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Abstract

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On the Mechano-Chemical Dissociation of Liquids on Freshly Formed Surfaces of Solids

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The dissociation of liquids adsorbed on the surface of quartz during its calcination in vacuum has already been reported ([1,2]). In works ([3,4]) it was established that the evolution of gases noncondensable at −195° during the calcination of hydrated quartz is due mainly to hydrogen dissolved in natural quartz crystals, or to contamination of the particle surface by organic substances, the oxidation and thermal dissociation of which lead to the appearance of carbon monoxide. The possibility of formation of gases noncondensable at −195° in the process of grinding solids as a result of mechano-chemical dissociation of molecules of liquids adsorbed on their surface has not been considered. Meanwhile, it is known that particles of solids, during fine grinding, undergo considerable deformations, leading to destruction of their crystalline structure and to a significant increase in the chemical activity of the amorphized surface layers ([5,6]). It could be assumed that molecules of liquids adsorbed on solid particles would also be destroyed in the course of grinding. The products of dissociation of liquids possess, at the moment of their formation, high activity and therefore can form strong compounds with molecules of solids located in the surface layers. Apparently, their penetration into the bulk of the particles through structural defects is also possible.

To test this assumption, powders obtained after grinding with various liquids were placed in a quartz ampoule connected to a vacuum installation, evacuated at a temperature of 150–200°, and then, to release the dissociation products, were calcined up to 1050°. It turned out that in this process a considerable quantity of gases is evolved from the powders, determined by the liquid introduced as an additive and by the grinding conditions. In many cases, the greater part of the evolved material does not condense at the boiling temperature of liquid nitrogen (−195°).

Before grinding, in order to remove organic contaminants, the powders were subjected to prolonged calcination at a temperature of $\sim 1000°$. It was shown that at this temperature the gases dissolved in the crystals are removed almost completely, irrespective of the crystal sizes ([4]). Consequently, the gases evolved were likewise not of geological origin. The experiments were carried out in such a way that part of the system was placed in liquid nitrogen, while the temperature

Fig. 1

Figure 1: Fig. 1

in the quartz ampoule was raised sufficiently slowly. This ensured the possibility of distillation of the liquid phase into the cold part of the apparatus, and, consequently, the appearance of gases noncondensable at −195° could not have been caused by ordinary high-temperature cracking. This is confirmed by experiments in which highly dispersed powders calcined at 900° were wetted with liquids and subjected to the treatment described above. Even under conditions in which, before repeated firing, the powders wetted with liquids were subjected to brief grinding, evolution in comparable quantities of gases noncondensable at −195° was not observed. If, however, freshly ground powders without

additive powders; under the same treatment (with short-term additional grinding or without it), a noticeable, but significantly smaller than usual, amount of gases not condensing at −195° was evolved from them.

The evolution of gases upon calcination of solids ground with liquids was studied by us using quartz, graphite, calcite, and corundum as examples,

Fig. 1. *a* —kinetics of gas evolution. $1, 2, 3, 4$ —respectively at 600, 900, and 1050° from quartz ground with 1.3% benzene for 16 min.; $5, 6$ —the fraction not condensed at −195°, respectively at 600 and 900°, from quartz ground with 1.3% benzene for 32 min.; 7 —at 900° from quartz ground with 0.4% benzene for 10 min. *b* —dependence of the amount of gases evolved on the calcination temperature: 1 —quartz ground with 1.3% benzene for 16 min.; 2 —quartz ground with 1.3% benzene for 32 min., the fraction not condensed at −195°, $\delta = 0.86$; 3 —quartz with 1.8% benzene, 12 min. of grinding, $\delta = 0.99$; 4 —corundum, ground for 10 min. with water, $\delta = 0.92$; 5 —quartz, 12 min. of grinding with 0.25% CCl_4, $\delta = 0.77$, the fraction not condensed at −195°

which had been dispersed with water, benzene, acetone, heptane, octane, alcohol, and carbon tetrachloride. In most experiments, pure pre-calcined quartz sand was used. In a number of experiments, the material together with the mill drums and balls was dried before grinding at 150°. In addition, some of the experiments were carried out under conditions excluding the influence of oxygen—in a nitrogen atmosphere. In some cases the powders were ground in a porcelain mill with corundum balls or were cleaned of wear products—iron—by treatment with hydrochloric acid.

The observed phenomenon is characterized by the following features:

1. Intensive evolution of gases not condensing at −195° begins at a temperature of about 400° and increases sharply with further increase in temperature. Evolution of gases condensing at −195° begins at $\sim 200°$. In the temperature interval up to 1050°, no decrease in the growth of gas evolution with increasing temperature is observed (Fig. 1). This indicates

that, under the conditions of our experiments, only part of the

products of dissociation of liquids, amounting in a number of cases to as much as 50-70% of the maximum possible quantity calculated from the condition of their complete decomposition.

The rate of gas evolution, as is seen from Fig. 1a, is rather low and is apparently limited by diffusion processes. At the same time, each temperature in the indicated interval corresponds to a certain practically established value of the amount of evolved gases. Moreover, the process is not reversible: when the temperature is lowered, the gases evolved by the powders are not absorbed in noticeable quantities and do not affect the degassing process. Consequently, the gas molecules undergoing thermal evolution possess different binding energies with the solid. An estimate of the magnitude of this energy on the basis of an analysis of the thermal-evolution curves for the gases gives approximately from 0.5 to 4 eV, which is several times higher than the maximum energy of physical adsorption on quartz.

2. Storage of the powders at room temperatures for several years does not noticeably affect their ability to evolve gases upon calcination.

Treatment of the powders (ground with organic additives) with hydrochloric acid during boiling and washing with water likewise does not destroy their ability to evolve gases upon calcination. Although the amount of gases evolved is thereby reduced by approximately a factor of 2, this process is accompanied by loss, together with the filtrate, of the finest particle fractions and, as a consequence, by an overall decrease in the dispersity of the powder.

3. The amount and composition of the gases evolved from the powder depend on the nature and content of the liquid additives, on the nature of the solid, and on the efficiency of its grinding. The data given as an example in Table 1 show that, with increasing duration of grinding (quartz with 1.3% benzene), the amount of gases evolved during calcination (900°) increases. At the same time, the amount of gas per unit surface area (V/S) of the disaggregated powders remains approximately constant. The value V/S at 800-900° corresponds to the formation of a saturated monolayer. At higher temperatures, considerably more gas is evolved than is necessary for the formation of a monolayer.

Table 1

Influence of the duration of grinding (τ) of quartz with an addition of 1.3% benzene on the specific quantity V of gases (cm^3/g) (NTP) evolved at $\sim 900^\circ$, and on the specific surface area S (m^2/g)

τ, min	2	4	8	11	16	32
S	10	17	28	36	45	62
V	2.3	4.6	6.0	12.0	12.6	16.2

τ, min	2	4	8	11	16	32
V/S	0.23	0.27	0.21	0.32	0.28	0.26
δ*	0.75	0.84	0.87	0.99	0.92	0.96

* δ is the fraction of gas noncondensable at −195°.

4. In the case of organic additives, as chemical and mass-spectrometric analysis shows, the main part of the gases noncondensable at −195° consists of CO and H_2. In the case of CCl_4 additives it consists of CO, whose oxygen was apparently obtained from air or at the expense of SiO_2. An analogous evolution of CO takes place upon calcination of finely ground graphite. Carbon atoms oxidized in air are rather strongly bound to the graphite substrate and are removed only at temperatures above 600°.

In addition to CO, quartz ground with an addition of CCl_4 evolves a certain amount of condensable gas, possibly chlorine. The main amount of chlorine, however, combines with iron—the product of wear of the mill. Upon heating, the iron chloride sublimes, forming a deposit in the cold part of the ampoule.

Evolution of oxygen was not observed in most experiments. Oxygen evolution as a result of thermal decomposition of Fe_2O_3 (oxidized products of mill wear) was also relatively small.

5. Dissociation of water on the surface of quartz is distinguished by a number of features. These include, as is seen from Table 2, first of all a sharp de-

Table 2

Effect of additions of water, benzene, and octane during grinding of quartz on the quantity of gases evolved at 800-900°

Additions, cm^3/g	0	0.5–1.0 · 10^{-3}	2.5 · 10^{-3}	5.0 · 10^{-3}	1.0–1.5 · 10^{-2}	2.0–2.5 · 10^{-2}	5–6 · 10^{-2}	0.10–0.12	1.0
Water, V	1.7	2.6	4.4	3.4	3.5		2.8	1.3	1.8
Water, δ	0.97	0.74	0.95	0.76	0.97		0.68	0.0	0.0
Benzene, V	1.7			8.2	12.0	11.2	7.03	6.9	8.2
Benzene, δ	0.97			0.77	0.99	0.95	–	0.96	0.85
Octane, V	1.7			7.4	9.4	10.2	9.2		
Octane, δ	0.97			0.92	0.94	0.94	0.89		

dependence of the composition and quantity of the decomposition products on the water content. This feature is apparently due to the formation and decomposition, in the presence of water vapor, of silanes, which constitute the main fraction of the vapors condensing at −195°. The dissociation of water during the grinding of corundum and calcite proceeds analogously to other hydrogen-containing liquids, with the liberation of a considerable quantity of gases that do not condense at −195° and a very small quantity of condensing gases (see Fig. 1).

Grinding quartz with small quantities of water and together with some other liquid, for example benzene, leads to a sharp decrease in gas evolution. Additional short-term regrinding with water of powders that had previously been ground with carbon tetrachloride, alcohol, acetone, and, especially, with small quantities of water also sharply reduces the gas content in the powders. At the same time, regrinding with water has no noticeable effect on gas evolution from powders previously ground with octane, heptane, and benzene.

Thus, in the experiments described here, in our opinion, the fact has been established of the dissociation of liquids adsorbed on freshly formed surfaces of solids during fine dispersion. It has been established that the dissociation products are bound rather strongly to the solid and, consequently, are capable of substantially lowering its surface energy. This phenomenon is also of interest for understanding the processes of interaction of liquids with freshly formed "clean" surfaces possessing an additional excess of free energy in connection with their mechanical amorphization.

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