords with our data obtained by the method of molecular dynamics [303,330,333] (Fig. 18, see below). The activation energy of desorption of the two types of adsorbed water (within the limits of a monolayer) lies approximately in the range $E_D = 6–8$ and 8–10 kcal mol^{-1} (Table 2, Fig. 12, see below).

Now we shall determine the exact value of the limiting temperature, T_B, which separates these two processes: dehydration and dehydroxylation.

Let us consider the ascending sectors in boundary thermogram 8 and in the neighboring thermogram 9 (Figs. 5 and 10, see below). In order to determine the activation energy E_D in the neighborhood of point A we used the non-isothermal method [341,346]. Experimentally obtained data on the position of point A for different rates of linear heating of the sample are summarized in Table 3. The graphic representation of the linear dependence of the difference $(2 \cdot \log T_A - \log \beta)$ as a function of the reciprocal of the maximum temperature $1/T_A$ yields 16.5 kcal mol^{-1} for the activation energy E_D.

To determine the reaction order n (for a given E_D), we used the method suggested by Smolyaninov et al. [344]. The reaction order for curve 8 was found to be $n = 2.00$ (Table 4). The kinetic parameters for thermograms 8 and 9 obtained by known methods [344–346] are also shown in Table 4.

An interpolation based on the data for thermograms 7 and 9 (Fig. 5) yields the temperature of the preliminary treatment of SiO_2 in the case where the ascending branch of the kinetic curve must exactly follow the boundary thermogram 8. The threshold temperature corresponding to the completion of dehydration and the beginning of dehydroxylation was found to be $T_B = 190 \pm 10$°C [302,303,332].

Thus, it was established that at T_B (for amorphous silica subjected to pretreatment in vacuo at 190°C) sharp changes of the parameters take place. These changes correspond to the change in the activation energy of desorption E_D approximately from 10 to 17 kcal mol^{-1} (and thus to changes in a number of other thermodynamic functions), and to the change in the kinetic order of the limiting stage of thermal desorption n from 1 to 2 (Tables 2 and 4, Figs. 11 and 12, see below).

Rebinder [44] examined earlier theoretically how the water layer is bound to the dispersed materials in the course of drying. The isothermic free energy (or characteristic binding strength of water on the surface) of the free water equals zero:

$$-\Delta F = A = RT\ \ln(p_0/p)\ \text{ at }\ p = p_0 \tag{2}$$

where R is the gas constant, and T is the temperature. In the region of removing of physically adsorbed water, the magnitude of A increases continuously (at $p_o > p$). In the case of chemically bound water (OH groups on the SiO_2 surface), the magnitude of A will increase abruptly. Thus, the leapwise increase in A was predicted by Rebinder [44] and experimentally confirmed by us (the sharp increase in the kinetic parameters, E_D and n, at $T_B = 190°C$, Figs. 11 and 12) [302,303,332].

A critical comparison of various data in literature regarding the threshold temperature at which the physically adsorbed water comes off from the hydroxylated surface of amorphous silica reveals the following. The value of $T_B = 190°C$ practically coincides with $T_B = 180°C$ obtained earlier by Young and Bursh [41,51]. In our opinion this value of $T_B = 190 \pm 10°C$ holds true for various amorphous silica samples having different structural characteristics.

3.2. Completely hydroxylated state of the silica surface. Structurally bound water inside the particles of amorphous silica

To develop a model describing the silica surface it is necessary first of all to have reliable quantitative data on the concentration of OH groups as a function of the preliminary thermal treatment in vacuum of SiO_2 samples. This is particularly important for the initial fully hydroxylated state of the silica surface.

At the same time it is well known that different types of amorphous dispersed silica contain not only OH groups on the surface, but also structurally bound water within the silica skeleton and inside the ultramicropores of the sample. It is necessary to make a distinction between internal water, which has no effect on the surface processes, and the hydroxyl coverage. The latter determines all variety of interactions of different substances with the active OH sites on the SiO_2 surface.

Let us consider the results obtained by the author, using the DE method [301–303]. In Table 5 are summarized values S, $\delta^{(S)}_{OH}$ and $\alpha_{OH} = \delta^{(S)}_{OH}/S$ that were obtained for 100 different samples of amorphous silica (the varieties 'a–i', see above). Each numerical value of $\delta^{(S)}_{OH}$ and, respectively, α_{OH} is an average of two or more measurements (altogether 231 measurements were carried out). The surface of these samples was subjected to the maximum degree of hydroxylation, i.e. the hydrated samples were thermally pretreated in vacuo at 180–200°C (see above $T_B = 190 \pm 10°C$).

In those cases where the biporous samples of SiO_2 contained very narrow pores (ultramicropores, $d < 1$ nm) in addition to wide pores (mesopores) [307,311,318–320,331], the samples were considered only to be wide-pore ones, and the very narrow pores were excluded from consideration in determining α_{OH} (see above).

At first, it would be pertinent to examine the value for the concentration of OH groups on the surface of SiO_2 per unit mass of the sample, $\delta^{(S)}_{OH}$, as a function of S (Fig. 6). It can be seen that the experimental values $\delta^{(S)}_{OH}$ are bounded by two slightly diverging straight (broken) lines passing through the origin of coordinates. There is a high value of the correlation coefficient of the linear regression equation between $\delta^{(S)}_{OH}$ and S, $\rho = 0.99$, that was calculated for the numbers (in 100 points) of these two independent each from other physical magnitudes, changing within very wide ranges: so, the surface S_{Kr} of such silica samples is changed within range of their values from 9.5 to 945 m^2 g^{-1} (Table 5), and the diameters, d, of

Table 5
Specific surface area, S (m^2 g^{-1}), and concentration of surface OH groups, $\delta_{OH}^{(S)}$ (mmole OH g^{-1}) and α_{OH} (OH nm^{-2}), for 100 different samples of amorphous silica whose surface was subjected to the maximum degree of hydroxylation[a]

No. sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
S	744	905	855	717	805	945	710	734	270	212	328	316	297	274	294	340	384	363	660	815
$\delta_{OH}^{(S)}$	5.56	6.61	6.39	5.12	6.55	6.41	5.54	5.73	2.56	1.90	2.78	2.94	2.71	2.46	2.34	2.94	3.51	3.38	5.70	6.77
α_{OH}	4.5	4.4	4.5	4.3	4.9	4.1	4.7	4.7	5.7	5.4	5.1	5.6	5.5	5.4	4.8	5.2	5.5	5.6	5.2	5.0
No. sample	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
S	558	670	120	400	545	750	38	96	39	121	62	48	39	20	9.5	498	129	155	161	161
$\delta_{OH}^{(S)}$	4.17	4.90	1.14	3.26	4.71	6.23	0.32	0.83	0.29	1.01	0.57	0.40	0.34	0.18	0.07	3.39	0.92	1.13	1.15	1.31
α_{OH}	4.5	4.4	5.7	4.9	5.2	5.0	5.1	5.2	4.5	5.0	5.5	5.0	5.3	5.4	4.3	4.1	4.3	4.4	4.3	4.9
No. sample	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
S	168	195	196	199	205	241	245	307	350	424	43	112	129	133	142	163	168	168	168	170
$\delta_{OH}^{(S)}$	1.42	1.39	1.37	1.36	1.43	1.92	1.87	2.55	3.31	3.03	0.39	0.80	0.86	0.91	1.06	1.08	1.26	1.28	1.26	1.44
α_{OH}	5.1	4.3	4.2	4.1	4.2	4.8	4.6	5.0	5.7	4.3	5.4	4.3	4.0	4.1	4.5	4.0	4.5	4.6	4.5	5.1
No. sample	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80
S	170	170	175	175	180	180	273	290	311	320	312	256	238	102	77	70	64	27	12	11
$\delta_{OH}^{(S)}$	1.21	1.41	1.45	1.22	1.44	1.47	2.27	2.02	2.43	2.66	2.38	2.00	1.90	0.97	0.73	0.60	0.59	0.27	0.11	0.10
α_{OH}	4.3	5.0	5.0	4.2	4.8	4.9	5.0	4.2	4.7	5.0	4.6	4.7	4.8	5.7	5.7	5.2	5.5	6.0	5.7	5.4
No. sample	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
S	262	270	270	270	270	241	250	262	262	283	298	305	47	108	133	142	145	11	42	45
$\delta_{OH}^{(S)}$	2.31	2.11	2.24	2.38	2.42	1.96	1.95	2.09	2.18	2.26	2.47	2.38	0.35	0.83	0.99	1.18	1.08	0.11	0.40	0.46
α_{OH}	5.3	4.7	5.0	5.3	5.4	4.9	4.7	4.8	5.0	4.8	5.0	4.7	4.5	4.6	4.5	5.0	4.5	5.8	5.7	6.1

[a] Note: nos. 1–26 of SiO_2 samples are the group (a); nos. 27–35, group (b); no. 36, group (c); nos. 37–50, group (d); nos. 51–70, group (e); nos. 71–80, group (f); nos. 81–92, group (g); nos. 93–97, group (h); nos. 98–100, group (i) (see text and Fig. 7).

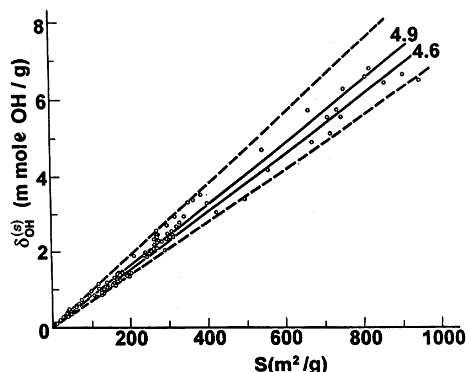


Fig. 6. Dependence of concentration of surface OH groups per unit mass of the sample SiO_2 determined by DE method, $\delta_{OH}^{(S)}$ (mmol OH g^{-1}), on the surface area of silica, S (m^2 g^{-1}) (Table 5). Straight (solid) lines passing through the origin of coordinates are average values of the silanol number (100 SiO_2 samples): $\alpha_{OH,AVER} = (\delta_{OH}^{(S)}/S)_{AVER} = 4.6$ OH nm^{-2} (least-squares method) and $\alpha_{OH,AVER} = 4.9$ OH nm^{-2} (arithmetical mean).

pores are changed within range from about 1.0 to 1000 nm and higher. This shows that the concentration of hydroxyl groups $\delta_{OH}^{(S)}$ is directly proportional to the specific surface area S of the amorphous silica samples under investigation. It means that we have indeed determined only the surface concentration of OH groups, $\delta_{OH}^{(S)}$. Straight (solid) lines passing through the origin of coordinates are average values of the silanol number (Fig. 6): $\alpha_{OH,AVER} = (\delta_{OH}^{(S)}/S)_{AVER} = 4.61 \cong 4.6 \pm 0.5$ OH nm^{-2} (least-squares method) and $\alpha_{OH,AVER} = 4.89 \cong 4.9 \pm 0.5$ OH nm^{-2} (arithmetical mean). The absolute error (the standard square divergence) of the silanol number α_{OH} forms value $\Delta\alpha_{OH} = \Delta(\delta_{OH}^{(S)}/S) = \pm 0.5$ OH nm^{-2} which characterizes a scatter of points concerning their mean magnitude. Besides, the high value of the coefficient of correlation ($\rho = 0.99$) confirms that the Brunauer–Emmett–Teller (BET) method [10] is the correct one and gives the opportunity to measure the real physical magnitude of the specific surface area S_{Kr} for the dispersed silica (and other oxide dispersed solids).

The values of the silanol number for 100 SiO_2 samples α_{OH}, depending on their specific surface area S, are shown in Fig. 7 [301–303]. The shaded horizontal band is the range of experimental data, and for a completely hydroxylated surface the silanol number α_{OH} is mainly between 4.2 and 5.7 OH nm^{-2} (Table 5). But, as already mentioned, the samples of amorphous silicas were prepared by different methods and had different structural characteristics. The horizontal (broken) lines are average values of the silanol number: $\alpha_{OH,AVER} = 4.6$ OH nm^{-2} (least-squares method) and $\alpha_{OH,AVER} = 4.9$ OH nm^{-2} (arithmetical mean) (see also Fig. 6). Thus, the silanol number α_{OH} is independent of the origin and structural characteristics of amorphous silica.

Our measurements carried out by DE and other methods showed that different types of amorphous dispersed silica contain not only surface OH groups ($\delta_{OH}^{(S)}$), but also structurally bound water inside the silica skeleton and inside the very fine ultramicropores ($\delta_{OH}^{(V)}$) [301–303,305–

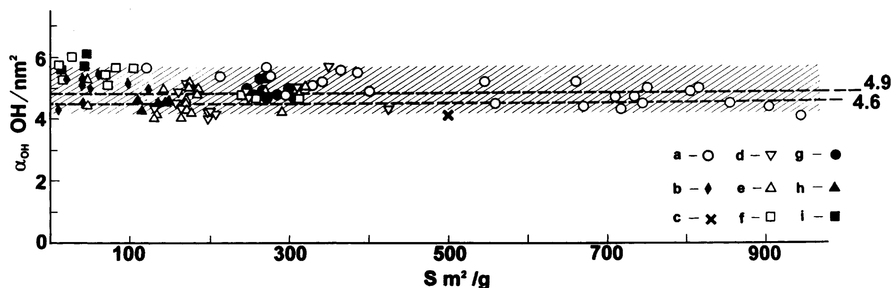


Fig. 7. Concentration of the surface hydroxyl groups (the silanol number) α_{OH} for silicas having different specific surface areas S, when the surface has been hydroxylated to a maximum degree: symbols 'a–i' indicate different types of amorphous silica (see Table 5 and text); the shaded area is the range of experimental data (100 samples of SiO_2 with different S_{Kr} values from 9.5 to 945 m^2 g^{-1}); broken lines are average values of the silanol number: $\alpha_{OH,AVER} = 4.6$ OH nm^{-2} (least-squares method) and $\alpha_{OH,AVER} = 4.9$ OH nm^{-2} (arithmetical mean) (see Fig. 6).

311,313,314,316–319]. Thus, the $\delta_{OH}^{(S)}$ value is only a part of the total content of OH groups δ_{OH} in silica; the other part of OH groups, $\delta_{OH}^{(V)} = \delta_{OH} - \delta_{OH}^{(S)}$, is contained within the bulk. According to our IR spectral measurements (together with Davydov and Kiselev) the latter consists of silanol groups inside the silica sample (the absorption band of stretching vibrations is about 3650 cm^{-1}) [309]. The distribution of OH groups between the surface and the volume of the sample depends on a number of factors, but mainly on the method of preparation of the silica sample and its subsequent treatment.

The total concentration of OH groups, g_{OH} (i.e. the number of OH groups), for one arbitrary SiO_2 particle can be represented as the sum [303,316]:

$$g_{OH} = k_1 v + k_2 s \quad (3)$$

where v and s are the volume and surface of the particle, respectively, k_1 and k_2 are the proportionality coefficients, within the volume and surface, respectively, for a certain standard maximum-hydroxylated state of silica both inside the bulk of the particle and on its surface. The magnitude of g_{OH} is related to the total concentration of the structural hydroxyl groups δ_{OH} per unit mass of silica by:

$$g_{OH} = \delta_{OH} v \gamma \quad (4)$$

where γ is the density of the silica skeleton and $m = v\gamma$ is the mass of this SiO_2 particle. Moreover, s is expressed through the specific surface area S as follows:

$$s = S v \gamma \quad (5)$$

By using Eqs. (4) and (5) we can determine the ratio δ_{OH}/S. This ratio describes the concentration of all OH groups within the bulk and on the surface of silica per unit surface area:

$$\delta_{OH}/S = k_1/S\gamma + k_2 \quad (6)$$

If coefficients k_1 and $k_2 = \alpha_{OH}$ are constant and are independent of the structure of silica, i.e. of the specific surface area S, then Eq. (6), within the coordinates δ_{OH}/S and S, stands for the equation of an equilateral hyperbola relative to the asymptotes δ_{OH}/S and $k_2 = \alpha_{OH}$. If we assume that the structural hydroxyl groups are located only on the surface, then $k_1 = 0$ and $\delta_{OH}/S = k_2 = \alpha_{OH} =$ constant.

Therefore within the coordinates δ_{OH}/S and S we obtain two boundary curves (Fig. 8(a)): a hyperbola B ($\delta_{OH}/S = k_1/S\gamma + \alpha_{OH}$), which expresses the dependence of the δ_{OH}/S ratio on the specific surface area S for a maximum-hydroxylated state both inside the bulk of the sample and on its surface, and a straight line A ($\delta_{OH}/S = \alpha_{OH}$), which describes only the surface concentration of hydroxyl groups, with no account being taken of the structurally bound water inside the silica skeleton.

An analysis of the experimental results describing the concentration of structurally bound water within the coordinates δ_{OH}/S and S, obtained by many authors for the maximum-hydroxylated silicas [1,16,20–27,31–34,37–39,45–49,53–58,65–67,71–83,88,92,97,99–102,106–109,130,159–161,194,214,215,233,234,253,254,280], including our data [301–311,313–320,323–327,334–338], shows the following (Fig. 8(b)). First, the values of $k_2 = \alpha_{OH}$, obtained in our work using the DE method for 100 different samples of amorphous silica (Fig. 8(a) and (b), open circles within a red band, cf. also Fig. 7), lie longitudinally with respect to the lower boundary straight line A, and $k_2 = \alpha_{OH} = 4.6$ (4.9) OH nm^{-2}. Secondly, the experimental points reported by other researchers and by us using different methods, for more than 170 different samples of SiO_2 with S in the range 4.3–960 $m^2\ g^{-1}$, are located throughout the space between the upper hyperbola B and the lower straight line A and represented the total content of OH groups (Fig. 8(a) and (b), black triangles within a green zone and a red band).

Thus the region of experimental points between the boundary curves A and B (Fig. 8(a)) should be considered to be the region of internal structurally water, i.e. of internal hydroxyl groups. Therefore, the experimental data reported in the literature, which are usually based on the loss of mass during calcination of the sample at high temperatures, describe the total concentration of OH groups in the sample, both within the bulk and on the surface (the ordinate of the points exceeds or equals $k_2 = \alpha_{OH}$, Fig. 8(a) and (b)). It is to be expected that with a decrease in S, i.e. with

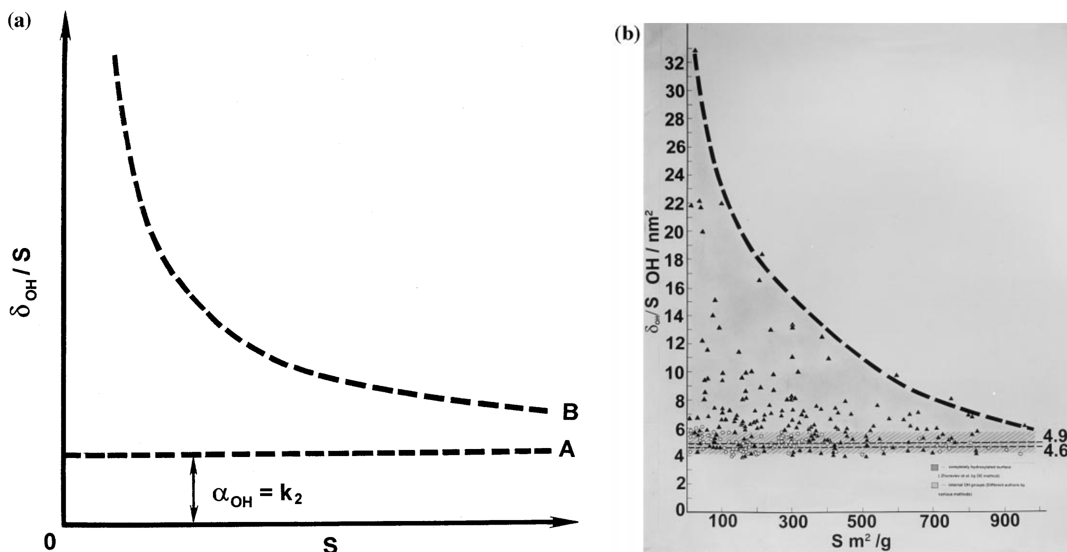


Fig. 8. (a) Theoretical dependence of δ_{OH}/S on the specific surface area S for a model sample of SiO_2 in a maximum-hydroxylated state both inside the bulk of the sample and on its surface [303,316]: (i) equilateral hyperbola B, the samples contain OH groups both in the bulk and on the surface of the sample (the upper boundary); (ii) straight line A, the samples contain only surface OH groups (the lower boundary). (b) δ_{OH}/S as function of the specific surface area S obtained by different researchers for different samples with a maximum-hydroxylated surface (see text): (i) a green zone, and also a red zone, corresponding to experimental data (black triangles, the total content of OH groups) obtained by different authors and by us (for more than 170 samples of SiO_2 with S in the range 4.3–960 $m^2\ g^{-1}$); (ii) only a red zone (band) corresponding to experimental data (open circles, the surface concentration of OH groups) obtained by us by the DE method (100 samples with S in the range 9.5–945 $m^2\ g^{-1}$, Fig. 7 and Table 5).

an increase in the size of the silica particles, the relative concentration of internal structurally bound water for freshly prepared samples can increase. This explains the shape of curve B for the maximum-hydroxylated sample. The constancy of $k_2 = \alpha_{OH}$, which is independent of S, shows that the silanol number for the maximum-hydroxylated state of surface is represented by a reproducible physico-chemical constant (Figs. 7 and 8(a) and (b)).

Next we shall examine the data reported in literature on the theoretical and crystallochemical estimates of the concentration of OH groups for different types of silica hydroxylated to a maximum degree. In 1950s Iler and De Boer and Vleeskens developed two basic models.

Based on the geometry of spherical SiO_2 particles and the density of amorphous silica ($\gamma = 2.20$ g cm^{-3}) Iler [1,23] estimated the number of Si atoms on the silica surface. The assumption was that for each surface Si atom there is one OH group, and Iler obtained the silanol numbers of $\alpha_{OH} = 7.85$ OH nm^{-2} [23] and 7.8 OH nm^{-2} [1] by using two calculation variants. However, as Boehm noted [80], only half of the free valency Si atoms are capable of holding OH groups. Therefore, Boehm gives $\alpha_{OH} = 3.93$ OH nm^{-2}.

Another model was proposed by De Boer and Vleeskens [38]. It is based on a concept that there is a similarity between the density and the refractive index of amorphous and crystalline modifications of silica — cristobalite and that of tridymite. The authors pointed out that since β-cristobalite crystallizes in octahedra, the silanol number should be calculated for the octahedral face {111}. The value for α_{OH} was found to be 4.55 OH nm^{-2}. The density of α- and β-cristobalite and that of α- and β-tridymite lie within a narrow range: from 2.20 to 2.34 g cm^{-3}. By considering the most probable cleft surface of these SiO_2 modifications the authors concluded that the silanol number, α_{OH}, lies in the range from 4.55 to 4.85 OH nm^{-2}. The minimal silanol number for completely hydroxylated SiO_2 surface

(both, for crystalline and amorphous modifications) is $\alpha_{OH} = 4.6 \pm 0.2$ OH nm^{-2}. The average area for a single Si atom on the surface holding one OH group is 0.217 ± 0.010 nm^2 [38]. Besides, De Boer et al. [37,38], in their thermogravimetric investigations of wide-pore amorphous SiO_2 it is subjected to pretreatment at ~ 600°C and then rehydroxylated in an autoclave, followed by the removal at 120°C of the physically adsorbed water, found that $\alpha_{OH} =$ 4.5–5.0 OH nm^{-2}. This experimental value is practically the same as the theoretical one. So, De Boer and Vleeskens were the first to obtain a reliable value for α_{OH}. However, owing to the non-correct thermogravimetric method they used (for determination of the concentration of OH groups on the SiO_2 surface), De Boer et al. [37,38] reached the erroneous conclusion that for the starting hydrated samples of amorphous silica which were not subjected to pretreatment at ~ 600°C and then rehydroxylated, $\alpha_{OH} = (6$–$8) > \alpha_{OH,MIN} = 4.6$ OH nm^{-2}. It is obvious that such a conclusion fails to take into account the presence of structural water inside the silica particles and attributes the total loss of mass of the sample after high-temperature annealing only to the loss of OH groups on the surface.

Zhuravlev, Kiselev et al. in their early works using the DE method [305–311] determined experimentally for the first time the value of α_{OH} in the small interval 4.8–5.2 OH nm^{-2} on the surface for the different initial, fully hydroxylated samples of the wide-pore silicas. These samples contained OH groups on the surface as well as structural water inside SiO_2 particles, and the authors observed that $\delta_{OH}/S > \alpha_{OH}$ or even $\delta_{OH}/S \gg \alpha_{OH}$, i.e. the total content of OH groups was much more than the content of silanols only on the surface.

The theoretical values were reported in literature for the concentration of OH groups on the surface of different types of silica [1,23,25,32, 38,80,92,159,160,265,285]. These data show that at present β-cristobalite model of De Boer and Vleeskens is accepted as the correct one. Thus, for instance, Branda et al. [265], Sindorf and Maciel [159,160] and Chuang and Maciel [285] when working out their models to describe the surface of amorphous silica, resorted to the concept developed by De Boer and Vleeskens, but in these models they also took into account the existence on the silica surface of a certain part of geminal silanols (besides the {111} face they considered the {100} face of β-cristobalite).

As can be seen from Figs. 6 and 7, our experimentally obtained averaged values $\alpha_{OH,AVER} =$ 4.6 (4.9) OH nm^{-2} show that at maximum-hydroxylated state of the amorphous silica surface, following the activation of SiO_2 in vacuum at 180–200°C, each Si atom holds approximately one or in some cases two OH groups (geminal silanols).

To sum up, the magnitude of the silanol number, which is independent of the origin and structural characteristics of amorphous silica, is considered to be a physico-chemical constant [301–303]. The results fully confirmed the idea predicted earlier by Kiselev and co-workers [31,32,48] on the constansy of the silanol number for a completely hydroxylated silica surface. This constant now has a numerical value: $\alpha_{OH,AVER} = 4.6$ (4.9) OH nm^{-2} (two calculation methods, see above) and is known in literature as the Kiselev–Zhuravlev constant.

The constant $\alpha_{OH,AVER} = 4.6$ OH nm^{-2} has a practical application: it can be used for determining the specific surface area S (m^2 g^{-1}) of amorphous dispersed silica with a maximum-hydroxylated surface [316,317] (it is necessary to remember about the high value of the correlation coefficient, $\rho \cong 1$, between $\delta_{OH}^{(S)}$ and S, see above). From Eq. (1′) we have the magnitude S:

$$S = K \cdot \delta_{OH}^{(S)}/\alpha_{OH,AVER} = K' \cdot \delta_{OH}^{(S)} \qquad (7)$$

where $K = 602.214$ and $K' = 130.916$ are constants, and $\delta_{OH}^{(S)}$ (mmol OH groups g^{-1} SiO_2) is the concentration of the silanol groups on the silica surface referred to unit mass of SiO_2, as determined by the DE method or by some other independent and correct method.

3.3. Dehydroxylation and rehydroxylation of the silica surface. Distribution of various types of surface groups. Energetic heteregeneity of the silica surface

Many papers have been published on the different aspects of the subject mentioned in the title. This is understandable since the chemistry of the silica surface as determined mainly by the concentration, the distribution and the reactivity of the surface silanol groups is of theoretical and practical importance.

Let us consider the dehydroxylation process of the silica surface. The DE method was used to determine the average value of the silanol number, depending on the temperature of pretreatment in vacuo. The experimental results obtained for 16 samples of amorphous silica are shown in Fig. 9. The samples differed from one another in the method of their synthesis and their structural characteristics: the specific surface area of the samples varied from 11 to 905 m^2 g^{-1}, and their porosity also varied within a wide range. Despite these differences the value of α_{OH} at a given temperature of treatment is similar for all the samples, and the decrease in the value of α_{OH} under similar heating conditions also follows approximately the same pattern. In Table 6 (column 2) are presented the most probable values of $\alpha_{OH} = \alpha_{OH,T}$ (concentration of the total OH groups averaged according to data in Fig. 9), beginning with the state of maximum hydroxylation (180–200°C, the first line), followed by the values for the degree of surface coverage with the total hydroxyl groups, $\theta_{OH} = \theta_{OH,T}$ (column 8) [301–303]. As can be seen from data in Fig. 9 and Table 6, the total values of α_{OH} decrease considerably in the range from 200 to about 400°C; between 400 and 1100°C decrease becomes notably smaller. Correspondingly the total value of θ_{OH} in the first steep section of the plot decreases from 1 to about 0.5, and in the second, more flat section it drops from 0.5 to very small values approaching zero.

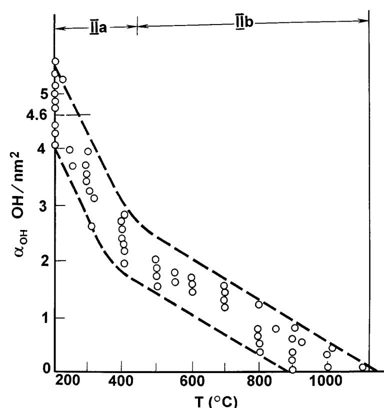


Fig. 9. Silanol number α_{OH} as a function of the temperature of pretreatment in vacuo for different samples of SiO_2. The broken lines delimit the range of experimental data (16 samples with different S from 11 to 905 m^2 g^{-1}). The subregions of dehydroxylation are: IIa from 200 to ~400°C, and IIb from 400 to 1100°C (see text).

Our results [301–303,305–311,313–315,317, 334–338] accord well with the data on the dehydroxylation of the amorphous silica surface obtained by Fripiat, Uytterhoeven et al. [58,74]. These authors determined the silanol number α_{OH} on the basis of the reaction of OH groups with organometallic reagents CH_3Li and CH_3MgI. Similarly, there is good agreement between our results and the data obtained by Taylor, Hockey et al. [73,82]. Here α_{OH} was determined by the weight loss upon the heating of the SiO_2 samples from 115 to 1100°C. Also, the data of Unger [112,146] derived from the reaction of OH groups with CH_3Li and the heavy water HTO accord well with our results. There is a qualitative agreement between our results and the data as reported by Papee [24], Gokcek and Boehm [80,81] and several other authors. The β-cristobalite models of dehydroxylation process as developed by Branda et al. [265], Sindorf and Maciel [159,160] and Chuang and Maciel [285] support the evidence of a two-stage temperature dependence of the silanol number α_{OH}.

Based on data in Table 6 (columns 2 and 8) it is possible to assess the most probable values of α_{OH} and θ_{OH} within a wide range of temperatures for the treatment of SiO_2 samples. These values are independent of the degree of silica dispersiveness if the starting samples have been obtained under the condition of a completely hydroxylated surface. Many researchers use in their studies our functionality of $\alpha_{OH} = f(T°C)$ and $\theta_{OH} = f(T°C)$

Table 6
Surface concentration of the different types of OH groups, Si atoms and SiOSi bridges (which are free of OH groups) and degree of coverage of the silica surface with these groups respectively[a] as a function of pretreatment temperature in vacuo, with the initial state corresponding to the maximum degree of surface hydroxylation (first line)

Temperature of vacuum pretreatment, T (°C)	Total OH groups, $\alpha_{OH,T}$ (OH nm^{-2})	Isolated OH groups, $\alpha_{OH,I}$ (OH nm^{-2})	Geminal OH groups, $\alpha_{OH,G}$[b] (OH nm^{-2})	Vicinal OH groups, $\alpha_{OH,V}$ (OH nm^{-2})	Si atoms, α_{Si} (Si nm^{-2})	SiOSi bridges, α_{SiOSi} (SiOSi nm^{-2})	$\theta_{OH,T}$	$\theta_{OH,I}$	$\theta_{OH,G}$[b]	$\theta_{OH,V}$	θ_{Si}
180–200	4.60	1.20	0.60	2.80	0	0	1.00	0.26	0.13	0.61	0
300	3.55	1.65	0.50	1.40	1.05	0.53	0.77	0.36	0.11	0.30	0.23
400	2.35	2.05	0.30	0	2.25	1.13	0.51	0.45	0.06	0	0.49
500	1.80	1.55	0.25	0	2.80	1.40	0.39	0.34	0.05	0	0.61
600	1.50	1.30	0.20	0	3.10	1.55	0.33	0.29	0.04	0	0.67
700	1.15	0.90	0.25	0	3.45	1.73	0.25	0.20	0.05	0	0.75
800	0.70	0.60	0.10	0	3.90	1.95	0.15	0.13	0.02	0	0.85
900	0.40	0.40	0	0	4.20	2.10	0.09	0.09	0	0	0.91
1000	0.25	0.25	0	0	4.35	2.18	0.05	0.05	0	0	0.95
1100	0.15	0.15	0	0	4.45	2.23	0.03	0.03	0	0	0.97
1200	0	0	0	0	4.60	2.30	0	0	0	0	1.00

[a] Indexes; T, total OH groups; I, isolated OH groups; G, geminal OH groups; V, vicinal OH groups.
[b] Data in columns 4 and 10 are the corrections for geminal OH groups [159,160].

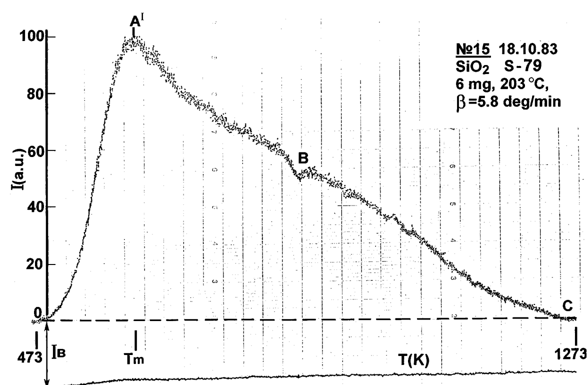


Fig. 10. Total mass thermogram 9 (rate of heating $\beta = 5.8$ grad min^{-1}): I, intensity of the H_2O peak (arbitrary units); I_B, intensity of the background signal (a.u.); T, temperature (K); T_m, characteristic point [temperature (K)] corresponding to the maximal rate of desorption; A^1, maximum of the differential curve; B, dip in the descending branch A^1BC (see Fig. 5 and text).

as a set of physico-chemical constants (at fixed temperatures).

Let us consider in detail the data obtained by the MTA-TPD method (Fig. 5). These data cover the entire region II which is confined to the left of the ascending section of the curve 8 and encompasses thermograms 9–17. After preliminary thermal treatment in vacuo under the given condition (Table 1) the standard silica samples S-79 were first subjected to cooling up to room temperature and then to linear heating in the 25–1000°C temperature range. It should be noted that the appearance of each separate mass thermogram within ± 0.5°C corresponded to the temperature of the preliminary treatment for a given sample. We have here a clear manifestation of 'the characteristic memory effect' of the silica surface and its hydroxyl coverage with respect to the temperature of preliminary thermal treatment in vacuo. Also, as noted above, with an increase in temperature of preliminary treatment of the S-79 sample there is an increase in temperature in region II which corresponds to the maximum of each individual mass thermogram (Fig. 5 and Table 1). All this confirms the fact that the silica surface which has been subjected to different degrees of hydroxylation is energetically non-uniform.

In Fig. 10 is shown the overall mass thermogram 9 obtained by the MTA-TPD method and recorded by an electronic potentiometer. This differential thermal desorption curve, owing to its nearness to the boundary curve 8 (Fig. 5), shows practically the complete spectrum of the hydroxyl groups removed from the silica surface. At first this surface corresponds to the maximum level of hydroxylation, while at the end of the heating at high temperature it becomes strongly dehydroxylated. In its appearance the thermogram (curve 9) is similar to the thermal kinetic curve obtained by Young [41]. Its asymmetric form also indicates the energetic non-uniformity of the surface.

It should be noted that both in the case of the thermogram curve 9 and in the case of other kinetic curves 1–7 and 10–13 (Figs. 5 and 10) there is a characteristic dip B on the descending ABC section. The differential curve 14 (Fig. 5) with a maximum in the region of the dip B was drawn by extrapolation, taking into account the form of the ascending section of the neighboring thermogram (curve 15). The beginning of this thermogram (curve 14) corresponds to about 400°C and coincides with the temperature corresponding to a change in the slope of two descending and approximately rectilinear sections of the temperature dependence of the silanol number α_{OH} (Fig. 9). Therefore both the dip B itself and the ascending section of curve 14 which passes through such a dip B practically delimit the different kinds of silanol groups on the silica surface (see below). The kinetic parameters for different thermograms 9–17 are summarized in Tables 4 and 8, and as can be seen from Fig. 11, the experimentally determined kinetic order of the thermal desorption reaction $n \cong 2$ for the whole region II.

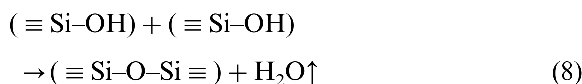
The dependence of the activation energy of desorption E_D on the temperature (Fig. 12) in region II is characterized by two approximately rectilinear sections: in the range from 190 to about 400°C (subregion IIa) and above 400°C (subregion IIb), with a notable change in the slope as one goes from the first to the second section. Here too, the change in the slope at ~ 400°C corresponds to the change in the slope at the same temperature between two sections of the temperature dependence of α_{OH} (Fig. 9).

Table 7
Values of the average area occupied by one OH group and the average distance between two adjacent OH groups following pretreatment in vacuo of amorphous silica at different temperatures

Temperature of vacuum pretreatment, T (°C)	Average value of the area occupied by one OH group, ω_{OH} (nm^2)		Average distance between two adjacent OH groups, L (nm)	
	Vicinal silanol	Isolated silanol	Between vicinal silanols	Between isolated silanols
180–200	0.068	0.45	0.295	0.76
300	0.068	0.42	0.295	0.73
400		0.43		0.74
500		0.55		0.84
600		0.67		0.92
700		0.87		1.05
800		1.43		1.35
900		2.50		1.79
1000		4.00		2.26
1100		6.67		2.91

From the known temperature dependences of the activation energy and the silanol number in region II we can obtain the dependence of the activation energy of dehydroxylation, E_D, on the concentration of OH groups, α_{OH}, or the dependence of E_D on the extent to which silica is covered with hydroxyl groups, θ_{OH}, as shown in Fig. 13 [302,303,332].

The second order of the reaction (Tables 4 and 8 and Fig. 11) observed for the entire region II is direct confirmation of associative desorption, which proceeds as a result of the reaction between the surface silanol groups (condensation) leading to the formation of siloxane bonds and molecular water:



$$(\equiv \text{Si–OH}) + (\equiv \text{Si–OH}) \rightarrow (\equiv \text{Si–O–Si} \equiv) + H_2O\uparrow \quad (8)$$

Thus, the condensation, Eq. (8), is characteristic of both subregions (IIa and IIb) despite the fact that the activation energies, E_D, for these sections differ significantly (Figs. 12 and 13).

The components of the silanol number — the silanol number of free isolated OH groups, $\alpha_{OH,I}$, and the silanol number of vicinal OH groups bound via the hydrogen bonds, $\alpha_{OH,V}$, on the surface of SiO_2 were determined (together with Agzamkhodzhaev and Galkin) by the DE method and IR spectroscopic measurements, depending on the temperature of the preliminary treatment in vacuo (Fig. 14) [302,303,315]. The sample consisted of compressed aerosilogel ($S = 330$ m^2 g^{-1}), which was free of narrow pores and having an initially fully hydroxylated surface. It has been shown that the vicinal hydroxyl groups can be removed from the SiO_2 surface by treatment in the temperature range of 200 to ~400°C. However, the intensity of the absorption band of free isolated hydroxyl groups increases in the temperature interval from 200 to about 400°C, while

Table 8
Dehydroxylation: determination of the kinetic parameters

Thermokinetic curve	Reaction order n	Activation energy of desorption E_D	
		kcal mol^{-1}	kJ mol^{-1}
10	(2.0)*	20.9	87.3
11	(2.0)*	21.1	88.5
12	(2.0)*	22.7	94.9
13	(2.0)*	24.2	101.9
15	2.00	25.0	104.7
15	(2.0)*	27.9	116.9
16	2.27	37.7	158.0
16	(2.0)*	44.8	187.4
17	1.97	49.1	205.4
17	2.26	50.3	210.7
17	(2.0)*	49.6	207.6

* Parentheses indicate that $n = 2$ is taken as a known value.

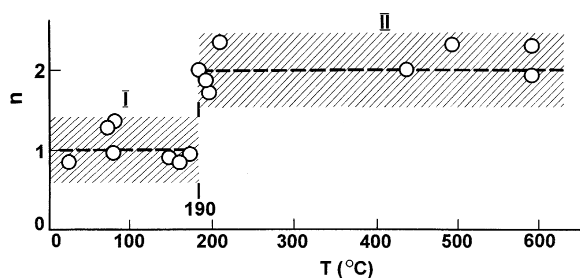


Fig. 11. Reaction order of the thermal desorption of water, n, as a function of temperature T (C°) of the pretreatment of silica in vacuo: region I, dehydration; region II, dehydroxylation; (Tables 2, 4 and 8 and Fig. 12); the shaded bands are the range of experimental data.

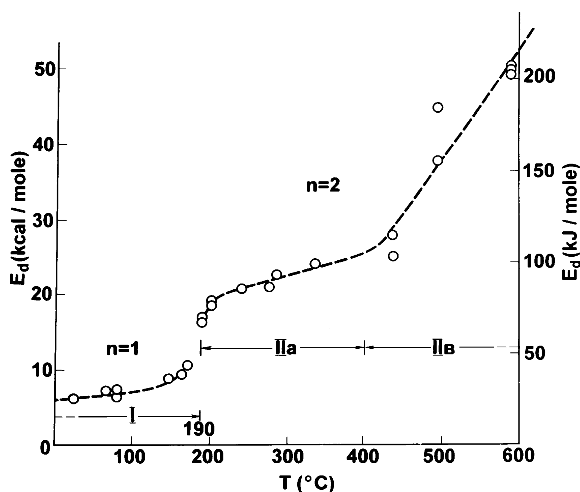


Fig. 12. Activation energy of water desorption, E_D, as a function of temperature T (C°) of the pretreatment of silica in vacuo: (i) region I, dehydration; (ii) IIa, IIb, subregions of region II, dehydroxylation (Tables 2, 4 and 8, see text).

above 400°C this intensity decreases. The correlation of data according to the silanol number at 400°C (Table 6, column 2) and the intensity of the IR absorption band of hydroxyl groups as shown in Fig. 14 is based on the fact that for the samples calcined in vacuo at 400°C there are practically only free isolated hydroxyl groups [315]. This means that the total concentration of silanol groups on the silica surface at 400°C, $\alpha_{OH,T}$, corresponds to the concentration of free isolated hydroxyl groups, $\alpha_{OH,I}$. The concentration of free isolated OH groups on the silica surface was calculated from the absorption coefficient (which also includes the values of α_{OH}) of OH groups on the surface of the sample, depending on the temperature of the pretreatment in vacuo. The con-

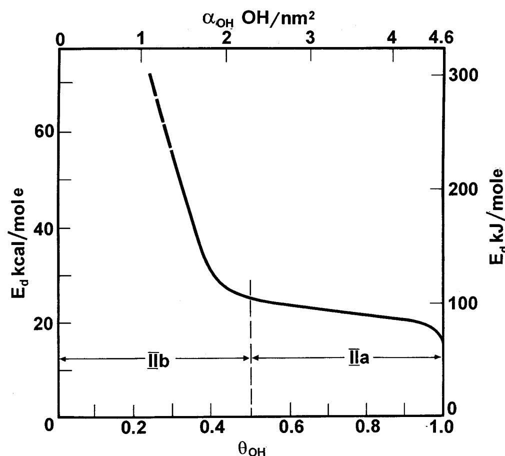


Fig. 13. Activation energy of water desorption, E_D (in region II): (i) as a function of the surface concentration of OH groups, α_{OH}; (ii) as a function of the surface coverage of SiO_2 with OH groups, θ_{OH} (see text).

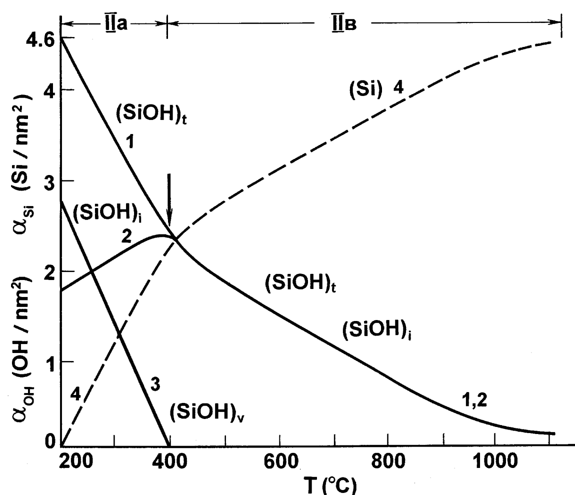


Fig. 14. Distribution of the surface groups as a function of the temperature of pretreatment in vacuo (Zhuravlev model-1): curve 1, average concentration of the total OH groups, $\alpha_{OH,T}$; curve 2, average concentration of the free isolated OH groups, $\alpha_{OH,I}$; curve 3, average concentration of vicinal OH groups bound through the hydrogen bonds, $\alpha_{OH,V}$; curve 4, average concentration of surface Si atoms that are part of the siloxane bridges and free of OH groups, α_{Si}. The arrow indicates the combined data obtained by the DE method and the IR spectroscopic method.

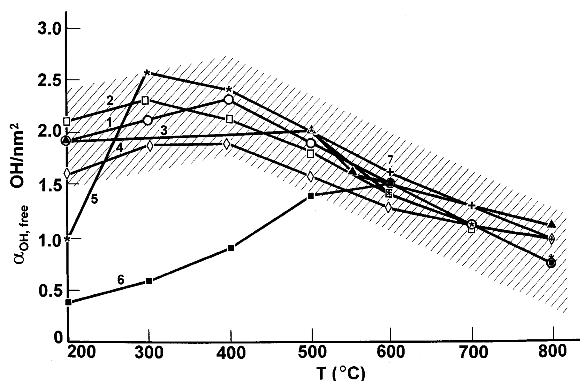


Fig. 15. Distribution of free isolated OH groups: survey of the different models (from Vansant et al. [263]): (1) Zhuravlev's model as a reference one (DE method) with an error region of ± 0.5 OH nm^{-2} (the shaded area); (2) Gillis-D'Hamers (pyridine); (3) Haukka (^{1}H NMR); (4) Gillis-D'Hamers (H_2O desorption); (5) Gillis-D'Hamers (IR band shift); (6) Van Der Voort (IR integration); (7) Fink (IR deconvolution) (see text).

centration of vicinal OH groups, $\alpha_{OH,V}$, at 200–400°C (Fig. 14, curve 3) and the concentration of surface Si atoms, α_{Si}, that are part of the siloxane bridges $\equiv$Si–O–Si$\equiv$ and free of hydroxyl groups, throughout the range of temperatures (Fig. 14, curve 4) can be determined from the total concentration of OH groups, $\alpha_{OH,T}$, and the concentration of free isolated OH groups, $\alpha_{OH,I}$.

On the basis of our data one can calculate the average value of the area occupied by one OH group, ω_{OH} (nm^2), as well as the average distance between these groups, L (nm), at temperature range of 200–1100°C (Table 7). Our IR spectroscopic investigations (together with Davydov and Kiselev) [309] showed that the difference in stretching vibrations between the band of free OH groups (3750 cm^{-1}) and the band due to vicinal OH groups (maximum at ~ 3550 cm^{-1}) is $\Delta\nu \approx 200$ cm^{-1}. According to Lippincott and Schroeder [347], the value for $\Delta\nu$ corresponds to a probable OH…O distance of ~ 0.295 nm. This gives $\omega_{OH} \cong 0{,}068$ nm^2 per one vicinal OH group. It is not difficult to calculate the other values of ω_{OH} and L. Since these OH groups are distributed at random, we can assume that their distribution is uniform throughout the silica surface. In this case, the average areas per one group, ω_{OH}, and the average distances, L, between them remain approximately constant up to 400°C, and then increase considerably. Thus, for example, at 1100°C the area occupied by one isolated OH group is $\omega_{OH} \cong 6.7$ nm^2 and the distance between two free isolated adjacent OH groups is $L \cong 2.9$ nm (Table 7, columns 3 and 5).

It is interesting to compare the shape of the distribution curve of free isolated OH groups, $\alpha_{OH,I}$, as a function of the pretreatment temperature of SiO_2, which we obtained by the DE method, with data reported in literature. Such a comparison (Fig. 15) has been made by Vansant, Van Der Voort and Vrancken in their monograph [263], where they considered seven different models: (1) the model of Zhuravlev [302,303] as a reference one with an error region of ± 0.5 OH nm^{-2} (the shaded band, Fig. 15); (2) the model of Gillis-D'Hamers et al. [238], which is based on pyridine desorption from the silica surface; (3) the model of Haukka et al. [253,254], which is based on ^{1}H NMR data for isolated and vicinal silanols; (4) the model of Gillis-D'Hamers et al. [263], which is based on the water desorption from the silica surface; (5) the model of Gillis-D'Hamers et al. [238], which is based on the IR band shift of free isolated OH groups as a function of temperature; (6) the model of Van Der Voort et al. [237,263], which is based on the integration of IR bands due to different types of OH groups; and (7) the model of Fink et al. [190], which is based on the deconvolution of the summed-up IR band into constituent components belonging to different types of silanol groups. It can be seen from Fig. 15 that almost all models 1–7 are situated in the error region. This shows good agreement between the data obtained by different researchers. Furthermore, it confirms the existence of a real temperature distribution of free isolated silanols, with a maximum at about 400°C. It is necessary to note that Yaroslavsky, by using the IR spectroscopy method, discovered for the first time [11] a qualitative temperature course of free isolated OH groups with the maximum at about 500°C.

Thus, our results (Figs. 9 and 12–14) indicate that the dehydroxylation of the silica surface proceeds via two stages: subregion IIa and subregion IIb.

Let us consider the case where the degree of coverage of the silica surface with OH groups is high, $1 \geq \theta_{OH} > 0.5$, which corresponds to subregion IIa (Fig. 13). This range is characterized by the linear energetic non-uniformity on the surface, which is described by the following empirical relationship:

$$E_D = 31.4 - 12.3\theta_{OH} \quad (9)$$

where E_D is the energy of activation in the range 19–25 kcal mol^{-1} (the values E_D for the initial non-linear section in Fig. 13 are from 16.5 to 19 kcal mol^{-1}). This activation energy E_D is almost independent of the silanol concentration and is determined mainly by a set of perturbations due to vicinal OH groups. These perturbations cease with the disappearance of the vicinal groups at ~400°C (at $\theta_{OH} \cong 0.5$). Thus, the subregion IIa is characterized by the presence of lateral interactions (hydrogen bonds) between the neighboring OH groups.

Let us consider the coverage of the silica surface with hydroxyl groups $\theta_{OH} < 0.5$, which corresponds to subregion IIb (Fig. 13). In this case, the main role is played by free isolated hydroxyl groups and siloxane bridges. This subregion E_D is strongly dependent on the concentration of hydroxyl groups, i.e. the activation energy of desorption is in the range from ~25 to 50 kcal mol^{-1} (and probably higher), and increases with a decrease in the concentration of the OH groups. When there are only free isolated silanols (and, perhaps, free geminals, see below) surrounded by siloxane SiOSi bridges, the latter bridges can acquire a relatively large area following high temperature treatment of SiO_2. Under these conditions the main mechanism describing the transfer of OH groups corresponds to condensation Eq. (8) via disordered migration of protons on the surface (a process of the activated diffusion of OH groups). At the final stage, water is evolved, owing to the interaction of two OH groups that accidentally approach each other to a distance of about 0.3 nm (a characteristic length of H-bond). The mechanism describing the migration of protons is not entirely clear. It probably involves the interaction of the protons at elevated temperatures with O atoms of the neighboring SiOSi bridges, resulting in the formation of new surface OH groups, which are displaced relative to their initial position. In other words, this mechanism can be represented as the transition from one local minimum of the potential energy into another by means of 'jumps' between the neighboring siloxane bridges. Obviously, at a low concentration of OH groups such a diffusion of protons along the silica surface will limit the condensation process Eq. (8).

In the monograph by Vansant et al. [263] are presented experimental results of Gillis-D'Hamers et al., obtained by the TPD method. These results pertain to the dehydration and the dehydroxylation of water from the surface of silica gel sample with a specific area of 400 m^2 g^{-1}. The obtained data on the dependence of the activation energy of water desorption, E_D, on the concentration of OH groups, α_{OH}, on the silica surface are in good quality agreement with our previously data [302,303,332], although the absolute values of E_D exceed our numerical values. Gillis-D'Hamers et al. have reported the appearance of three approximately linear sections. At high values of α_{OH} (from 4.5 to 5.0 OH nm^{-2}) a sharp decline in E_D is attributed to the transition from dehydration to dehydroxylation (cf. section in the region of 190°C in Fig. 12). At values of α_{OH} from approximately 4.5 to 2.0 OH nm^{-2} there appears a weakly sloping section of E_D which is due to the condensation of bridged vicinal OH groups. This corresponds to the subregion IIa in Figs. 12 and 13. Finally, at silanol values of $\alpha_{OH} < 2.0$ OH nm^{-2} the sharply ascending section of E_D is due to the condensation of free hydroxyl groups on the SiO_2 surface, which correspond to the subregion IIb in Figs. 12 and 13 of our work.

In the last two decades, owing first of all to the investigations carried out by Sindorf and Maciel [159,160] and others based on ^{29}Si NMR spectroscopic measurements, it became possible to differentiate between single silanols and geminal silanols on the silica surface. These results confirmed the hypothesis proposed earlier by Peri and Hensley [79,92].

Therefore, it was necessary to correct our results on the distribution of silanols with account taken of the presence of geminal silanols on the

SiO_2 surface. Data on the content of geminal silanols we took from the works of Sindorf and Maciel, and this correction is based on the temperature dependence of the relative concentration of geminal silanols (%) on the SiO_2 surface [159,160,263]. In Table 6 (columns 2–7 and 8–12), the surface concentrations of all the different types of silanol groups and the degree of surface coverage by these groups on amorphous silica that has been thermally pretrated in vacuo at a temperature range from 180–200 to ~1200°C, are summarized. Also are shown the concentrations and the degree of surface coverage of Si atoms and SiOSi groups, which are free of OH groups, on the silica surface. In Fig. 16 a graphic representation of our model is shown (model-2): the distribution of all total OH groups and the separate distribution of three types of silanol groups (isolated, geminal and vicinal silanols), and Si atoms and SiOSi groups, as a function of the pretreatment temperature in vacuo.

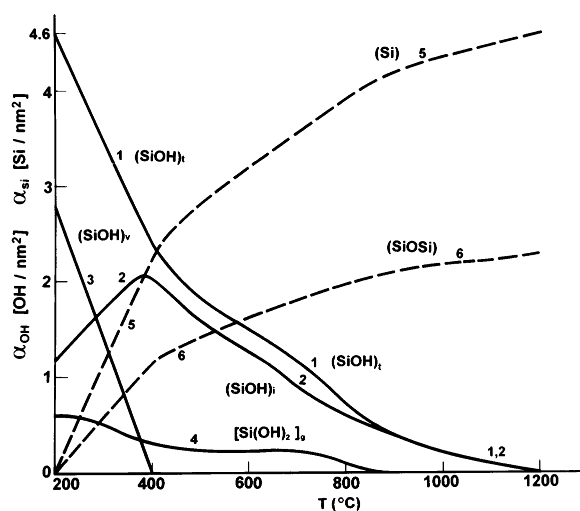


Fig. 16. Distribution of the surface groups as a function of the temperature of pretreatment in vacuo (Zhuravlev model-2): curve 1, average concentration of the total OH groups, $\alpha_{OH,T}$ (column 2, Table 6); curve 2, average concentration of the free isolated OH groups, $\alpha_{OH,I}$ (column 3); curve 3, average concentration of vicinal OH groups bound through the hydrogen bonds, $\alpha_{OH,V}$ (column 5); curve 4, average concentration of geminal OH groups, $\alpha_{OH,G}$ (column 4); curve 5, average concentration of surface Si atoms that are part of the siloxane bridges and free of OH groups, α_{Si} (column 6); curve 6, average concentration of surface SiOSi bridges, which are free of OH groups, α_{SiOSi} (column 7).

The correction, introduced for the geminal OH groups, indicates (Table 6) that at temperatures ≥400°C the concentration curve for the single free OH groups (model-1, Fig. 14, curve 2) is decomposed in single isolated (free) and geminal (free) curves for the silanol groups (model-2, Fig. 16, curves 2 and 4, respectively). With regard to free isolated and free geminal OH groups, it can be considered that in the first approximation these groups occupy about the same area ω_{OH} at a given pretreatment temperature (see Table 7).

Next we shall consider the rehydroxylation process of the SiO_2 surface. When the dehydroxylated surface of silica reacts with water in a vapor or liquid state silanol groups are formed, or, in other words, rehydroxylation takes place (Fig. 1(b)). It has been pointed out in the literature [35,37,38,41,121] that complete hydroxylation of the surface can be achieved only for those samples of silica which were subjected to preliminary treatment at temperatures below ~400°C. After calcination at higher temperature only partial rehydroxylation takes place.

However, as has been shown in our work [326], the dehydroxylated surface of silica samples first activated in the range from 400 to 1000–1100°C can be completely restored to the maximum hydroxylated state ($\alpha_{OH} = 4.6$ OH nm^{-2}) by treatment with water at room temperature. For samples subjected to more extensive dehydroxylation, it takes more time to obtain complete rehydroxylation. Thus, for a starting wide-pore silica sample ($S = 340$ m^2 g^{-1}) that had been calcined in air at 900°C ($\alpha_{OH} = 0.66$ OH nm^{-2}) it took about 5 years, during which the sample was in contact with liquid water at room temperature, before the complete rehydroxylation of its surface was achieved ($\alpha_{OH} = 5.30$ OH nm^{-2}). To accelerate rehydroxylation we subjected the silica samples to hydrothermal treatment at 100°C (samples were boiled in water) [307,311,326]. The starting aerosilogel ($S = 168$ m^2 g^{-1}) was calcined in vacuo at 1100°C for 10 h ($\alpha_{OH} = 0.06$ OH nm^{-2}). Then the sample was boiled in water for 60 h and its specific surface area was found to be $S = 108$ m^2 g^{-1} and the silanol number $\alpha_{OH} = 4.60$ OH nm^{-2} (Table 5).

The rehydroxylation of a wide-pore silica gel sample (calcined in air at 850°C and held in water at 100°C for 1, 5, 10, 30 and 100 h) was found to take 5–10 h to achieve complete rehydroxylation [326]. These and other results [326] indicate that rehydroxylation, in the presence of water, of dehydroxylated silica (calcined at above 400°C) requires considerable energy to activate the process of dissociative adsorption, E_A. In other words, what we have here is the chemisorption of water resulting in the formation of hydroxyl groups bound through valence bonds to the SiO_2 surface. The reaction which takes place on the surface is the opposite of the condensation reaction Eq. (8) and involves the breaking of the surface siloxane bonds.

Thus the rehydroxylation of silica should be considered to be a process taking place in two subregions: below and above the temperature of the preliminary treatment (about 400°C). This accords well with the two subregions, IIa and IIb, observed in the dehydroxylation process (Figs. 12 and 13).

In subregion IIb the silica surface is occupied only by free hydroxyl groups and siloxane bridges. In suregion IIa, however, there are also vicinal OH groups bound together by hydrogen bonds.

In analyzing the silica surface we should take into account the non-uniform nature of the Si–O bonds belonging to silanol groups and siloxane bridges. As is known, the presence of an additional donor–acceptor $(d-p)_\pi$ interaction of the Si–O bond determines the specific nature of these bonds [135].

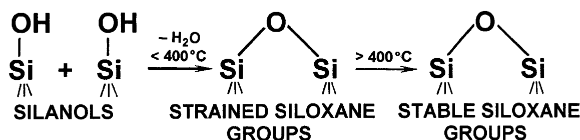
For strongly dehydroxylated silica the surface concentration of siloxane groups is high (Figs. 14 and 16). As a result of the $(d-p)_\pi$ conjugation in the siloxane group, due to the shift in the electronic density as one goes from O atom to Si atom, it is impossible for oxygen which is on the surface of the sample to form a hydrogen bond with the adsorbed water molecules, i.e. the siloxane surface is hydrophobic [135].

The hydroxylated surface with a predominance of silanol groups is hydrophilic in nature. In the silanol $\equiv$Si–O–H group, owing to the same $(d-p)_\pi$ interaction, the electronic density becomes delocalized from the O–H bond to the neighboring Si–O bond [135]. This makes it possible for the silanol groups to form strong hydrogen bonds with water molecules.

It follows from the data in Figs. 12–14 and 16 that the high rate of rehydroxylation of silica subjected to preliminary activation at 200–400°C (subregion IIa) is apparently due to the fact that the concentration of the siloxane bridges is still low and each $\equiv$Si–O–Si$\equiv$ bridge is surrounded by OH groups. Such a location of the surface groups weakens the Si–O bond in the siloxane bridge itself. During the rehydroxylation process, additionally introduced water molecules first become adsorbed on silanol groups and have a direct effect on the neighboring weakened strained siloxane groups. This results in the splitting of these siloxane groups and the formation of new OH groups on the surface of silica.

Upon a preliminary activation of SiO_2 at above 400°C (subregion IIb) the concentration of the siloxane bridges increases sharply. These bridges form whole hydrophobic regions on the surface, while the concentration of OH groups drops with an increase in temperature (Figs. 9, 12–14 and 16). But even under the condition of maximum activation (1000–1100°C), free OH groups can still exist, but are at a large distance from one another (Tables 6 and 7). These OH groups act as the centers of adsorption when an additional amount of water is introduced, and rehydroxylation takes place first in the vicinity of the silanol groups. The hydroxylated sections that are localized in the shape of small spots gradually expand. Subsequent rehydroxylation proceeds along the boundary separating the hydrophilic and hydrophobic sections. Such rehydroxylation of the surface is due to the considerable energy of activation of adsorption, E_A [302,303,326]. This means that rehydroxylation, due to dissociative adsorption (chemisorption) of H_2O with the splitting of siloxane bridges and the formation of new OH groups, proceeds according to a different mechanism, depending on the coverage of the surface with OH groups, θ_{OH}.

At $1 \geq \theta_{OH} > 0.5$ (subregion IIa, Fig. 13) the activation energy of chemisorption, E_A, is close to zero. For this subregion we can write that $E_D \approx$



Scheme 2. Bergna's scheme.

Q_A [70], where Q_A is a heat of chemisorbption which varies from 16.5 to $\sim$25 kcal mol^{-1} (see Eq. (9)). The heat of chemisorption Q_A decreases insignificantly with an increase in θ_{OH}.

At $\theta_{OH} < 0.5$ (subregion IIb, Fig. 13) chemisorption proceeds very slowly at room temperature, but the rate of reaction increases sharply with an increase in the reaction temperature to 100°C. The physical adsorption of water on silanol groups precedes chemisorption. The latter is strongly activated, or $E_A > 0$. It can be expressed as

$$E_A = E_D - Q_A \quad (10)$$

where E_D varies from 25 to about 50 kcal mol^{-1} and probably higher (Fig. 13).

An analysis has been carried out of data reported in literature from the point of view of whether stable or strained siloxane bridges and siloxane rings are located on the surface of amorphous silica. This analysis shows that at present there is still no agreement among the researchers on this question. On the basis of our experimental data described above we are of the same opinion which has been stated in a review by Bergna [256] and which can be seen in Scheme 2.

According to this scheme strained weakened siloxane bridges are formed on the hydroxylated silica surface owing to a thermally induced condensation process of vicinal silanols. Such ≡Si–O–Si≡ bridges exist at temperatures up to approximately 400°C. At high concentrations of OH groups which surround the bridges and act on the Si–O bonds these strained weakened siloxane bridges are readily broken and the surface is completely rehydroxylated in the presence of an additional amount of water (subregion IIa, Fig. 13). At higher temperatures and without vicinal OH groups on the surface, the strained siloxane groups are converted into stable siloxane bridges and rings, which are also able to rehydroxylate but more hardly and at a slower rate (subregion IIb, Fig. 13).

Thus, it is necessary to emphasize that the rehydroxylation process, which is due to the dissociative adsorption of water involving the splitting of siloxane bridges and the formation of new OH groups, takes place via: (a) the rapid nonactivated (or weakly activated) chemisorption (subregion IIa); and (b) the slow strongly activated chemisorption (subregion IIb).

3.4. Physico-chemical model of amorphous silica surface: main stages

Let us consider the main stages of our physico-chemical model of the SiO_2 surface.

3.4.1. Stage 1: the initial stage (25°C, in vacuo):

- the SiO_2 surface is in a maximum state of hydroxylation ($\theta_{OH} = 1$, $\alpha_{OH} = 4.60$ OH nm^{-2});
- all the different types of silanol groups (isolated singles, geminals, vicinals) are present;
- the SiO_2 surface is covered with physically adsorbed water (multiple layers of H_2O), $\theta_{H_2O} > 1$;
- the surface OH groups and adsorbed water are permeated with a H-bond network;
- the internal OH groups are present inside the SiO_2 skeleton.

3.4.2. Transition from stage 1 to stage 2 (Fig. 17)

- the first threshold temperature ($T_1 = 25$°C, in vacuo);
- complete removal of multiple layers of physically adsorbed water;
- the process is readily reversible upon the introduction of an excess of water.

3.4.3. Stage 2 (25–190°C, in vacuo, the region I, Fig. 12)

- the SiO_2 surface is in a maximum state of hydroxylation ($\theta_{OH} = 1$, $\alpha_{OH} = 4.60$ OH nm^{-2});

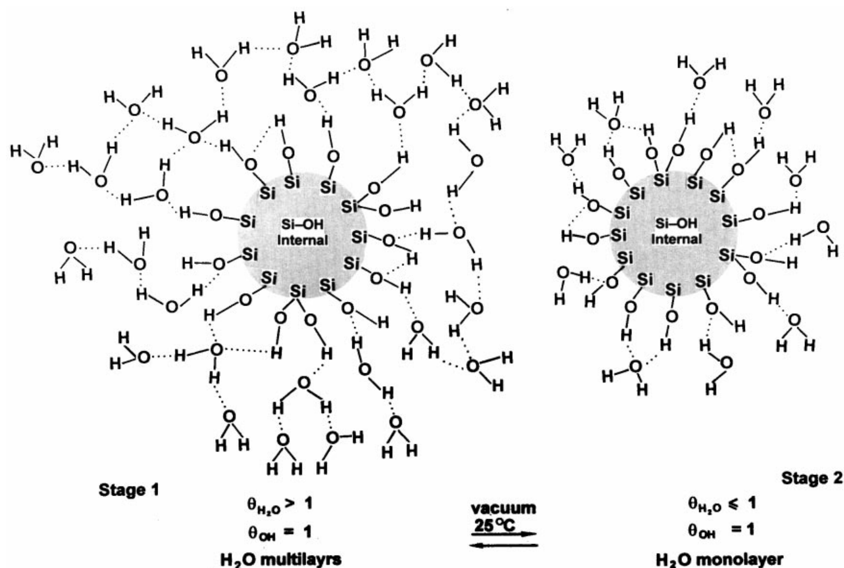


Fig. 17. Transition from stage 1 to 2 ($T_1 = 25°C$, see text).

- all the different types of silanol groups (isolated singles, geminals, vicinals) are present;
- the surface is covered with a single or less layer of adsorbed water, which completely disappears towards the end of the stage 2 ($1 \geq \theta_{H_2O} \geq 0$);
- the surface silanol groups and the molecules of adsorbed water at a low degree of coverage (less than the H_2O monolayer) are predominantly bound via H-bonds, according to the types shown in Fig. 18, as it was suggested by us by the method of molecular dynamics and the MTA-TPD method [303,330,333];
- the internal OH groups are present inside the SiO_2 skeleton.

3.4.4. Transition from stage 2 to stage 3 (Fig. 19)

- the second threshold temperature ($T_2 = T_B = 190°C$, in vacuo, Fig. 12);
- complete removal of H_2O monolayer while the SiO_2 surface remains in a state of maximum hydroxylation (the dry SiO_2 surface);
- the process is readily reversible upon the introduction of an excess of water.

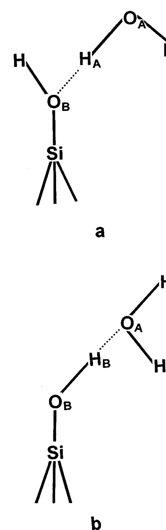


Fig. 18. Two basic types of orientation of the water molecule with respect to the silanol group on the SiO_2 surface [303,333]: (a) The hydrogen atom H_A in the H_2O molecule bonded to the oxygen atom O_B of the ≡Si–OH group (the hydrogen bond); (b) The oxygen atom O_A in the H_2O molecule bonded to the hydrogen atom H_B of the ≡Si-OH group (the hydrogen bond).

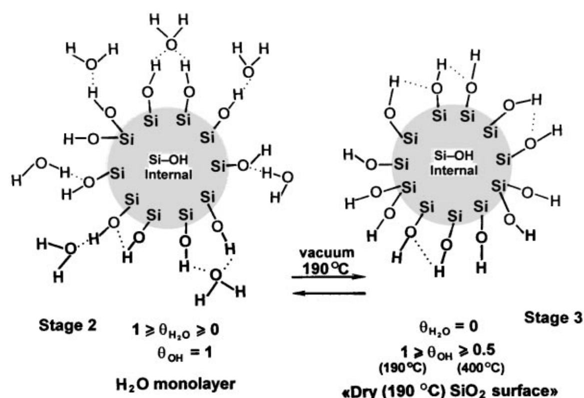


Fig. 19. Transition from stage 2 to 3 ($T_2 = 190°C$, see text).

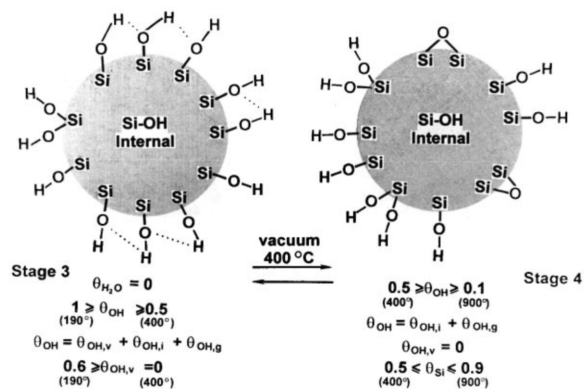


Fig. 20. Transition from stage 3 to 4 ($T_3 = 400°C$, see text).

3.4.5. Stage 3 (190–400°C, in vacuo, the subregion IIa, Fig. 12)

- the overall degree of surface hydroxylation decreases significantly ($1 \geq \theta_{OH} \geq 0.5$, $4.60 \geq \alpha_{OH} \geq 2.35$ OH nm^{-2});
- all the different types of silanol groups (isolated singles, geminals, vicinals) are present;
- the concentration of isolated single OH groups, $\alpha_{OH,I}$, increases (from 1.20 to 2.05 OH nm^{-2}), reaching a maximum at 400°C;
- the concentration of vicinal bridged OH groups, $\alpha_{OH,V}$, decreases (from 2.80 to 0.0 OH nm^{-2}), and these silanols disappear at about 400°C;
- internal OH groups gradually disappear with an increase in the temperature and duration of silica thermal treatment;
- the range of activation energy of dehydroxylation, E_D, for subregion IIa (Fig. 13) changes very slightly (from 19 to ~ 25 kcal mol^{-1}) and is determined mainly by a set of perturbations due to H-bonded OH groups;
- the activation energy of dissociative adsorption of H_2O, E_A, is close to zero, i.e. there is the rapid, nonactivated (or weakly activated) chemisorption of water in subregion IIa.

3.4.6. Transition from stage 3 to stage 4 (Fig. 20)

- the third threshold temperature ($T_3 = 400°C$, in vacuo, Fig. 12);
- complete removal of the vicinal OH groups while free single and free geminal OH groups remain on the silica surface;
- the process is readily reversible upon the introduction of an excess of water, and the complete rehydroxylation takes place owing to the splitting of weakened strained SiOSi bridges.

3.4.7. Stage 4 (400–900°C, in vacuo, the subregion IIb, Fig. 12)

- the overall degree of surface hydroxylation continues to decrease but the downward slope is more gradual ($0.5 \geq \theta_{OH} > 0.1$, $2.35 \geq \alpha_{OH} > 0.40$ OH nm^{-2});
- there are only isolated single (free) and geminal (free) OH groups on the surface;
- the concentration of isolated single and geminal OH groups decreases, respectively, in ranges: $2.05 \geq \alpha_{OH,I} > 0.40$ and $0.30 \geq \alpha_{OH,G} \geq 0.0$ OH nm^{-2};
- at temperatures close to about 800–900°C the silica surface becomes free of geminal OH groups;
- the internal OH groups disappear completely from the silica skeleton;
- the concentration of siloxane bridges increases considerably (Figs. 14 and 16), and whole areas on the silica surface become covered by SiOSi groups;
- with a decrease in the concentration of OH groups, α_{OH}, the activation energy of dehydroxylation, E_D, sharply increases from 25 to 50 kcal mol^{-1} (and probably higher);

- there are the shrinkage and sintering of the SiO_2 matrix;
- in the subregion IIb the restoration of the hydroxyl coverage is determined by the mechanism of the slow, strongly activated chemisiorption of water ($E_A > 0$).

3.4.8. Transition from stage 4 to stage 5 (Fig. 21)

- the fourth threshold temperature ($T_4 \approx 900°C$);
- there is a complete removal of surface geminal silanols and internal OH groups, while isolated single silanols remain still on the surface;
- at room temperature the process is hardly reversible upon the introduction of an excess of water, and it takes a very long time for the reverse process to be completed; but at 100°C this process becomes reversible and it proceeds quite rapidly.

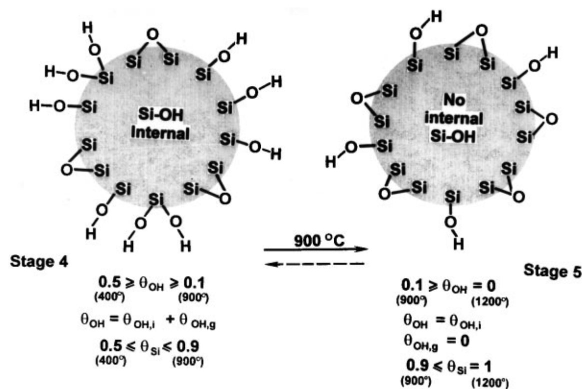


Fig. 21. Transition from stage 4 to 5 ($T_4 \approx 900°C$, see text).

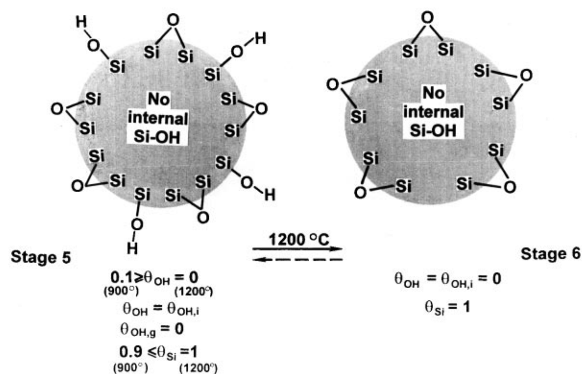


Fig. 22. Transition from stage 5 to 6 ($T_5 \approx 1200°C$, see text).

3.4.9. Stage 5 (900–1200°C, the subregion IIb)

- the degree of surface coverage and the concentration of isolated single (free) OH groups continue to decrease till the entire disappearance of these silanols ($0.1 \geq \theta_{OH,I} \geq 0.0$, $0.40 \geq \alpha_{OH,I} \geq 0.0$ OH nm^{-2});
- the degree of surface coverage and the concentration of siloxane bridges continue to increase till the entire silica surface is covered by these SiOSi groups and Si atoms ($0.9 \leq \theta_{Si} \leq 1.0$, $4.20 \leq \alpha_{Si} \leq 4.60$ Si nm^{-2});
- the shrinkage and sintering of the SiO_2 matrix continue;
- as in stage 4, the activation energy of dehydroxylation, E_D, continues to increase, and the restoration of the hydroxylated coverage is determined by the mechanism of the slow, strongly activated chemisorption of water ($E_A > 0$).

3.4.10. Transition from stage 5 to stage 6 (Fig. 22)

- the fifth threshold temperature ($T_5 \approx 1200°C$);
- complete removal of all OH groups from the silica surface;
- complete coverage of the SiO_2 surface with SiOSi groups.

3.4.11. Stage 6, the final stage (≥ 1200°C, the subregion IIb)

- the silica surface consists of siloxane bridges only ($\theta_{Si} = 1$, $\alpha_{Si} = 4.60$ Si nm^{-2}).

4. Conclusions

The results of our experimental and theoretical studies, together with the data published in literature, permitted to construct the model for describing the surface chemistry of amorphous silica [301–303,332,334,336–338].

It has been shown that in any description of the surface of amorphous silica the hydroxylation of the surface is of critical importance. There is a difference between the surface hydroxyl (silanol)

groups and other types of bound water such as physically adsorbed water and hydroxyl groups inside the silica skeleton and the very narrow ultramicropores. An analysis was made of the processes of dehydration (the removal of physically adsorbed water), dehydroxylation (the removal of silanol groups from the silica surface), and rehydroxylation (the restoration of the hydroxylated covering). The probable mechanisms for explaining the observed processes are described.

The main advantage of our physico-chemical model (model-1, model-2) lies in the possibility of determination the concentration and the distribution of different types of silanol and siloxane groups on the silica surface as a function of the pretreatment temperature of SiO_2 samples, and in the possibility assessing of OH groups inside the silica particles. This model also makes it possible to characterize the energetic heterogeneity of the silica surface and to determine the kind of the chemisorption of water (rapid, weakly activated or slow, strongly activated) under the restoration of the hydroxyl coverage, within a wide temperature interval of thermal treatment in vacuo.

On the basis of the surface concentration of silanol groups we have established that adsorbtion and other surface properties per unit surface area of silica are identical (except for very fine pores).

The high value of the correlation coefficient ($\rho = 0.99$) of the linear regression equation between the surface concentration of OH groups per unit mass of the SiO_2 sample, $\delta^{(S)}_{OH}$, and the specific surface area of the SiO_2 sample, S_{Kr}, i.e. between numbers of two independent each from other physical magnitudes, changing within very wide ranges, confirms that the BET method is the correct method and gives the opportunity to measure the real physical size of the specific surface area for dispersed silicas (and other oxide dispersed solids).

Based on data reported in literature, our model of the amorphous silica surface is today the most advanced model. It has been found useful in solving various applied and theoretical problems in the field of adsorption, catalysis, chromatography, chemical modification, etc.

The regularities established for the amorphous silica surface in the proposed model can be applied to other, more complex silica containing systems and related materials (silicates) as well to various solid oxide substances containing OH groups on their surface.

In the future, for a more detailed analysis of the chemical properties of the silica surface it is necessary to take into account the presence on the silica surface of the following: other possible functional groups and active sites, radicals, structural defects, impurities, etc.

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