

Structurally bound water and surface characterization of amorphous silica

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Abstract - The dehydration and the dehydroxylation of the surface of amorphous silica have been investigated by using the mass spectrometric thermal analysis method with the employment of temperature-programmed desorption.

INTRODUCTION

As has been noted by Rebinder: "...the interaction of water with different substances is of great scientific interest" (1). Among various systems a special place is occupied by the silica-water system, which consists of two most abundant substances in nature (2).

The study of the so-called structurally or chemically bound water (1) in amorphous silica is of paramount importance for understanding the behavior of this system. Structurally bound water is chemisorbed water, i.e., valent bound with the surface of SiO₂ hydroxyl (silanol) groups ≡Si-OH (2). Information about the concentration of hydroxyl groups and the energetic nonuniformity of the silica surface are of importance for solving various scientific and practical problems.

In addition to the layer of OH groups account should be taken of the presence of physically adsorbed water on the surface and the presence inside silica particles of structurally bound water (OH groups inside the SiO₂ skeleton and inside the thinnest ultramicropores whose diameter is comparable to that of a water molecule).

Previously we have investigated the concentration of hydroxyl groups on the surface of amorphous silicas (3). By the deuterio-exchange method, the concentration of hydroxyl groups (the silanol number), α_{OH} , has been estimated on the fully hydroxylated surfaces of different samples of amorphous silica (silica gels, aerosilogels, porous glasses). The silanol number α_{OH} is about 5.0 OH groups nm⁻², independent of the origin and structural characteristics (specific surface area, type of the pores, size distribution of the pores, particle packing density, structure of SiO₂ skeleton). The α_{OH} value is considered as a physicochemical constant. A silanol group ≡SiOH (one OH group per one surface Si atom) is the most probable compound on the fully hydroxylated surface of amorphous silica. The deuterio-exchange method was used for measuring the silanol number of different samples of amorphous silica, depending on the temperature of vacuum treatment. The values of α_{OH} at a certain temperature of vacuum treatment are close for all samples under study and lowering of the concentration of hydroxyl groups on the surfaces of different silicas under similar conditions of the heat treatment also proceeds similarly (3).

In addition we have investigated structurally bound water inside silica particles for different types of amorphous silica (4-6). It has been shown that the distribution of OH groups between the surface and bulk depends on the processes of silica preparation and treatment (5).

In the present work the dehydration (removal of physically adsorbed water) and dehydroxylation (removal of the surface OH groups) have been investigated by using the mass spectrometric thermal analysis method with the employment of temperature-programmed desorption (7, 8).

EXPERIMENTAL SECTION

The object of investigation: amorphous silica

In order to investigate the dehydration and dehydroxylation of an amorphous silica surface free of any side effects it had been necessary to prepare SiO₂ sample that would meet the following requirements: (a) The

surface of the starting sample must be completely hydroxylated. (b) The diameter of the pores must be much larger than the dimension of the water molecule. This is necessary in order to suppress to a maximum extent the effect of diffusive retardation and the effect of readorption. (c) There must be no structurally bound water inside the silica particles. This is necessary in order to suppress the side effect due to evolution of water from the bulk of silica sample at elevated temperatures. (d) The silica sample must be sufficiently pure (free of admixtures on the surface and inside the sample).

The most suitable type of SiO_2 which meets the above-stated requirements is aerosilogel, an amorphous silica with uniform large pores (9). The sample was prepared from water suspension of pure pyrogenic silica, aerosil. The pores of the sample were distributed according to their diameter within a narrow range with a maximum at 51 nm. The specific surface area of the sample was $S=79 \text{ m}^2/\text{g}$ as determined by the BET method from low-temperature adsorption of Kr (the area covered by one krypton molecule $W_{m,Kr}=21.5 \text{ \AA}^2$ (10)).

Method of mass spectrometric thermal analysis using temperature-programmed desorption (the MTA-TPD method)

The author worked out the version of the MTA-TPD method for the investigation of the removal process of molecularly adsorbed water and hydroxyl groups from the surface of amorphous silica (7, 8). The equipment consisted of a mass spectrometer MAT-311A made by the Varian Co. The setup also included a pyrolytic attachment (designed by the Institute of Physical Chemistry) which consisted of the following: (a) A connector unit and a pyrolysis chamber. (b) A programmed temperature regulator. (c) An electronic unit for plotting time marks (to establish a precise correspondence between each mass spectrum of the gaseous products evolved and the sample temperature).

At low rates of heating the temperature of the little crucible containing the sample, which varied with time, was measured with a precision of $\pm 1.5^\circ\text{C}$. The Chromel-Alumel thermocouple simultaneously served as a holder for the little crucible.

By using the MTA-TPD method under a dynamic regime in vacuo the following conditions were fulfilled: (a) Small ($< 10 \text{ mg}$) weighed allotment of the sample. (b) Precise determination of the sample's temperature, which varies linearly with time from 25 to 1000°C . (c) A rapid and complete mass transfer of gaseous products from the sample surface to the ion source of the mass spectrometer.

Various methods were used for analyzing of the obtained mass thermograms (or the differential thermal curves): the method of Kissinger (11), the difference-differential method of Freeman and Carroll (12), and others (13-15). These methods made it possible to estimate the kinetic parameters of thermodesorption. The processing of data and calculation of kinetic parameters were carried out with the aid of a computer according to the corresponding programs.

RESULTS AND DISCUSSION

In Fig. 1 is shown a series of the individual, reduced mass thermograms of water. They have been recorded at the same linear rate of heating ($\beta = 5.8 \text{ deg/min}$). Curves 1-17 (Table 1) correspond to silica samples that were subjected to a treatment in vacuo under different conditions before measurements were carried out by the MTA-TPD method.

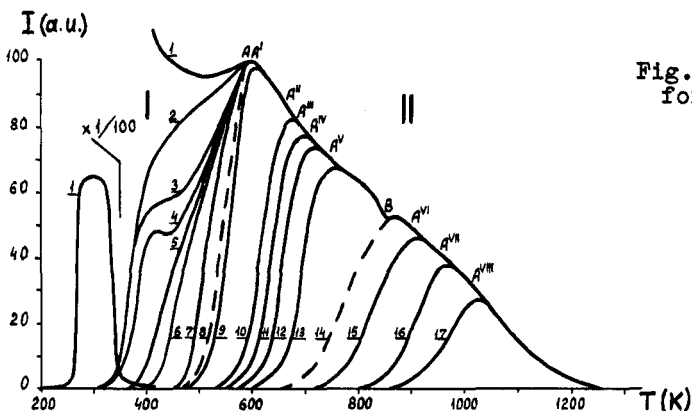


Fig. 1. Mass thermograms of water for the silica sample:

T - temperature (K);
I - normalized intensity of the peak due to water ion, $m/Z=18$ (arbitrary units);
A - maximum of kinetic curves 1-8;
 A^I - maxima of kinetic curves 9-13 and 15-17 ($i = I, II, \dots, VIII$);
8 and 14 - boundary curves.

Table 1. Conditions for treatment in vacuo of amorphous silica prior to its investigation by the MTA-TPD method, and the temperature corresponding to the maximum of the differential mass thermogram (at $\beta = 5.8$ deg/min)

Thermo-gram No.	Conditions for pretreatment in vacuo	Temperature (K)
1	Suspension of SiO ₂ in an excess of water frozen at -196°C; evacuation for 1 hr at -196°C; gradual warming up from -196 to 0°C; 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 hrs 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 hrs at 25°C	600
4	Ditto, with evacuation for 306 hrs at 25°C	600
5	Ditto, with evacuation for 14 hrs at 107°C	600
6	Ditto, with evacuation for 2 hrs at 136°C	600
7	Ditto, with evacuation for 1 hr at 169°C	600
8	Dotted line (curve 8) - calculated data (cf. text)	(600)
9	Loading of the wet sample; evacuation for 14 hrs 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 hrs at 240°C	688
11	Ditto, with evacuation for 12 hrs at 276°C	711
12	Ditto, with evacuation for 14 hrs at 286°C	718
13	Ditto, with evacuation for 16 hrs at 335°C	769
14	Dotted line (curve 14) - calculated data (cf. text)	(875)
15	Loading of the wet sample; evacuation for 13 hrs 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 hrs at 495°C	972
17	Ditto, with evacuation for 14 hrs at 588°C	1037

An important experimental fact was established: the maxima of all thermal curves 1-7 occurred at the same temperature T_A (point A in Fig.1). It is to be noted that for curves 1-7, which differ from one another with respect to conditions of pretreatment, the temperature of such a treatment did not exceed 200°C (Table 1). If the pretreatment of a silica sample was carried out at temperature above 200°C, then the maxima of the individual thermograms were shifted into the region of temperatures higher than T_A (to the right of point A). Such a shift is the greater, the higher the temperature of the pretreatment (curves 9-17).

Boundary curves 8 and 14 were not recorded experimentally. Curve 8 was plotted by interpolation with account taken of the shape of the neighboring thermograms 7 and 9. Curve 14 with a maximum in the region of the characteristic point B (a dip in the decreasing section of ABC thermograms, Fig.1) was plotted by extrapolation with account taken of the shape of the neighboring thermogram 15.

It is reasonable to assume that the region to the left of the dotted curve 8 (Fig.1), which represents a multitude of ascending branches of mass thermograms, each passing through the same common point A, corresponds to the state of silica when in addition to hydroxyl surface coverage there is physical adsorption of water. The removal of such physically adsorbed water at different initial values of the silica surface coverage (with molecularly adsorbed water, curves 1-7) has no effect whatsoever on the position of point A. This means that the characteristic point A, which represents the maximal rate of thermal desorption of water from the silica surface, indicates dehydroxylation and not dehydration of the surface.

To determine the kinetic parameters characterizing the dehydration we used graphic plotting of the subtractive thermokinetic curves. In so doing we assumed that for each subtractive curve the kinetic parameters remain constant within a relatively narrow temperature range, and therefore, the subtractive curve can be treated according to the method of Freeman and Carroll (12).

In Fig.2 as an example is shown the total mass thermogram 9 (in the form as it was recorded on the chart of an electronic potentiometer). It represents a complete spectrum of hydroxyl groups that have been removed from the SiO₂ surface in the course of thermodesorption. In its external appearance this kinetic curve resembles the differential thermokinetic curve obtained by Young (16). It demonstrates by its strongly asymmetrical form the energetically nonuniform surface of SiO₂. The energetic nonuniformity of an amorphous silica surface covered with silanol groups has been pointed out by

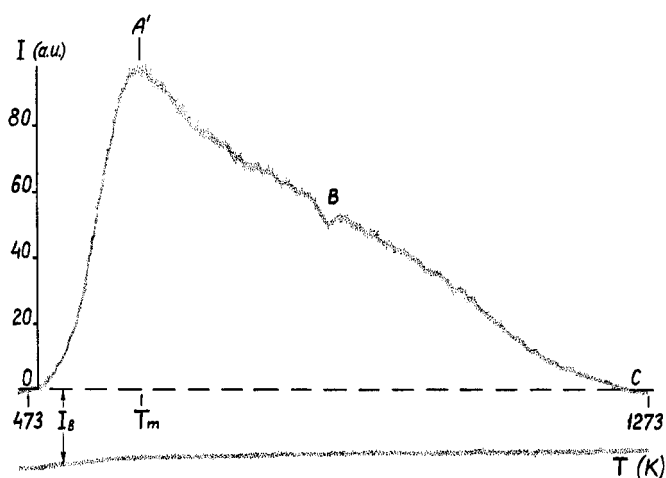


Fig.2. Total mass thermogram 9 (cf., Fig.1): I_b - background intensity; T_m - the characteristic point (temperature, K) corresponding to the maximal rate of desorption; A' - maximum of the differential curve; B - dip on the descending branch $A'BC$.

Baikova, et al. (17). It should be noted that as in the case of thermogram 9 (Fig.2), as well as of others registered kinetic curves, the descending branch has a characteristic dip B . This dip marks the division between the different types of silanol groups that are present on the silica surface.

Dehydration

We shall consider the dehydration region I (Fig.1) which is separated on the right by an ascending branch of the boundary curve 8. Curve 1 reflects the behavior of a thermogram for a silica sample introduced into a pyrolyzer in the form of a suspension of SiO_2 in the presence of a large excess of liquid water (Table 1). It can be seen that within the 270-350 K temperature range an extraordinarily large increase in the intensity is registered. The observed effect is directly related to the evaporation of the excess of the liquid phase of water (free water) which was in suspension, and is not yet due to the removal of adsorbed water. Upon a further increase in temperature the thermogram 1 passes through a second, a weaker, but clearly defined maximum - through a characteristic point A (Fig.1).

Mass thermograms 2-8 (ascending branches) open the possibility of investigating the removal of molecularly adsorbed water monolayer from the silica surface. Curves 2-4 belong to samples treated in vacuo at room temperature, with the period of treatment increasing for each curve, respectively. Curve 5 belongs to the sample that has been activated already at ca. 100°C (Table 1). It can be seen that in this subregion between curves 2 and 5 the initial section of the thermogram decreases, and there appears a weak maximum (curves 3 and 4) at ca. 400-420 K. For the next subregion between curves 5 and 8 the ascending branches pass through the same common point A . With an increase in the temperature of pretreatment from 100 to 200°C the ascending section becomes steeper in the shape.

The results given in Table 2 (8) indicate that the activation energy of desorption, E_d , increases approximately from 6 to 10 kcal/mole with a decrease in the surface coverage of silica with physically adsorbed water. Here, the experimentally obtained first order of reaction (column 2) accords with the reported data (18).

On the basis of the ratio of areas (Fig.1) we can conclude that under the experimental conditions employed the amount of physically adsorbed water (the limited area between the ascending branches 2 and 8) is less than one 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 2), is removed in vacuo at room temperature. However, a small amount of physically adsorbed water, within the limits of a monolayer, is retained on the hydroxylated surface of silica up to ca. 200°C.

As noted above, we can identify on the basis of the shape of the thermograms two subregions, which correspond to the presence on the surface of two types of physically adsorbed water. It accords with our data obtained by the method of molecular dynamics (19). The activation energy of desorption for these two types of adsorbed water lies approximately in the ranges: $E_d = 6-7$ and $E_d = 9-10$ kcal/mole (Table 2).

An increase in E_d with a decrease in surface coverage by adsorbed water is close to the observed changes in pure differential heat of adsorption of water vapor ($Q_a - L$), where, Q_a - differential heat of adsorption and L - heat of condensation at low surface coverage of hydroxylated silica by adsorbed water, as it has been obtained by Kiselev, et al.(20).

Table 2. Dehydration. Determination of kinetic parameters by the method of Freeman and Carroll (12)

Subtractive thermokinetic curve i/j *	Reaction order n	Activation energy of desorption E_d		Pre-exponential factor Z (min^{-1})
		(kcal/mole)	(kJ/mole)	
2/3	0.85	6.2	25.9	$0.5 \cdot 10^2$
2/5	1.25	7.3	30.6	$7.5 \cdot 10^2$
2/6	1.34	7.3	30.7	$4.9 \cdot 10^2$
3/6	0.97	6.4	26.9	$2.3 \cdot 10^2$
5/8	0.85	8.9	37.1	$5.3 \cdot 10^2$
6/8	0.84	9.4	39.3	$9.0 \cdot 10^2$
6/9	0.91	10.4	44.2	$2.8 \cdot 10^3$

* 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.1).

Table 3. Rate of heating of a SiO_2 sample and the temperature corresponding to the maximum (point A)

β (deg/min)	5.8	12.3	25.0
T_A (K) (average of several determinations)	599.8	630.9	659.0

Table 4. Kinetic parameters determined for thermodesorption processes on the basis of the shape of the ascending branches of the boundary thermogram 8 and the thermogram 9 (between regions I and II, Fig.1)

Thermokinetic curve	Reaction order n	Activation energy E_d		Pre-exponential factor Z (min^{-1})	Method (Ref.)
		(kcal/mole)	(kJ/mole)		
8	2.00	16.5	69.1	$1.4 \cdot 10^5$	11, 15
Ditto	(2.0)*	17.0	71.1	$2.1 \cdot 10^5$	13-15
9	1.70	18.8	78.6	$5.8 \cdot 10^5$	13, 14
Ditto	(2.0)*	19.2	80.6	$8.7 \cdot 10^5$	13-15

* In parentheses the reaction order $n=2$ is assumed to be known.

Temperature boundary of dehydration

Next we shall consider the ascending branch of the boundary thermogram 8, as well as thermogram 9 which is located nearby (Fig.1). To determine E_d in the vicinity of point A we shall use the nonisothermal method (11, 13). In Table 3 are summarized the experimentally obtained positions of point A at different linear rates of heating of the silica sample. The graphic representation of the linear dependence of the difference ($2\log T_A - \log \beta$) on the inverse temperature at the maximum, $1/T_A$, enables us to obtain the activation energy of desorption, E_d , which was 16.5 kcal/mole.

To determine the order of the reaction, n (at a known energy, E_d), we used the method proposed by Smolyaninov, et al. (15). The reaction order, obtained by us, is $n=2$ (Table 4). In the Table 4 are also shown the kinetic parameters for curves 8 and 9, obtained by the known methods (13-15).

A correct interpolation made it possible (on the basis of the data for thermograms 7 and 9, Fig.1) to determine the temperature of the pre-treatment of a SiO_2 sample in the case where the ascending branch of a kinetic curve must exactly follow along the boundary thermogram 8. This threshold temperature, which corresponds to the final temperature of dehydration and to the initial temperature of dehydroxylation, was found to be $T_b = 190 \pm 10^\circ\text{C}$ (8). Previously, by using the thermogravimetric method and mass spectrometric analysis in experiments with large-pore silica gel (21) and by using the method of derivatography (22), we have found that physically adsorbed water is removed from the surface of silica when the samples are heated in vacuo from room temperature to 200°C .

Thus, in the present work (8) it is shown that at temperature T_b (for amorphous silica that has been subjected beforehand to activation in vacuo at 190°C) abrupt changes have been observed in the activation energy of desorption, E_d (and therefore also of a series of other thermodynamic functions); in the kinetic order of the limiting stage of the thermodesorption, n ; and in the pre-exponential factor Z (cf. Table 2 and Table 4).

Dehydroxylation

Now we shall consider region II which is limited on the left by the ascending branch of thermogram 8 (Fig.1). In Table 5 are summarized the kinetic parameters for different thermograms forming region II. Curves 15-17 were processed according to the above-mentioned method of Freeman and Carroll (12). However, thermograms 10-13, which resemble the thermogram 9 (Figs 1 and 2) with its sharply defined asymmetry, cannot be processed by this method. Therefore, by considering that region II corresponds to differential kinetic curves with reaction order $n=2$ (Tables 4 and 5, Fig.3), we determined the kinetic parameters, E_d and Z , for the thermograms 10-13 on the basis of the characteristic points T_m and $T_{0.5m}$ according to the methods (13-15).

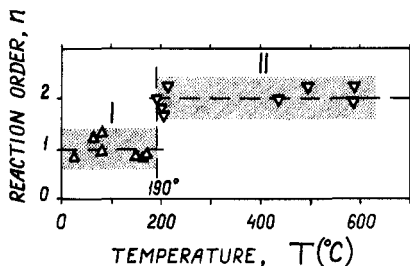


Fig.3. The order of the water thermodesorption reaction, n , as a function of the temperature, T ($^{\circ}\text{C}$), used in pretreatment of silica in vacuo (Tables 1, 2, 4 and 5).

Table 5. Dehydroxylation. Determination of kinetic parameters

Thermo-kinetic curve	Reaction order n^*	Activation energy (kcal/mole)	E_d (kJ/mole)	Pre-exponential factor Z (min^{-1})	Method (Ref.)
10	(2.0)	20.9	87.3	$5.5 \cdot 10^5$	13-15
11	(2.0)	21.1	88.5	$3.8 \cdot 10^5$	13-15
12	(2.0)	22.7	94.9	$1.0 \cdot 10^6$	13-15
13	(2.0)	24.2	101.4	$9.3 \cdot 10^5$	13-15
15	2.00	25.0	104.7	$8.1 \cdot 10^4$	12
Ditto	(2.0)	27.9	116.9	$4.5 \cdot 10^5$	13-15
16	2.27	37.7	158.0	$3.6 \cdot 10^7$	12
Ditto	(2.0)	44.8	187.4	$1.6 \cdot 10^9$	13-15
17	1.97	49.1	205.4	$2.9 \cdot 10^9$	12
Ditto	2.26	50.3	210.7	$5.6 \cdot 10^9$	13, 14
Ditto	(2.0)	49.6	207.6	$3.9 \cdot 10^9$	13-15

* In parentheses the reaction order $n=2$ is assumed to be known.

In Fig.3. are shown also two experimental points for region II. They were obtained at a lower heating rate ($\beta=2.9$ deg/min). The samples were subjected to pre-treatment in vacuo: one sample for 12 hrs at 201°C ($n=1.84$), and the other - for 14 hrs at 213°C ($n=2.32$)

As can be seen from data in Fig.4, the temperature dependence of the activation energy, E_d , in region II is characterized by two approximately rectilinear sections: in the range from 200 to 400-450 $^{\circ}\text{C}$ (subregions IIa and IIb) and above 400-450 $^{\circ}\text{C}$ (subregion IIc). These sections show a notably increasing inclination angle relative to the temperature axis when going from the first to the second section. This abrupt change in terms of temperature approximately corresponds to the beginning of the ascending branch of the boundary curve 14 which has a maximum near the characteristic B point (Fig.1).

The deuterio-exchange method with mass spectrometric analysis was used for measuring the concentration of hydroxyl groups (the silanol number), α_{OH} , of different samples of amorphous silica, depending on the temperature of vacuum treatment (see Table 1, Ref.3). It has been noted that there is a rapid decrease in α_{OH} with an increase in temperature from 200 to 400-500 $^{\circ}\text{C}$. At higher temperatures the rate of decrease in α_{OH} slows down (3). Thus, the temperature dependences shown for E_d (Fig.4) and for α_{OH} (Table 1, Ref.3) in the form of two linear sections with different slopes accord well with one another.

Spectroscopic investigations (23) show that a rapid decrease in the value of α_{OH} at 200-500 $^{\circ}\text{C}$ is due to the relative ease of removing the hydroxyl groups bound via a mutual hydrogen bond. Then, at a temperature above 400-500 $^{\circ}\text{C}$, dehydroxylation is slowed down owing to an increase in the average distance between the neighboring free hydroxyl groups on the silica surface.

A knowledge of the temperature dependences of the activation energy, E_d (in region II, Fig.4), and of the silanol number, α_{OH} (Table 1, Ref.3), make it possible to obtain the activation energy, E_d , of the dehydroxylation process as a function of the concentration of the silanol surface groups, α_{OH} , or as a function of the surface coverage with such groups, θ , as it is shown in Fig.5 (8).

The 2nd reaction order (Tables 4 and 5, Fig.3) observed for the entire region II directly confirms the associative desorption of the surface silanol groups due to the interaction between these groups (or the condensation reaction of such OH groups), which is accompanied by the formation of siloxane bonds and molecular water:



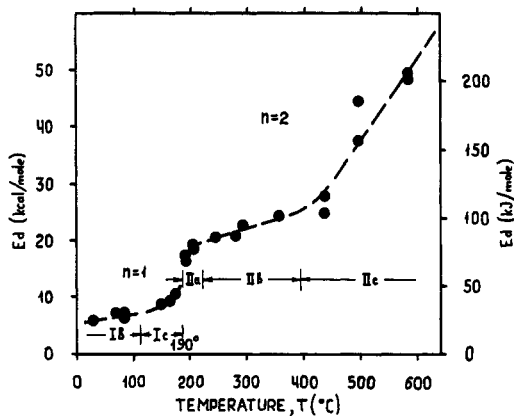


Fig. 4. Activation energy of water desorption, E_d , as a function of the temperature, T ($^{\circ}\text{C}$), used in pretreatment of silica in vacuo (Tables 1, 2, 4 and 5). Ia, Ib, Ic - subregions of region I; IIa, IIb, IIc - subregions of region II (see also text).

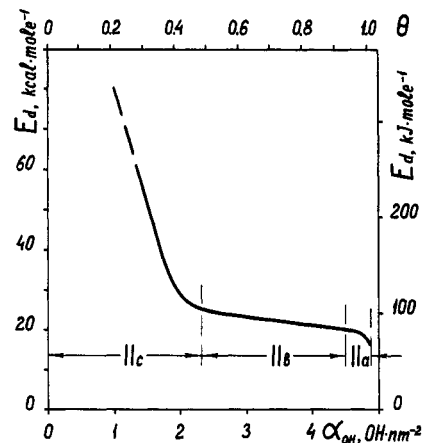


Fig. 5. Activation energy of water desorption, E_d (in region II), as a function of the surface concentration of OH groups, α_{OH} , or as a function of the surface coverage of SiO_2 with OH groups, θ .

Thus, the condensation reaction (1) is characteristic of all three subregions, IIa, IIb, and IIc, inspite of the fact that the activation energy, E_d , differs considerably (Fig. 5).

We shall consider the interval of a high degree of surface coverage with OH groups, $1 \geq \theta > 0.5$, which corresponds to subregions IIa and IIb (Fig. 5). This interval is characterized by a linear energetic nonuniformity of the surface which is defined by an empirical relationship:

$$E_d = 31.4 - 12.3 \cdot \theta \quad (2)$$

where, E_d - activation energy of desorption at an approximate range from 19 to 25 kcal/mole (the values E_d for the initial nonlinear section IIa are from 16.5 to 19 kcal/mole). This range of activation energy is not so great and is determined by a set of perturbations due to hydrogen-bonded OH groups. Thus, characteristic of subregions IIa and IIb is the presence of lateral interactions (of hydrogen bonds) between the neighboring OH groups.

Now we shall analyze the silica surface at low coverage with hydroxyl groups, $\theta < 0.5$, which corresponds to subregion IIc (Fig. 5). In this case the main role is played by free hydroxyl groups and siloxane bridges. This subregion is characterized by a strong concentrational dependence of E_d , i.e., by a considerable increase in the desorption activation energy in the range ca. from 25 to 50 kcal/mole (and probably greater) with a decrease in the surface coverage with OH groups. Under conditions where only free OH groups surrounded by siloxane areas exist these areas can cover a large area after a high-temperature treatment of the sample. In this case the main mechanism of OH groups transfer via the condensation eq.1 is due to the disordered migration of protons along the surface (the process of activated diffusion of OH groups). As a result of this migration water is evolved at the final stage owing to the paired reaction of two OH groups which encounter each other by chance (on approaching each other at a distance of about 0.3 nm). We still do not have a detailed picture of the mechanism describing the migration of protons. It probably involves a reaction of protons with oxygen atoms of strained siloxane bridges resulting in the formation of new surface OH groups that are shifted relative to the starting groups. In other words, this mechanism can be represented as a "jump" between the neighboring siloxane bridges. Thus, at a low surface coverage with hydroxyl groups the diffusion of protons along the surface will limit the condensation eq.1.

CONCLUSIONS

An investigation of the dehydration and dehydroxylation of an amorphous silica surface was carried out by the MTA-TFD method. An analysis of the thermograms makes it possible to draw the following conclusions.

Firstly, the obtained 1st order of the thermodesorption reaction, $n=1$, lies below 190°C (the temperature of a preliminary treatment of silica). This indicates that desorption in this temperature range proceeds via

a monomolecular reaction. In this case only a direct breaking off of water molecules from the silica surface takes place without their mutual interaction. Two forms of molecularly adsorbed water were established.

Second, at the temperature of pretreatment $190 \pm 10^\circ\text{C}$ a sharp change occurs in the order of the reaction, n , the activation energy, E_d , and the pre-exponential factor, Z . This means that physically adsorbed water is practically completely removed by such a treatment.

Third, the obtained 2nd order of the reaction in the range exceeding 190°C indicates that the thermal desorption of water proceeds owing to the interaction between the surface silanol groups (the condensation reaction), which results in the formation of siloxane bonds. We have established the relationship between the activation energy of dehydroxylation, E_d , and the concentration of the surface silanol groups, α_{OH} , or the surface coverage of SiO_2 with OH groups, θ . At $1 \gg \theta > 0.5$ the values E_d are changed from 16.5 to 25 kcal/mole. This interval is characterized by a linear energetic nonuniformity of the surface. There is the presence of lateral interactions (of hydrogen bonds) between the neighboring OH groups in this range. A considerable increase in E_d in subregion at $\theta < 0.5$ is due to the fact that for the condensation reaction to take place the protons must migrate along the surface, with the evolution of water at the final stage of the process as a result of a paired interaction of OH groups that form the hydrogen bonds.

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