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ON THE DEHYDRATION AND REHYDRATION OF THE SURFACE OF QUARTZ

(Presented by Academician M. M. Dubinin, 11 VII 1958)

Under the usual conditions for obtaining quartz powders, the surface of quartz particles, like the surface of silica gels, is hydrated and bears hydroxyl groups valently bonded to silicon atoms ([1,2]). The formation on the surface of quartz, as a result of its hydration, of tetrahedral silicic-oxygen groups whose free apices emerging at the surface are occupied by monovalent OH groups leads to valence saturation and normal coordination of the surface Si and O atoms. As is known, the hydration reaction of the SiO_2 surface is exothermic. As a result of the transition of an ultimately dehydrated surface of amorphous SiO_2 into an ultimately hydrated one, according to Brunauer et al. ([3]), the total surface energy decreases by approximately 130 erg/cm^2. Therefore one may expect that, when a newly formed quartz surface comes into contact with water, as occurs when quartz powders are treated in aqueous acid solutions to remove impurities or when they are elutriated in water for separation into fractions, the quartz surface should be in a state of ultimate hydration, in which the number of hydroxyls per unit surface is maximal and corresponds to the number of Si–O–Si bonds broken in the formation of the surface; it should be close for different quartz samples because of the identity of their crystal structure.

On the basis of crystal-chemical data it can be shown that possible changes in the number of hydroxyls per unit surface of quartz in the state of ultimate hydration, depending on the choice of cleavage planes, are limited to the range 9.9–16.0 μM/m^2 ([2]). If the manifestation of anisotropy during cleavage, noted by Engelhardt ([4]), is taken into account, then the upper limit of the surface concentration of hydroxyls should be lowered to 12.6 μM/m^2. However, determinations of the hydroxyl content per unit surface of quartz, from thermal dehydration data, usually lead to considerably larger and, moreover, different values. It does not seem possible to interpret the experimental results if one assumes that surface hydroxyls are the only source of the water released on calcination of quartz.

In the present work, the dehydration in vacuum of a powder of opaque quartz

Fig. 1. Dehydration curves of various quartz samples in vacuum

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(s = 5.4 m^2/g) and of rock crystal (s = 0.58 m^2/g) was investigated, as well as the rehydration of the surface of rock crystal after calcination at 1150°, and a comparison was made of the adsorption properties of the initial (ultimately hydrated), ultimately dehydrated, and rehydrated surfaces of rock crystal with respect to the adsorption of water vapor. Calcination of the quartz powders was carried out in a quartz ampoule sealed to a vacuum apparatus. The water evolved in each temperature interval of calcination was condensed in a trap cooled with liquid nitrogen and was quantitatively determined either by a gravimetric method, by absorbing it with magnesium perchlorate, or by a volumetric method.

The apparatus for studying dehydration also made it possible to quantitatively determine the hydrogen released during the ignition of quartz ([1]).

Figure 1 presents dehydration curves in vacuum for various quartz samples with an extremely hydrated surface. Curves 2 and 5 were obtained in the present work; curves 1, 3, and 4 were taken from the work of Stöber ([1]). Although the amount of water released during ignition, referred to unit surface area, varies for different quartz samples over a very wide range (from 5 to 50 µM/m^2). In contrast, during ignition of silica gels only slight fluctuations are observed in the content of structural water per unit surface area, if the values of the specific surfaces have been determined sufficiently reliably ([5]).

Fig. 1. Dehydration curves of various quartz samples in vacuum

Since all the curves in Fig. 1 refer to quartz samples whose surface, according to the conditions of preparation, should correspond to the state of limiting hydration, it is evident that the divergence of the curves in Fig. 1 cannot be associated with possible differences in the degree of hydration of quartz surfaces. This is all the more improbable because the possible limiting content of hydroxyls per unit surface area of quartz, determined by the structural features of the crystal lattice and by the mechanical anisotropy of the crystals, is, as indicated, only 12.6 µM/m^2. Stöber ([1]) considers the cause of the divergence of the dehydration curves he obtained to be the presence of impurities of clay minerals in the quartz, which may be sources of water release during ignition. However, the possibility should not be excluded that quartz crystals contain free (molecular) water that is not removed when powders are evacuated without heating. This water may be adsorbed in the finest cracks, or may be present in the adsorbed state, or in the state of a solid solution in the crystal lattice itself. It is known that water is often detected spectroscopically in quartz crystals.

Fig. 2. Comparison of dehydration curves obtained on initial and rehydrated quartz.
1 –initial, unignited quartz; 2 –ignited at 1150° and rehydrated

Fig. 2. Comparison of dehydration curves obtained on initial and rehydrated quartz. 1 —initial, unignited quartz; 2 —ignited at 1150° and rehydrated

Figure 2: Fig. 2. Comparison of dehydration curves obtained on initial and rehydrated quartz. 1 —initial, unignited quartz; 2 —ignited at 1150° and rehydrated

Fig. 3

Figure 3: Fig. 3

The steep rise of curve 5 in Fig. 1 in the interval 100-200° may be associated with the release of water irreversibly adsorbed in the finest cracks of molecular dimensions. The presence of such cracks in crystals of this quartz sample is confirmed by the fact that its ignition at 200° leads to a substantial increase in water adsorption, whereas the surface measured by nitrogen remains practically unchanged ([6]). In the presence of cracks whose hydrated surface is only partially accessible to nitrogen, the magnitude of the specific surface of quartz powders determined by nitrogen adsorption will be smaller than the true one, and the amounts of structural water calculated per 1 m^2 may turn out to be su—

substantially overestimated. This circumstance may also be one of the possible reasons for the discrepancy in the amounts of structural water determined from dehydration curves of different quartz samples (Fig. 1). Determinations of the content of structural water on the rehydrated surface of quartz and studies of water adsorption on such a surface indicate that a considerable part of the water evolved on ignition of some quartz samples is formed not at the expense of surface hydroxyls.

In Fig. 2 are shown dehydration curves for rock crystal III (s = 0.58 m^2/g). Curve 1 corresponds to the initial powder, which had not previously been ignited, while curve 2 was obtained on the same sample after its surface had been completely dehydrated by ignition at 1150°, and then rehydrated by keeping it in water for 1 month at room temperature. As follows from comparison of the curves in Fig. 2, as a result of rehydration a considerable number of hydroxyls was restored on the quartz surface. However, the amount of water evolved on ignition from the rehydrated quartz surface, at all temperatures above 200°, proves to be considerably smaller than for the initial quartz powder with a completely hydrated surface.

Fig. 3. Initial portions of water adsorption isotherms on the same quartz powder treated under different conditions. **1a** —initial, completely hydrated sample; **1b** —ignited at 1150° and then kept in water for 1 month; **2** —ignited at 1150° in vacuum; **3** —kept after ignition at 1150° in water vapor (at $p/p_s = 1$) for 48 h.

If these differences are connected with unequal contents of hydroxyls per unit surface of the initial and rehydrated samples, then a different degree of hydration

of the surface should be revealed in the water adsorption isotherms, since water adsorption is very sensitive to the degree of hydration of the surface of silica gels ([8],[5],[2],[7]). However, as is seen from Fig. 3, the water adsorption isotherms, referred to unit surface area, on the initial (1a) and rehydrated (1b) quartzes in the region of monolayer filling practically coincide. This can evidently occur only when the chemical structure and degree of hydration of the surface are close in both cases. From these data it follows that during the first ignition of the rock-crystal powder, together with water formed at the expense of surface OH groups, a considerable amount of water was irreversibly evolved which was located, evidently, not on the surface but in the interior of the quartz crystals.

The amount of hydroxyls per unit surface of the rehydrated quartz, determined from dehydration curve 2 of Fig. 2, taking into account 0.48 $\mu M/m^2$ of H_2 evolved during its ignition in the temperature interval 500-1100°, is 9.44 $\mu M/m^2$.

This value is only slightly less than the lower limit of the possible content of hydroxyls per unit surface of quartz in a state of complete hydration (9.9 $\mu M/m^2$). Rehydration of the surface of quartz ignited at 1150° also occurs upon keeping it in water vapor at $p/p_s = 1$. As is seen from isotherms 2 and 3 in Fig. 3, water adsorption increases noticeably as a result of keeping in vapor, which indicates a partial restoration of hydroxyls on the surface. However, the process of rehydration upon keeping in vapor is not completed, and for its completion a longer time, and perhaps other conditions as well, are required.

From the results presented in the present work it follows that one must be especially cautious in estimating the number of hydroxyls on the surface of quartz from thermal-dehydration data. The evolution of hydrogen observed upon calcination of quartz is of interest from various points of view and deserves special consideration.

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