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The Influence of Aggregation of Quartz Particles during Grinding on Its Adsorption Properties

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It was recently shown (1) that, in the process of grinding quartz in an air-dry state, the magnitude of its specific surface area, determined from the low-temperature adsorption of nitrogen, ceases to increase with increasing grinding time and may even decrease. This phenomenon was explained by aggregation of quartz particles, in which part of the surface becomes inaccessible to nitrogen molecules. It is of interest to examine the influence of aggregation on the adsorption properties of quartz with respect to other adsorbates and, in particular, to determine to what extent aggregation of quartz particles affects its adsorption properties with respect to water vapor, the molecular dimensions and adsorption character of which differ substantially from the molecular dimensions and adsorption character of nitrogen.

The adsorption properties of a unit surface of quartz with respect to water and methanol vapors have been studied repeatedly (2–8). The heats of adsorption and wetting by these liquids have also been investigated (4,9–12). Comparison of the results obtained for adsorption isotherms of water vapor (8) and for heats of wetting by water (12) indicates a large discrepancy in these adsorption characteristics for different quartz samples. In the case of water-vapor adsorption isotherms this was explained (8) by the presence, in some natural quartz samples, of "submicroscopic" cracks accessible to water molecules but inaccessible to nitrogen molecules, which leads to underestimated values of the specific surface area determined from nitrogen adsorption isotherms and, consequently, to overestimated "absolute" values (i.e., referred to a unit surface) of water-vapor adsorption. Such an explanation seems unlikely to us, since in the process of fine grinding the splitting of quartz particles should occur predominantly along microcracks, which are the weakest points of the lattice, and, consequently, dispersion should promote a decrease in the porosity of powders of different origin, which, however, is not confirmed (8). No independent experimental data on the presence of ultraporosity in the samples studied are given (8). In (12) a substantial increase in the specific heats of wetting of quartz by water with decreasing dispersity is noted. An analogous dependence, though less sharply expressed, was observed by us earlier (13–16) for silica gels. It was also pointed out that the methods of preparation of silica gels and quartz powders have a marked

Figure 1

Figure 1: Figure 1

influence on their adsorption properties. Thus, the reasons for the considerable divergence, reported in the literature for different quartz samples, of the specific values of adsorption and adsorption energy have not yet been firmly established.

In the present work we used two samples of highly dispersed quartz. The first sample, Kv-4, was obtained by grinding transparent crystalline quartz with excess water (1) in a steel vibratory mill. The second sample, Kv-4A ···

was obtained by further grinding the well-dried first sample (Kv-4) for 16 min in air. Both quartz samples were purified of iron impurities by treatment with hydrochloric acid, followed by passing the suspension through a chromatographic column filled with cation exchanger (18). The adsorption of water vapor and nitrogen was measured on a volumetric apparatus. The amount of structural water in the samples was determined on the same apparatus from the volume of water vapor evolved when the sample was calcined from 300 to 1000°. The specific surface area was calculated by BET from the isotherms of low-temperature adsorption of nitrogen. The data obtained are given in Table 1.

Fig. 1. **A** –adsorption isotherms of water vapor (open points) and nitrogen (black points) on quartz samples Kv-4A (1) and Kv-4 (2). **B** –adsorption isotherms of water vapor on the same samples, referred to the content of structural water in these samples

Figure 1 presents the reversible branches of the adsorption isotherms of water vapor and nitrogen on samples Kv-4 and Kv-4A, calculated per 1 g of adsorbent. As is seen from Fig. 1, the adsorption isotherm of nitrogen vapor on the aggregated sample Kv-4A lies considerably lower than that for the original sample. Accordingly, during further grinding of the dry powder Kv-4 its specific surface area with respect to nitrogen decreased by a factor of 1.5 due to aggregation of the particles (1) (Table 1). The water-vapor isotherm on the aggregated sample Kv-4A, on the contrary, lies higher than on sample Kv-4, which may be explained by an increase in the true surface of the sample as a result of its additional grinding. Thus, these experiments show that, as a result of particle aggregation during quartz grinding, its adsorption properties change differently with respect to water and nitrogen vapors. The ultraporous structure of the aggregated particles formed in this case is evidently not connected with the original quartz sample, but has a secondary origin.

Table 1

Adsorption characteristics of quartz powders

Fig. 2

Figure 2: Fig. 2

Sample	Specific surface, m^2/g	Structural-water content, μM/m^2	Grinding conditions
Kv-4	53.0	5.4	With excess water
Kv-4A	35.4	14.8	Additional grinding of dry powder Kv-4

The absence in all studies (2–12) on quartz of data on the grinding conditions and the failure to take into account the aggregation effect, which leads to underestimated values of the specific surface area calculated from the isotherms of low-temperature adsorption of nitrogen, do not permit comparison among themselves of the specific adsorption values (2–8), heats of adsorption (4), and heats of wetting (9, 12) calculated in these works, as was done previously (8, 12). It is possible that this is one of the causes of the considerable discrepancies in both adsorption and energetic-

characteristics obtained for quartz powders in different studies.

As follows from Fig. 2, the "absolute" isotherms of adsorption of water vapor on two quartz samples of the same origin, differing only in the conditions of their grinding, differ sharply. This is due to the fact that part of the surface of the aggregated sample proves to be inaccessible to nitrogen molecules, but accessible to water molecules. In this case it would naturally be appropriate to determine the value of the specific surface area of the aggregated sample from the isotherms of adsorption of water vapor. However, this approach may lead to significant errors, since the area occupied by water molecules on the surface of silica depends on the degree of its hydration, which differs noticeably for samples of different origin ([14–16]). Calculation of the area occupied by a water molecule from crystallographic sections of quartz ([17]) is not justified, since even earlier ([21]) the presence of an amorphous layer on the surface of crystalline quartz had been established. The facts of coincidence of the "absolute" isotherms ([4,8]) on different quartz and silica gel samples when using the specific surface area calculated from these same data still say nothing about the identity of the surfaces of the objects studied. In this case the "absolute" isotherms coincide only because, when calculating the specific surface area, qualitative differences in the nature of the surface of different samples are taken into account by its magnitude ([19]). Thus, for example, with such a method of calculation the "absolute" isotherms coincide on ordinary silica gel and on silica gel with a modified surface, in which part of the OH groups had been replaced by CH_3 groups, i.e., on samples whose surface nature is substantially different ([20]).

Fig. 2. Specific adsorption isotherms of water vapor (open points) and nitrogen (black points) on quartz samples Kv-4A (1) and Kv-4 (2)

Since the value of the true specific surface area of the aggregated quartz powder remained unknown, we related the measured values of adsorption of water vapor directly to the amount of structural water contained in the samples studied ([14]). As can be seen from Fig. 1B, in the initial region P/P_s the isotherms coincide, which testifies in favor of the fact that the entire surface of the aggregated quartz powder is accessible to water molecules.

At present it is not yet possible to give a substantiated explanation of the aggregation phenomenon observed in ([1]) and in the present work. Apparently, when particles approach one another during grinding, contacts are formed between them owing to interaction of active sites of neighboring particles. Such active sites may, in particular, be free radicals arising on fracture surfaces. In this process comparatively dense aggregates are formed, consisting of primary particles, which are not destroyed by treatment with water or by heating. However, their mechanical strength is considerably lower than that of the original quartz particles. Short-term grinding of aggregated quartz in water leads to disaggregation of the particles and to a sharp increase in the specific surface area. The fact noted above that water molecules are distributed over the entire surface of the aggregated particles is consistent with the dispersing (peptizing) properties of water with respect to these systems. It should be noted that the phenomenon of particle aggregation during grinding is observed not only for crystalline quartz, but also for a number of other solids—corundum, fused quartz, calcite, etc.—and also for silica gel, whose specific surface area during dry crushing in a vibratory mill in some cases decreases by more than a factor of 10.

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