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Abstract

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ON THE THERMAL DEHYDRATION OF SILICA AND CERTAIN PROPERTIES OF ITS SURFACE

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In connection with the hypothetical scheme proposed in (1) for the mechanism of dehydration of the silica surface, attempts were made (2,3) to clarify the composition of the products evolved during its thermal treatment. In (3) it was found that, when powders of crystalline quartz are heated, in addition to water, in some cases CO_2 and a combustible gas not frozen out by liquid air are evolved; on the basis of these characteristics, the latter was identified as hydrogen. The amount of hydrogen determined in this way varied for different quartz samples within the range of 10-40% of the amount of water evolved. Repeating these experiments, the author (4) likewise observed the evolution of hydrogen both from the original quartz powder and after its rehydration. Assuming that free dissolved hydrogen may be present in natural quartz crystals, the author (4) attributed the hydrogen evolved from the rehydrated sample to dissociation of surface OH groups.

It had previously been shown (5) that the surface of silica, upon its thermal dehydration, possesses oxidizing properties, i.e., contains some excess of oxygen atoms over the stoichiometric ratio. In order to establish the nature and mechanism of formation of these centers, it was necessary to undertake a detailed study of the composition of the gas phase formed in the process of thermal dehydration of silica, as well as of the properties of the dehydrated surface obtained in this way. For solving the first problem, the method of mass-spectrometric analysis proved very convenient (6,7). As a result of a detailed study of the dehydration products of a number of samples of amorphous and crystalline silicas, it was established that the evolution of H_2 in appreciable quantities does not occur. The supposition was made (7) that the authors of (2,3) observed the evolution not of H_2, but chiefly of CO, arising from organic contaminants.

Instead of H_2, during the dehydration of several varieties of crystalline quartz powder and silica gel, the evolution of molecular oxygen was unexpectedly detected (6). The temperature dependence of this process had two maxima: in the region of intermediate temperatures (500-550°) and in the region of high temperatures (900-950°). The origin of the oxygen evolved at intermediate temperatures was readily established. It appeared as a consequence of treating silicas with HNO_3 vapors, which was usually carried out in order to clean the surface of organic contaminants. Evidently, a certain amount of nitrogen oxides was retained in this process, forming a comparatively strong bond with the silica surface ([8]). As for the evolution of O_2 at high temperatures (the second maximum), when the main mass of "structural" water had already been removed, it was assumed that the oxygen is organically bound to the silica surface and that the process of its liberation may be regarded as a reflection of certain changes in the indicated surface. On this basis the term "structural" oxygen was used ([6]). It was emphasized, however, that there is apparently no direct connection between the amount of structural water contained in silicas and the amount of O_2 evolved at high temperatures.

With respect to the evolution of O_2, the behavior of one of the silica-gel samples (K-2) was unusual. It was prepared under laboratory conditions by hydrolysis of $SiCl_4$, with maximum attention to cleanliness and care in the operations, and, apart from prolonged washing with bidistilled water, was not subjected to any additional purification. Mass-spectrometric study of the dehydration products of this sample showed the absence of both O_2 and H_2 in appreciable amounts.

Thus, the data obtained up to that time proved contradictory: for different silica preparations, depending on the methods of their preparation, purification, and investigation, in some cases ([2,3]) evolution of H_2 was observed, in others there was absence of H_2 and presence of O_2 ([6,7]), and, finally, there was practically complete absence of both (silica gel K-2). The evolution of O_2 during thermal treatment of silicas could not be reconciled with the fact that the surface of silica thereby acquires oxidizing properties ([5]). It must also be emphasized that in ([2–4]) no evolution of hydrogen from silica gels was observed, but only from crystalline silicas, which may indicate a different, non-surface origin of H_2.

Clarity on all these questions was obtained as a result of additional experiments with mass analysis of the dehydration products of silicas, varying the conditions of their preparation and treatment. In particular, it seemed necessary to verify that the evolution of H_2, if it occurs, is not eliminated as a result of treating silicas with HNO_3. New mass-analysis experiments were carried out using an external heating system ([7]), but without freezing out H_2O vapors along their path into the mass spectrometer, in order to estimate the relative content of the other components of the gas evolution with respect to H_2O.

A freshly prepared sample of silica gel of type K-2 was studied in the purest possible form, both without additional treatment and after treatment with HNO_3. In both cases the mass spectrum showed a small amount of H_2, amounting to 1-2% relative to the evolved H_2O, irrespective of temperature. In the first case O_2 was completely absent over the entire temperature range, whereas in the second, as previously in similar cases ([7]), evolution of a certain amount of O_2 and NO was observed in the region of intermediate temperatures. It should be noted that also in the earlier experiments ([7]), with other varieties of silica gel and with quartz powders that evolved O_2, hydrogen appeared in the mass spectrum when water vapor was not frozen out. The magnitude of the ratio of the ion currents H_2 and H_2O always remained approximately the same, varying within 1-3%. This evidently indicates that in the experiments mentioned the so-called residual hydrogen was observed, arising during fragmentation of molecules by electron impact in the ion source of the mass spectrometer. Special experiments with vapors of pure water, introduced from the heating system into the mass spectrometer, showed, under an unchanged operating regime of the latter, that the ratio ${H_2}^+/H_2O^+$ in this case has a value practically coinciding with that indicated above. Thus, the absence of H_2 in the dehydration products of silica gels was definitively confirmed.

As crystalline silica, a powder of rock crystal with a specific surface area of 1.5 m^2/g was studied; it was obtained by grinding large crystals in a porcelain mortar under a layer of water. In this case mass analysis of the gases in the course of powder dehydration showed evolution of a considerable amount of H_2, which rapidly increased with increasing calcination temperature (at 1000°, the ratio ${H_2}^+/H_2O^+$ was about 200%). Evolution of O_2 was not observed. This powder also evolved H_2 after treatment with nitric acid, although to a somewhat lesser extent.

A more detailed study of the evolution of H_2 from the rock-crystal powder (without HNO_3 treatment) was carried out with one and the same charge, which was subjected to fourfold calcination up to 1000-1100° at one- or two-day intervals. During this time the sample was either rehydrated or remained in vacuum. It turned out that hydrogen was evolved during each successive calcination of the powder, regardless of whether its surface had been hydrated or not. The amount of H_2 evolved in each subsequent experiment (both in absolute magnitude and relative to H_2O) decreased monotonically as the total duration of heating increased (Fig. 1). The phenomenon proceeded as though the hydrogen evolved on heating the quartz powder were not of surface origin, but were dissolved in the lattice of natural rock-crystal crystals. This assumption was confirmed quite simply. An equal sample by weight of the same rock crystal was taken, but in the form of large pieces, whose total surface area was approximately 10^4 times smaller than the surface area of the fine powder. On heating these pieces, mass analysis showed the presence of H_2 in an amount close to that observed for the fine powder. Upon repeated heating (without rehydration), appreciable evolution of H_2 was again recorded, although in a smaller amount (Fig. 1).

Fig. 1. Intensity of H_2 evolution from powder (1) and large pieces (2) of rock crystal (in arbitrary units), as a function of calcination duration (number of successive experiments) at 1000°. Experiment No. 1—initial state; No. 2—powder after secondary hydration (large crystals—without rehydration); No. 3—powder without preliminary rehydration; No. 4—powder after the third hydration.

Thus, it should be considered beyond doubt that in all cases of H_2 evolution from crystalline silicas (²-⁴) the observations referred to hydrogen of bulk origin, whose evolution was not connected with the hydroxyl covering of the surface. At the same time, some fraction of the non-freezable combustible gas apparently belonged to CO, since mass analysis invariably showed its presence among the dehydration components of all silicas without exception.

The origin of the oxygen evolved on heating certain silica samples in the high-temperature region remained unclear (⁶,⁷). Since O_2 evolution did not occur from the purest silica gel K-2, nor from rock-crystal powder prepared in the laboratory and not subjected to additional purification, the supposition arose that this phenomenon was caused by the decomposition, on heating, of certain impurities that could not be eliminated even by the most thorough purification. Such impurities could be iron oxides, Fe_2O_3 and others, entering the crystalline quartz powder and technical silica gel during their preparation.

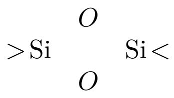
To test this supposition, a sample of pure silica gel (K-2), from which O_2 evolution had not been observed, was contaminated by immersion in a $FeCl_3$ solution and then washed until the reaction for chlorine disappeared. Subsequent mass-spectral investigation of the dehydration of this sample showed evolution of O_2 in appreciable amounts, beginning at 800° and higher, i.e., precisely in the region of the second maximum. NO and H_2 were not detected. Thus, the evolution of O_2 on heating silicas to high temperature was explained as the result of decomposition of an iron oxide impurity.

The investigations carried out show that during thermal decomposition of the surface hydrate of silica nothing other than water is

is released, i.e., centers are formed on the surface in an equivalent amount,

$$>\mathrm{Si{-}O}\cdot \quad (I) \qquad \text{and} \qquad >\mathrm{Si}\cdot \quad (II)$$

Such a surface, irrespective of whether the radicals formed close according to the scheme



$$>\mathrm{Si}\overset{O}{\underset{O}{\qquad}}\mathrm{Si}<$$

or not, cannot possess the oxidizing properties previously found (⁵) for silica-gel samples calcined in air. From this standpoint it was natural to seek the cause of the appearance of the oxidizing properties of the silica surface in the interaction of atmospheric oxygen with dehydrated regions. In this connection we attempted to detect the formation of active forms of oxygen upon contact of atmospheric air with the silica surface under high-temperature conditions. The experiment was carried out as follows: a stream of purified air was passed through a sample located in a quartz tube placed in a furnace, and then through a KI solution. For silica gels treated with HNO_3 vapors at a furnace temperature of 400–500°, liberation of I_2 was observed, which could be attributed to nitrogen oxides in accordance with mass-spectrometric data. For all secondarily hydrated samples, pure silica gel, and quartz, up to a temperature of 900°, liberation of I_2 from the KI solution was not detected.

The formation of a surface possessing oxidizing properties could occur through interaction of atmospheric oxygen with centers (II) and formation of centers (I). In order to exclude possible chemisorption of oxygen from the air, experiments on dehydration of silica gel under high-vacuum conditions were also carried out. The silica gel was calcined in a quartz ampoule connected to a glass comb, to which an ampoule with a previously vacuum-degassed KI solution had been sealed. After cooling, silica gel calcined at 700° was flooded in vacuo with the KI solution by breaking the glass partition separating the solution from the silica gel. The silica gel flooded with KI solution was removed from the ampoule, and the liberated I_2 was titrated with a hyposulfite solution. As these experiments showed, the surface of silica gel dehydrated in vacuo possesses oxidizing properties, just as when it is dehydrated in air. For the sample studied, the oxidizing properties of the surface averaged $1 \cdot 10^{-2}$ μeq/m^2. Thus, the oxidizing properties of the silica surface are not connected with oxygen chemisorption. In accordance with the best shielding of Si^{4+}, as was indicated in (9), oxygen atoms must be located on the silica surface. From this point of view centers (II) are unstable formations. As noted earlier (5), most of centers (I) and (II) close with one another, forming strained regions of the siloxane surface. On the other hand, isolated incomplete SiO_3 tetrahedra (II) apparently change their orientation in such a way that oxygen atoms appear on the surface. This leads to the manifestation of oxidizing properties by the surface of dehydrated silica, and also to the formation of bulk defects.

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CITED LITERATURE

1. W. A. Weyl, Research, 3, 230 (1950).
2. L. Müller, Koll. Zs., 142, No. 2/3, 117 (1955).
3. W. Stöber, Koll. Zs., 145, No. 1, 17 (1956).
4. S. P. Zhdanov, Izv. AN SSSR, OKhN, No. 2, 352 (1959).
5. V. F. Kiselev, K. G. Krasilnikov, E. A. Sysoev, DAN, 116, 990 (1957).
6. A. V. Bondarenko, DAN, 125, No. 3, 573 (1959).

7. A. V. Bondarenko, Vestn. Moskovsk. univ., ser. III, No. 1, 11 (1960).

8. L. M. Roev, A. N. Terenin, DAN, 125, No. 3, 588 (1959).

9. W. A. Weyl, A New Approach to the Chemistry of the Solid State and its Application to Problems in the Field of Silicate Industries, Pennsylvania, 1958.

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