



Soviet-era science, translated into English

**L. G. GANICHENKO, M.
M. EGOROV, V. F.
KISELEV,**

K. G. KRASILNIKOV, and G. S. KHODAKOV

1960

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196001.64015>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

PHYSICAL CHEMISTRY

L. G. GANICHENKO, M. M. EGOROV, V. F. KISELEV,
K. G. KRASILNIKOV, and G. S. KHODAKOV

**ON THE PROPERTIES OF THE SURFACE OF
HIGHLY DISPERSED QUARTZ**

(Presented by Academician M. M. Dubinin, 8 XII 1959)

As is known, the adsorption and energetic properties of a unit surface of silica depend substantially on the degree of its hydration, which is determined by the crystallochemical features of the surface structure. In most adsorption studies carried out on quartz, questions concerning the nature and structure of the surface and its influence on adsorption properties have not been subjected to special study. The available literature data indicate a considerable discrepancy in the values for the degree of surface hydration and the specific adsorption isotherms; this has been explained either by the influence of clay impurities in the samples ⁽¹⁾, or by the presence of submicroscopic cracks in individual quartz crystals ⁽²⁾. As was shown in ⁽³⁾, one of the reasons for these discrepancies may be the effect of aggregation of quartz particles during dry grinding. The absence, in all works on the study of adsorption and the degree of hydration of the quartz surface, including in the work ⁽²⁾, of indications concerning the method of grinding quartz, and the failure to take into account the possible effect of particle aggregation, makes it difficult to interpret and compare the experimental data obtained. Questions concerning the relation of the degree of surface hydration to the structure of the surface layer and to the features of its structure for samples of highly dispersed quartz cannot at present yet be considered clarified.

In the present work we set ourselves the aim of studying the adsorption of water vapor (since the adsorption of water is very sensitive to the state of the surface ⁽⁴⁾), and the degree of hydration of the surface of quartz powders of different dispersity, obtained by grinding one and the same initial sample. To eliminate the aggregation effect ⁽³⁾, all initial powders were obtained by grinding transparent crystalline quartz with an excess of water in a steel vibratory mill. The most coarsely dispersed sample, Kv-6, was prepared by crushing quartz crystals in a mortar, also in the presence of an excess of water. The powders obtained under different grinding conditions, as in ⁽³⁾, were purified from iron impurities. Measurements of the adsorption of water and nitrogen vapors, as well as determination of structural water, were carried out on a volumetric apparatus. The data obtained are presented in Table 1 and in Fig. 1.

Fig. 1. Isotherms of primary adsorption (A) and reversible adsorption (B) of water vapor on quartz samples Kv-3 (1), Kv-5 (2), Kv-4 (3), Kv-6 (4)

Figure 1: Fig. 1. Isotherms of primary adsorption (A) and reversible adsorption (B) of water vapor on quartz samples Kv-3 (1), Kv-5 (2), Kv-4 (3), Kv-6 (4)

Fig. 1. Isotherms of primary adsorption (A) and reversible adsorption (B) of water vapor on quartz samples Kv-3 (1), Kv-5 (2), Kv-4 (3), Kv-6 (4).

As can be seen from Fig. 1, the initial portions of the primary isotherms for all samples calcined at 200° lie considerably above the corresponding

reversible isotherms obtained after prolonged holding of the samples in water vapor at $p/p_s = 1$ and a temperature of 20°. This occurs, apparently, because reversible adsorption of water vapor on such samples proceeds with a lower energy than on samples calcined at 200°⁽⁵⁾. At a low evacuation temperature, owing to the high content of silanol groups on the surface, hydrogen bonds may arise between neighboring groups, which leads to a decrease in the energy of adsorption^{(5)*}. The values of irreversible adsorption on quartz (Table 1) are considerably

Table 1

Adsorption and structural characteristics of the samples

Sample	Calcination temp., °C	Specific surface, m ² /g	Particle diameter, mμ	Degree of surface hydration, μM/m ²	Content of amorphous phase, %	Thickness of amorphous layer, Å	Irreversible adsorption, μM/m ²	
Kv-3	200	300	50.8	44	5.85.3	50	45	0.7
Kv-4	200	300	53.0	43	6.75.4	45	39	0.9
Kv-5	200	300	31.7	72	9.97.4	28	40	1.7
Kv-6	200	300	2.4	960	12.48.2	10	190	—

higher than for silica gels calcined at the same temperatures⁽⁴⁾. From Table 1 and Fig. 1 it follows that the degree of surface hydration and the specific adsorption values in the initial part of the isotherm, under identical pretreatment conditions, are not the same for different samples. The indicated discrepancy between the values of the degree of hydration and the specific adsorption values in the present case cannot be explained by the different origin of the samples and a possible aggregation effect, as was the case in^(1,2), and is apparently associated with differences in the structure of the surface of the samples studied.

Detailed calculations of the degree of surface hydration on the basis of consideration of crystallographic sections of an ideal quartz crystal were given in⁽⁷⁾.

The authors of ⁽⁷⁾ point out that it is difficult to use these calculations for quartz powders, since in this case the distribution of the particle surface over their crystallographic sections is unknown. The data obtained can give only an idea of the upper and lower limits (in the absence of thermal treatment) within which the degree of hydration of the surface of quartz powders may lie. Attempts to refine these data, made in ^(1,8), proceeding from an assumption concerning some probable distribution of the particle surface over their crystallographic sections, led to a certain limiting hydration which, in the opinion of the authors ⁽⁸⁾, characterizes not only the surface of quartz but also the surface of other modifications of silica, for example silica gel. Thus the independence of the degree of surface hydration and, consequently, of its structure from a number of factors determined by the “biography” of the sample was recognized.

According to modern concepts ⁽⁹⁾, the surface of a crystal, in principle, cannot be regarded as an undisturbed structure. Weyl ^(9,10), proceeding from the conditions for optimum shielding of the Si^{4+} ion, indicates that one of the ways of lowering the surface energy of a crystal is destruction of its lattice, leading to better shielding of the cation; in the case of silica, the rearrangement of the surface tetrahedra SiO_4 occurs in such a way that oxygen atoms will always be present on the surface—

* In addition, on the surface of silica at low treatment temperatures, coordinatively bound water may also be present ⁽⁶⁾.

water. When quartz crystals are crushed, as a result of mechanical action an amorphized layer appears on the surface of the particles, similar to Beilby layers*. The presence of such a layer on the surface of crushed quartz has been confirmed by various methods, including X-ray and electron-diffraction studies, differential thermal-analysis data, investigation of IR spectra, and solubility measurements ^(12–14). Thus, in the process of grinding quartz, a change occurs in the packing of the surface SiO_4 tetrahedra. The relatively easy mobility of SiO_4 tetrahedra in the bulk is indicated by the existence of polymorphic transformations for crystalline silica, proceeding at comparatively low temperatures of 117–250° ($\gamma \rightarrow \beta$ -tridymite, $\alpha \rightarrow \beta$ -cristobalite). It may be assumed that the rearrangement of SiO_4 tetrahedra at the surface will be facilitated by the conditions of their one-sided bonding with the bulk. According to the data of ⁽¹²⁾, no crystalline modifications of SiO_2 were found in the surface layer of ground quartz. The density of the amorphized layer is less than that of crystalline α -quartz, but greater than that of fused quartz.

Fig. 2. Dependence of solubility (1), content of the amorphous phase (2), and specific surface area (3) of quartz on the duration of its grinding in a vibratory mill.

To estimate the fraction of the amorphous layer in the quartz samples we investigated, we used differential thermal analysis ⁽¹²⁾, which makes it possible, from the heat of the $\alpha \rightleftharpoons \beta$ transition in quartz, to determine the percentage content of crystalline quartz capable of undergoing this transition. The data obtained,

Fig. 2. Dependence of solubility (1), content of the amorphous phase (2), and specific surface area (3) of quartz on the duration of its grinding in a vibratory mill.

Figure 2: Fig. 2. Dependence of solubility (1), content of the amorphous phase (2), and specific surface area (3) of quartz on the duration of its grinding in a vibratory mill.

as well as the calculated thicknesses of the amorphous layer, are presented in Table 1. To clarify the factors affecting the amorphization of quartz, special investigations were carried out. As is seen from Fig. 2, the content of the amorphous phase and the magnitude of the specific surface area of quartz increase with increasing grinding time. The thickness of the amorphized layer changes only insignificantly. Prolonged grinding in a mortar led to sample Kv-6 (Table 1), with a small specific surface area but a greater thickness of the amorphous layer (in this case, apparently, the mechanical work was expended mainly not on splitting the crystals but on their deformation). Disorder of the lattice leads to an increase in its free energy. Investigation of the equilibrium solubility (Fig. 2) shows an increase in the concentration of SiO_2 in solution as the grinding time and the percentage content of the amorphous phase increase.

The degree of hydration of the surface is determined by the number of free corners of SiO_4 tetrahedra at the surface and, consequently, depends on their packing. It follows from the above that the magnitude of the degree of hydration, even under completely identical preparation conditions, cannot be the same for different silica samples, but is determined mainly by the structure of their surface. As follows from Table 1, samples with a smaller specific surface area have greater surface hydration. Accordingly, the adsorption capacity per unit surface increases somewhat with decreasing dispersion of the silica. If one relies on the data of ⁽¹⁵⁾, according to which the surface energy of a siloxane surface is 259 erg/cm^2 , and that of a silanol surface 129 erg/cm^2 , then for partially hydrated silica the specific surface energy will increase with deca-

* In 1921 Beilby ⁽¹¹⁾ discovered the destruction of crystals during the polishing of metallic surfaces.

the degree of hydration of the surface. From Table 1 and the data obtained for silica gels ⁽¹⁶⁾, it follows that the specific surface energy tends to increase with increasing dispersion of the sample and, correspondingly, with decreasing degree of hydration of the surface. These data confirm Weyl's point of view ^(9,10), according to which an increase in specific surface energy should be observed for very small crystals. In the case of semiconductors, the dependence of adsorption properties on the dispersion of the adsorbent was substantiated in ⁽¹⁷⁾.

The data we have obtained do not agree with the conclusions ^(2,18) concerning the identity of the adsorption properties and limiting hydration of silica gels and

crystalline quartz. S. P. Zhdanov ⁽²⁾ sees confirmation of this point of view in the coincidence of the “absolute” isotherms of water-vapor adsorption on samples of quartz and silica gel. In his calculations he used values of specific surface area calculated from the same isotherms for which the “absolute” isotherm is then constructed. It was shown in ⁽¹⁹⁾ that an isotherm with a close value of the BET constant C will in this case always coincide, since the qualitative difference of the surface is automatically taken into account by its magnitude. With such a calculation, for example, the “absolute” isotherms coincide on hydrated and methylated silica gels, which have qualitatively different surfaces ⁽²⁰⁾. Thus, the data presented in ^(2,18) cannot be regarded as confirmation of an identical degree of hydration and, consequently, of the state of the surface of different silicas.

Moscow State University
named after M. V. Lomonosov

Research Institute
of New Building Materials

Received
20 XI 1959

REFERENCES

1. W. Stöber, *Koll. Zs.*, **145**, 117 (1956).
2. S. P. Zhdanov, *DAN*, **120**, 103 (1958).
3. V. F. Kiselev, K. G. Krasilnikov, G. S. Khodakov, *DAN*, **130**, No. 6 (1960).
4. M. M. Egorov, G. S. Egorova, *ZhFKh*, **32**, 2624 (1958).
5. M. M. Egorov, K. G. Krasilnikov et al., *ZhFKh*, **33**, 65 (1959).
6. E. A. Hauser, W. A. Weyl, *Koll. Zs.*, **124**, 72 (1951).
7. H. Seifert, R. Buhl, K. F. Seifert, *Koll. Zs.*, **141**, 146 (1955).
8. S. P. Zhdanov, A. V. Kiselev, *ZhFKh*, **31**, 2213 (1957).
9. W. A. Weyl, E. C. Marboe, *Some Mechanical Properties of Glasses and Crystals as Affected by Changes in Chemical Binding Forces*, Munich, 1959.
10. W. A. Weyl, *Structure and Properties of Solid Surfaces*, Chicago, 1953, p. 147.
11. G. T. Beilby, *Aggregation and Flow in Solids*, N. Y., 1921.

12. P. B. Dempster, P. D. Ritchie, *J. Appl. Chem.*, **3**, 182 (1953).
13. M. Cignitti, A. Uva, *Ricerca scient.*, **28**, 1915 (1958).
14. G. S. Khodakov, E. R. Plyushch, *DAN*, **123**, 725 (1958).
15. S. Brunauer, D. L. Kantro, C. H. Weise, *Canad. J. Chem.*, **34**, 1483 (1956).
16. M. M. Egorov, K. G. Krasilnikov, V. F. Kiselev, *ZhFKh*, **32**, 2448 (1958).
17. Sh. M. Kogan, *Problems of the Kinetics and Catalysis*, 1960.
18. A. V. Kiselev, G. G. Muttik, *Koll. zhurn.*, **19**, 562 (1957).
19. V. F. Kiselev, K. G. Krasilnikov, *ZhFKh*, **33**, 2621 (1959).
20. L. G. Ganichenko, M. M. Dubinin, E. D. Zaverina, V. F. Kiselev, K. G. Krasilnikov, *Izv. AN SSSR, OKhN*, 1960, No. 3.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.