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Abstract

Full Text

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On the Nature of the Surface of Dehydrated Silica Gel

(Presented by Academician M. M. Dubinin, May 4, 1957)

Proceeding from the principles of the construction of the atomic structure of silica and silicates, it was indicated in work (^{1}) that, during thermal dehydration of silica, the formation is possible of a surface containing an excess of oxygen atoms over the stoichiometric ratio. Some experimental data confirming this consideration are given in work (^{2}). It could be expected that such a surface would possess oxidizing properties. We had long ago observed that, upon adsorption by silica gel calcined in air of a number of organic substances that give colored oxidation products, the silica gel became colored, and the intensity of the coloration increased as the calcination temperature was raised. It was of interest to carry out quantitative determinations of the oxidizing capacity of the silica-gel surface as a function of the temperature of its calcination.

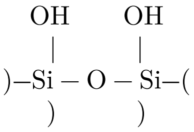
Fig. 1. Oxidizing capacity (A) and oxygen sorption (B) by silica gels KSK-2 (1) and K-2 (2) as a function of their calcination temperature

As objects of investigation we used samples of coarse-pored silica gel KSK-2 ($S = 400$ m^2/g) and K-2 ($S = 695$ m^2/g), studied in detail previously in works (^{3}–^{5}). The specific surface area of all samples was determined by the BET method from adsorption isotherms of nitrogen vapor at its boiling temperature. The oxidizing capacity of silica gel was determined quantitatively by titration, with a 0.01 N solution of hyposulfite, of iodine liberated from an acidified KI solution when the given silica-gel sample was immersed in it. In Fig. 1A are presented the results of measurements of the oxidizing capacity of a unit surface of silica gels calcined at different temperatures in air, simultaneously with the samples used in work (^{3}). As follows from the data obtained, the oxidizing capacity of the surface is very small; the number of oxidizing eq-

valences is three orders of magnitude smaller than the number of equivalents of

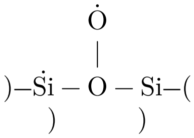
OH groups on the same surface (3). From Fig. 1A it is seen that the oxidizing ability of the surface is different for samples of different degrees of hydration: it is greater for sample KSK-2, with a smaller specific surface area and greater hydration. The number of oxidizing equivalents increases for each of the samples as the calcination temperature is raised.

During thermal dehydration in vacuum of an element of the hydrated surface of silica gel:



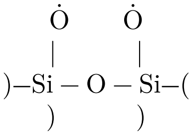
$$\begin{array}{ccccc}\mathrm{OH}&&&&\mathrm{OH}\\|&&&&|\\)\!-\!\mathrm{Si}&-&\mathrm{O}&-&\mathrm{Si}\!-\!(\\)&&&&)\end{array}$$

the formation of the following surface radicals or free valences is possible (1):



$$\begin{array}{ccccc}&&\dot{\mathrm{O}}&&\\&&|&&\\)\!-\!\dot{\mathrm{Si}}&-&\mathrm{O}&-&\mathrm{Si}\!-\!(\\)&&&&)\end{array}$$

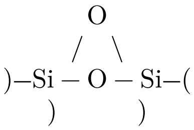
(I)



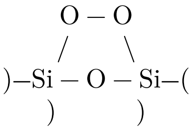
$$\begin{array}{ccccc}\dot{\mathrm{O}}&&&&\dot{\mathrm{O}}\\|&&&&|\\)\!-\!\mathrm{Si}&-&\mathrm{O}&-&\mathrm{Si}\!-\!(\\)&&&&)\end{array}$$

(II)

accompanied by the evolution of water (I) or hydrogen (II). Mass-spectroscopic studies of the dehydration process of silica gel (sample K-2), as well as chemical analysis (6–7) of the gas not condensed by liquid air, established that, in addition to water, hydrogen is present in the products evolved during dehydration of silica gel. The decrease in adsorption activity during dehydration of silica gel in vacuum (8) indicates that the greater part of the free radicals apparently closes up:

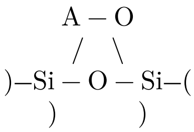


(III)

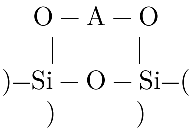


(IV)

During dehydration of the surface in the atmosphere of some gas (A), the interaction of molecules of this gas with active centers of the surface may lead to surfaces of a quite different kind than (I-IV), for example:



(V) or



$$\begin{array}{ccccc}\mathrm{O}&-&\mathrm{A}&-&\mathrm{O}\\|&&&&|\\)\!-\!\mathrm{Si}&-&\mathrm{O}&-&\mathrm{Si}\!-\!(\\)&&&&)\end{array}$$

(VI)

Thus, in the case of thermal dehydration of silica gel in air, as was done in works (3–5), the possible adsorption of nitrogen and oxygen leads to a surface substantially different from the surface obtained in vacuum.

Fig. 2. Heats of wetting of silica gels KSK-2 (1) and K-2 (2), calcined in air (open points) and in vacuum (solid points), as a function of their surface hydration. The dashed line shows data corresponding to standard treatment of silica-gel surfaces (3).

Figure 2: Fig. 2. Heats of wetting of silica gels KSK-2 (1) and K-2 (2), calcined in air (open points) and in vacuum (solid points), as a function of their surface hydration. The dashed line shows data corresponding to standard treatment of silica-gel surfaces (3).

To clarify these questions we carried out quantitative measurements of the adsorption of nitrogen and oxygen on silica gels dehydrated under conditions of high vacuum. The adsorption was measured by the volumetric method. A sample of silica gel was placed in a quartz ampoule and, after preliminary conditioning at 300°, was calcined at the specified temperature to constant vacuum; then a prepared portion of the gas under study was admitted into the ampoule, and the corresponding measurements were made at 20°. As our experiments showed, under these conditions nitrogen is not adsorbed within the accuracy of the measurements ($1 \cdot 10^{-4}\ \mu M/\mathrm{m}^2$). In the case of oxygen (Fig. 1B), the surface of silica gel dehydrated in vacuum at temperatures from 300 to 900° noticeably adsorbs oxygen, and the amount of oxygen adsorbed increases with increasing calcination temperature. The small magnitude of oxygen adsorption, which, apparently,

is adsorbed on surface radicals indicates that the number of the latter is small. It is obvious that the oxidizing properties of the silica surface are manifested through elements (II) and (VI) upon hydration of the latter. Comparison of the data on the oxidizing properties of the surface and on oxygen adsorption on it for the same samples and treatment temperatures shows that, in all the cases studied, the number of oxidizing equivalents is twice the number of moles of adsorbed oxygen. The parallel character of the change in the oxidizing capacity of the surface and in the adsorption of oxygen on it indicates that the same surface centers are probably responsible for both phenomena. If the surface elements (II) are such centers for oxygen adsorption, then, obviously, there must be a definite dependence between the amount of hydrogen evolved from the surface during its dehydration and the amount of oxygen adsorbed on it. In this connection, however, it should be borne in mind that the amount of hydrogen evolved may exceed the amount of adsorbed oxygen owing to the disappearance of a certain amount of radicals formed as a result of surface contraction during calcination, and also owing to the closing of bonds with formation of surface elements (IV). Preliminary experiments carried out by calcination in vacuum up to 800° of silica-gel samples previously pumped off at 300° showed that the amount of hydrogen evolved in this process, taking as such the gas not frozen out at the temperature of liquid nitrogen (6, 7), exceeds by a factor of 2–3 the amount of oxygen subsequently adsorbed on the same surface.

Fig. 2. Heats of wetting of silica gels KSK-2 (1) and K-2 (2), calcined in air (open points) and in vacuum (solid points), as a function of their surface hydration. The dashed line gives data corresponding to standard treatment of the surface of silica gels (3).

Earlier studies (9) showed that, when silica is irradiated with ultraviolet light, free valences are formed on its surface (scheme II), which are centers for oxygen adsorption. Our measurements of photodesorption and subsequent oxygen adsorption after irradiation of silica gel K-2 with light from a PRK-4 mercury lamp fully confirmed these results. The action of short-wavelength radiation and thermal dehydration apparently ultimately lead to surfaces identical in their properties. Contrary to (10), free radicals can form not only as a result of irradiation, but also upon calcination of silica in vacuum.

In connection with the presence, on the surface of silica dehydrated in vacuum, of adsorption centers of high activity, the energetic properties of such samples should differ from the corresponding properties of samples calcined in air. To this end we investigated the heats of wetting by water of silica gels calcined in vacuum at different temperatures, up to 800°. Calcination of the silica gel was carried out in a quartz ampoule connected to a glass manifold with ampoules soldered to it for determining the structural water, the specific surface area, and the heats of wetting. The manifold was sealed off from the vacuum apparatus, and the silica gel in vacuum was poured into ampoules, which were then sealed off. From the data obtained, presented in Fig. 2, it is seen that both silica gels, after calcination in vacuum, give a higher heat of wetting than the same samples calcined in air (3). The difference between the heat of wetting of samples calcined in air

and in vacuum, is considerably greater for KSK-2 silica gel, which has a larger number of active centers than K-2 silica gel, in agreement with the data on oxidizing capacity and oxygen adsorption (see Fig. 1). The heat of wetting of KSK-2 silica gel, in contrast to the case of its calcination in air, increases as the surface is dehydrated. It follows from this that on the surface of silica gel dehydrated in vacuum, centers are formed with higher adsorption activity than OH groups.

The data we have obtained agree with the conclusions of the authors of works ([11], [12]), in which, on the basis of a study of the infrared spectra of water adsorbed on porous glass calcined in vacuum, centers of high activity (centers of the second type) were established. It should be noted that the difference between the surfaces obtained upon dehydration of silica gel in air and in vacuum is not exhausted solely by the centers on which oxygen adsorption occurs, but apparently also extends to other regions of the dehydrated surface. The study of these questions will be the subject of a separate communication.

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