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1962

SovietRxiv

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Abstract

Full Text

PHYSICAL CHEMISTRY

K. G. KRASILNIKOV

ON THE SORPTION OF WATER VAPOR ON CALCIUM HYDROSILICATES

(Presented by Academician P. A. Rehbinder, 28 XI 1961)

Most work on the investigation of the system $CaO—SiO_2—H_2O$* at temperatures of 15–30° and atmospheric pressure has been directed mainly toward clarifying the ratios of the first two components in the precipitates and determining the composition of the corresponding equilibrium solutions. The question of the nature of the bond of water in the hydrosilicates formed remained least clear. In the few works devoted to the investigation of equilibrium states between hydrosilicates of various composition and water vapors ([1,2]), because of the small number of measurements carried out and the imperfection of the method used, sufficiently clear data had not yet been obtained. In this connection, we undertook systematic studies of the equilibrium isotherms of sorption and desorption of water vapors on samples of low-temperature forms of calcium hydrosilicates of different basicity (C/S = 0.1–1.0).

The samples were obtained by interaction of pure coarse-pored silica gel with calcium hydroxide in pre-calculated ratios. The powders were placed in glass vessels, flooded with water, and periodically shaken at room temperature for 6 months. During this time, as analyses of the solutions above the precipitates showed, in accordance with ([3]), equilibrium states were reached up to compositions with C/S = 0.8. The precipitates obtained were filtered off and dried over $CaCl_2$. Then all samples were degassed on a vacuum apparatus to $1 \cdot 10^{-2}$ mm Hg and used for determining the content of "structural" water (by igniting weighed portions at 1150° ([4])), as well as the value of the specific surface area (from data on low-temperature adsorption of nitrogen by BET).

Fig. 1. Sorption isotherms of water vapor at 18° on: **1** –the initial silica gel, **2** –a sample with C/S = 0.35, **3** –a sample with C/S = 1.0. Black dots –desorption.

Fig. 2. Initial sections of water-vapor sorption isotherms at 18° on samples with C/S = 0.1–1.0. Black points–desorption.

Figure 2: Fig. 2. Initial sections of water-vapor sorption isotherms at 18° on samples with C/S = 0.1–1.0. Black points–desorption.

The sorption and desorption isotherms of water vapor were obtained on an adsorption apparatus with quartz spring balances. The equilibrium state for each experimental point was established in a time of about 6 h. In all operations, measures were taken to protect the preparations from the action of atmospheric CO_2.

The processes occurring during the interaction of silica gel with a $Ca(OH)_2$ solution lead to a disturbance of its initial structure. As follows from comparison of the capillary-condensation region of the isotherms shown in Fig. 1, the porosity characteristic of the initial silica gel decreases noticeably, reaching a minimum value for the sample with C/S = 1.0. The change in sorption capacity (from the desorption branch of the isotherm) in the interval $P/P_s = 0.7$—1.0 is 0.75 cm^3/g for silica gel, and only 0.16 cm^3/g for the sample with C/S = 1.0. With increasing basicity of the samples, their specific surface area also decreases: thus, for the initial silica gel $s = 245$ m^2/g, while for the sample with C/S = 1.0 it is 43 m^2/g.

Fig. 2. Initial sections of water-vapor sorption isotherms at 18° on samples with $C/S = 0.1$—1.0. Black points–desorption.

The noted change in the structure of the samples is associated with an increase in the volume of the solid phase–siliceous material–at the expense of the other two components that are included in the newly formed solid phases. The crystals of hydrosilicate, as they grow, first of all fill the pore spaces between individual particles and, in the case of contact, fuse with one another. An increase in the size of the hydrosilicate crystals in comparison with the primary particles of the initial silica gel was also established by electron-microscopic observations (5). The sorption hysteresis for all samples, in contrast to pure silica gel, extends down to the very lowest pressures and is at the same time completely reversible. This phenomenon is usually observed for sorbents whose structure changes during vapor sorption. It is known that "swelling" crystals of calcium hydrosilicate when the water content in them changes leads to a change in the parameters of the crystal lattice (2).

Attention is drawn to the appearance of steps on the desorption branch of the isotherms at $P/P_s = 0.35$ (5.4 mm Hg, 18°) for all the samples studied, and the

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* In what follows, the following conventional designations are adopted: CaO – C, SiO_2 –S, and H_2O –H.

Fig. 3. Water content in samples with different C/S ratios: 1 –total at $P/P_s = 0.37$; 2 –in the original samples after evacuation; 3 –corresponding to the vertical sections in the isotherms of Fig. 2 ($P/P_s = 0.30$—0.37).

Figure 3: Fig. 3. Water content in samples with different C/S ratios: 1 –total at $P/P_s = 0.37$; 2 –in the original samples after evacuation; 3 –corresponding to the vertical sections in the isotherms of Fig. 2 ($P/P_s = 0.30$—0.37).

height of the vertical section of the step increases as the C/S ratio increases. This effect is evidently caused by the properties of the crystals of calcium hydrosilicate present in the preparations. It may be assumed that the step we have found appears owing to a bulk hydrate that is stable at high values of P/P_s, and that, when the relative pressure is lowered to $P/P_s = 0.35$, decomposes at a constant vapor pressure. On the other hand, these hydrosilicates may also be regarded as porous crystals which, unlike zeolites, do not possess a rigid framework, but form a mobile layered structure. Water molecules, penetrating between the layers, are apparently bound, as in zeolites, by the cations of the lattice. The distance between the layers changes depending on the amount of water absorbed. From this point of view, hydrosilicate crystals possess an external surface, determined, for example, from the nitrogen adsorption isotherm, and an internal surface, which is accessible only to water molecules. The sorption hysteresis observed for the hydrosilicates (Fig. 1) is due in origin to such a "bidisperse" structure of the samples–relatively large gaps between individual crystals and cavities associated with the structure of the crystals themselves. As already indicated, the specific surface area of the samples, calculated from nitrogen-vapor adsorption data, decreases with increasing basicity, whereas the adsorption of water vapor, on the contrary, increases.

Fig. 3. Water content in samples with different C/S ratios:
1 –total at $P/P_s = 0.37$; **2** –in the original samples after evacuation; **3** –corresponding to the vertical sections in the isotherms of Fig. 2 ($P/P_s = 0.30$—0.37).

Applying the concepts of the BET theory formally to the case of adsorption of water vapor, one can obtain the value of the capacity of the "monomolecular layer," which for a sample with $C/S = 1.0$ is about 2.8 mM/g or 65 μM/m^2, based on the specific surface area of the sample given above. Since this value considerably exceeds the possible limit determined by the surface concentration of oxygen or hydroxyl ions at the closest packing (for example, corundum (^{6}), etc.), it must be considered that water in the hydrosilicates studied by us enters into their bulk structure. Thus, sorption of water vapor on the hydrosilicates studied occurs mainly not at the expense of the external surface of the crystals, but is determined by the peculiarities of their crystal structure.

The data obtained show that water in hydrosilicates of this series is bound in different ways. Most strongly bound is the water which is not removed in vacuum and can be released only by heat treatment at high temperatures. Apparently, the release of this water occurs at the expense of OH groups entering into the structure of the hydrosilicate crystals. The amount of such water for samples with $C/S = 0.8—1.0$ is 1.0–1.1 H/S. Figure 2 gives the initial portions of the isotherms for all the samples studied, where the total water content, as in (^{2}), was referred to 1 mole of SiO_2. Considering the desorption branches of the isotherms (Fig. 2), it can be seen that the beginning of dissociation of the crystalline hydrate corresponds to the transition to the vertical part of the step on the isotherm. In this case, for samples with $C/S = 0.8—1.0$ the H/S ratio is 2.5–2.8. The water contained in the samples at $P/P_s = 0.34—0$ probably enters into the composition of the defective structure, without forming

in this case, of a regular crystalline hydrate as an individual solid phase (7).

Figure 3 shows the dependence of the molar ratios H/S on C/S in the range 0.1-1.0. It follows from Fig. 3 that the amount of firmly bound water (curve 2) is not proportional to the amount of calcium oxide absorbed, as would be expected if only one hydrosilicate were formed in this region. The initial slope of the straight line $dH/dC = 1.4$ decreases by a factor of two at $C/S = 0.5$ and thereafter is 0.7. The same is true for the water corresponding to the regular crystalline hydrate. In Fig. 3 (curve 3), vertical segments are plotted on the desorption isotherms (Fig. 2) in the interval P/P_s = 0.305-0.370. As can be seen, curve 3 also undergoes a break at $C/S = 0.5$, its initial slope $dH/dC = 0.63$ increasing by a factor of two and becoming equal to 1.3. The total amount of water, however, depends almost linearly on the basicity (curve 1). It follows from this that, beginning with $C/S = 0.5$, a redistribution of water among the forms of binding takes place: water from the more strongly bound form passes into a crystalline hydrate with a weaker bond. In the studied region of C/S, at least two solid phases are formed, differing in their composition and structure: a hydrosilicate with the limiting ratio $C/S = 0.5$ and a hydrosilicate (hydrosilicates) existing in the interval C/S = 0.5-1.0. This conclusion agrees with earlier studies of the composition of solutions in equilibrium with precipitates in the same interval of C/S (3).

The author expresses gratitude to Academician P. A. Rehbinder and O. I. Lukyanova for their interest in this work and for discussion of the results.

Moscow State University
named after M. V. Lomonosov

Received
23 XI 1961

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