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Fig. 1. Adsorption isotherms of water on the surface of α-quartz obtained by crushing in vacuum. a —first adsorption, b —repeated adsorption, v —desorption. I—II —15 h; III—IV —17 h; V—VI —45 h.

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Abstract

Full Text

Physical Chemistry

S. P. Zhdanov

Adsorption of Water on Quartz Crushed in Vacuum

(Presented by Academician M. M. Dubinin on 21 III 1957)

It is known that under ordinary conditions the surface of silica particles, in both its crystalline and amorphous states, is hydrated and bears OH groups valently bound to surface silicon atoms. Consequently, in studying adsorption on SiO_2 one always has to deal with a surface hydrated to one degree or another. More or less complete dehydration of the surface can be achieved only by calcination at high temperatures, about 1100-1200°. However, with such treatment, together with removal of residual hydroxyls, there may occur not only a substantial rearrangement of the structure of the surface layer (in the case of nonporous SiO_2 powders), but also complete disappearance of the entire developed internal surface (in the case of silica gels and porous glasses).

Studies of the adsorption of water on silica gel and porous glasses show that the magnitude of adsorption at low vapor pressures depends very substantially on the degree of hydration of the surface. In the dehydrated state, obtained by calcination in vacuum at 600-650°, the surface of amorphous silica proves to be only slightly active with respect to water vapor and adsorbs the latter very weakly at low values of P/P_s (^{1}). It is of interest to obtain a SiO_2 surface devoid of hydroxyls without the use of thermal treatment at high temperatures, and to compare the adsorption properties of such a surface with those of a surface dehydrated by calcination. Studies in this direction could provide some information concerning the structure of the silica surface in its different states.

Fig. 1. Isotherms of adsorption of water on the surface of α-quartz obtained by crushing in vacuum. *a* —first adsorption, *b* —repeated adsorption, *v* —desorption. I—II —15 h; III—IV —17 h; V—VI —45 h.

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Figure 2

Figure 2: Figure 2

One of the possible ways of obtaining a SiO_2 surface free from hydroxyls, without requiring calcination, is crushing in vacuum. Under these conditions, not only hydration by atmospheric moisture is excluded, but also the action of atmospheric gases on the freshly formed surface. In the present work, results are reported for a study of the adsorption of water on a powder of low-temperature α-quartz obtained by crushing crystals of rock crystal in vacuum, and the adsorption properties of SiO_2 surfaces obtained under different conditions with respect to water vapor are also compared.

The crushing of rock crystal was carried out by means of a solenoid in an agate mortar placed in a sealed glass cylinder, connected to a mercury diffusion pump through a trap cooled with liquid nitrogen, which prevented vapors of vacuum grease and mercury from reaching the freshly formed quartz surface. Pumping was continued throughout the entire crushing period, up to the sealing-off of the cylinder with the mortar. After sealing-off, the quartz powder was transferred from the mortar (under vacuum) into a special ampoule, which was sealed off from the cylinder and sealed onto the adsorption apparatus. With the aid of a small steel rod and a solenoid, the glass diaphragm was broken and the contents of the ampoule were brought into communication with the measuring part of the apparatus, evacuated to high vacuum.

Adsorption was measured by the volumetric method at a temperature of 18°. The total surface area of the powder was determined from the adsorption isotherm of argon at a temperature of $-195.6°$ and from methyl alcohol at a temperature of 18°. In both cases close values were obtained: 16.0 m^2 from argon (ω_0 was taken as 15.5 $Å^2$) and 15.5 m^2 from methanol ($\omega_0 = 23.7$ $Å^2$). Measurements of the adsorption of Ar and CH_3OH were made after the experiments on water adsorption.

Figure 1 gives the isotherms of the first and repeated adsorption and desorption of water, obtained on α-quartz crushed in vacuum. The isotherm of the first adsorption has a not entirely usual form, with characteristic steps that appear upon prolonged holding of the adsorbent in contact with water vapor at the given pressure*. The appearance of such steps indicates that, in addition to purely physical adsorption with rapidly established equilibrium, a slow absorption process also takes place, evidently connected with a chemical reaction between water and the surface of silica. This interaction should lead to hydration of the surface, i.e., should be accompanied by irreversible absorption of water, which is confirmed by the position of the desorption branch of the isotherm, which lies considerably above the adsorption branch.

Fig. 2. Initial portions of the isotherms of water adsorption on the surface of SiO_2 obtained under different conditions. 1 —α-quartz with a hydrated surface:

a –first adsorption, *b* –repeated adsorption; 2 –silica gel dehydrated by heating in vacuum at 650°; 3 –porous glass dehydrated in vacuum at 600°; 4 and 5 – α-quartz crushed in vacuum

The repeated isotherm already has a more usual form and is characterized only by insignificant hysteresis. The presence of the latter indicates, however, the continuing chemical interaction of water with the surface of α-quartz. Hydration of the quartz surface was not completely finished, although the total time during which the adsorbent remained in an atmosphere of water vapor exceeded 17 days (the time elapsed between the beginning of the first and the repeated adsorption experiment). At the same time, the closeness of this isotherm to the isotherm of water adsorption on α-quartz with a hydrated surface (see Fig. 2) indicates that, before the start of the repeated adsorption experiment, the surface obtained by crushing in vacuum had in practice already been almost completely hydrated.

* The duration of holding is indicated in Fig. 1.

In Fig. 2 the initial portions of the isotherms of water adsorption on silica surfaces obtained under different conditions are compared. Quartz with a maximally hydrated surface was obtained by prolonged treatment of rock-crystal powder with water at a temperature of about 100°. Thermal dehydration of the SiO_2 surface was carried out by calcination in vacuum at 600–650°. The isotherms shown in Fig. 2 refer to previously studied samples of porous glass and silica gel ([1],[2]). Under such calcination conditions, as may be concluded from the water losses, only about 15% of the amount of hydroxyl groups present on the surface in the state of its maximum hydration remains per unit surface area. The adsorption values in all cases have been calculated per unit surface area, and the curves of Fig. 2 describe properties of the adsorbents that depend only on the state and properties of their surface, and not on the magnitude of the specific surface area.

The sharp differences in the properties of the SiO_2 surface obtained by calcination and by grinding in vacuum attract attention. The hydroxyl-free SiO_2 surface formed by grinding in vacuum proves to be considerably more active with respect to water vapor than the surface dehydrated by calcination. These differences cannot be explained by the presence of residual hydroxyls on the surface dehydrated by calcination. They are evidently due to other features of the structure of the silica surfaces obtained under vacuum conditions by grinding and by calcination. The state of the silica surface dehydrated by calcination has been discussed in works ([1]-[4],[7]).

It seems to us that the liberation of water during calcination at the expense of surface OH groups must, ultimately, lead to the formation on the surface of electrostatically and valence-saturated silicon–oxygen groups of two types

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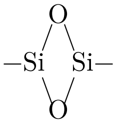
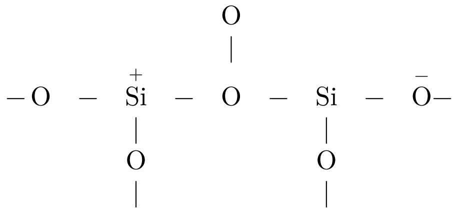


or $> \mathrm{Si} = \mathrm{O}$

depending on whether the water molecule is formed from hydroxyls belonging to two silicon atoms or to only one. The formation of charges on the surface during thermal dehydration of a hydrated surface (silica gels, porous glasses), as assumed in work (^{3}), is unlikely (^{2},^{4}). In this case water is apparently liberated not by rupture, but by redistribution of bonds, ensuring the electrical neutrality of the surface and compensation of valences, which is facilitated under heating conditions.

When α-quartz is ground in vacuum, the state of the newly formed surface will depend on the direction of the fracture surface relative to the faces and axes of the crystal. Since α-quartz has cleavage (^{4},^{5}), fracture should occur predominantly along the cleavage plane $(10\bar{1}1)$. Analysis of the structure of α-quartz shows that in this case, in each pair of tetrahedra connected by vertices, one Si—O bond is broken, and charged groups of the type should form on the surface



$$\begin{array}{ccccccccc} & & & & \mathrm{O} & & & & \\ & & & & | & & & & \\ -\mathrm{O} & - & \overset{+}{\mathrm{Si}} & - & \mathrm{O} & - & \mathrm{Si} & - & \overset{-}{\mathrm{O}}- \\ & & | & & & & | & & \\ & & \mathrm{O} & & & & \mathrm{O} & & \\ & & | & & & & | & & \end{array}$$

in which the charges or the sites of rupture of Si—O bonds are localized in such a way as

shown here and in Fig. 3*. Such an arrangement of the structural elements bearing charges or free valences does not favor saturation of the valences by formation of a second Si—O—Si bond, since this requires not only considerable deformation of the bonds, but also rearrangement of the structure of the surface layer. It must be assumed that, for the rigid Si—O—Si bonds, these processes are very difficult under room-temperature conditions. Therefore, the charges and unsaturated valences formed on the quartz surface when it is crushed in vacuum may remain uncompensated for a long time under vacuum conditions.

Since the cleavage of quartz is very imperfect, other fracture surfaces are evidently also possible, different from the rhombohedron planes $(10\bar{1}1)$. In all such cases, silicon-oxygen groups may also form on the fracture surface, differing in their structure from those given above, for example groups $> \mathrm{Si}^{+}$—O^{-}, which then, with compensation of charges and valences, pass into the more stable groups $> \mathrm{Si} = \mathrm{O}$ (7).

Fig. 3. Position of the sites of rupture of Si—O—Si bonds in neighboring surface tetrahedra [$\mathrm{SiO}^{4/2}$] upon splitting along the rhombohedron plane (10$\bar{1}$1).

Figure 3: Fig. 3. Position of the sites of rupture of Si—O—Si bonds in neighboring surface tetrahedra [$\mathrm{SiO}^{4/2}$] upon splitting along the rhombohedron plane (10$\bar{1}$1).

Fig. 3. Position of the sites of rupture of Si—O—Si bonds in neighboring surface tetrahedra [$\mathrm{SiO}^{4/2}$] upon splitting along the rhombohedron plane (10$\bar{1}$1). **a** —Si; **b** —vertices of tetrahedra along which Si—O—Si bonds are broken; **c** —vertices of tetrahedra that remain bonded.

The presence of charges and unsaturated valences on the surface of α-quartz crushed in vacuum is one of the principal structural features of this surface, distinguishing it from the structure of the surface of silica gel dehydrated by calcination. It is likely that this structural feature of the α-quartz surface formed by crushing in vacuum is responsible for its high activity with respect to adsorption of polar water molecules; it exceeds even that of the maximally hydrated hydrophilic quartz surface (curve 1, Fig. 2). However, as can be seen from comparison of isotherms 1 and 4 in Fig. 2, at low vapor pressures the activity per unit surface of α-quartz crushed in vacuum only slightly exceeds the activity of the hydrated surface. This indicates that the number of primary adsorption centers per unit surface is close in both cases. The greater increase in adsorption with increasing vapor pressure in the first case, already in the very initial part of the isotherm, is probably connected with the superposition of chemical absorption caused by hydration. The appearance of charges on freshly formed mica surfaces upon its splitting in vacuum was observed by I. V. Obreimov (6).

In conclusion, I consider it my duty to thank Acad. M. M. Dubinin and Prof. A. V. Kiselev for their support of the present work and for the interest they showed in it.

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* Evidently, the formation of like charges at neighboring silicon-oxygen groups is also possible.

Note: Figure translations are in progress. See original paper for figures.

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