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SELECTIVE SORPTION ON POROUS GLASSES

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Selective sorption, caused by the molecular-sieve action of an adsorbent, is usually considered a specific property of porous crystals—zeolites. However, studies of the sorption of various substances carried out by us earlier ([1],[2]) and in the present work on porous glasses indicate that the capacity for selective sorption is also characteristic of certain porous glasses, which behave as typical molecular sieves. Such porous glasses can be obtained as a result of leaching, in acid solutions, two-component alkali-silicate glasses, as well as alkali-borosilicate glasses of definite compositions.

Figures 1 and 2 give the sorption isotherms of water, alcohols, nitrogen, and certain hydrocarbons on porous glasses Nos. 2 and 3, obtained by treatment with 1N HCl of potassium-silicate glasses differing in their content of K_2O. Figure 3 refers to porous glass No. 1, obtained in an analogous manner from sodium-silicate glass. Separately, in Fig. 3a, are shown the sorption isotherms of water and nitrogen belonging to another sample of porous glass No. 1. Measurements of the adsorption of water, alcohols, and hydrocarbons were made at 18°, and of nitrogen adsorption at −195.6°, on gravimetric (water, alcohols) and volumetric (hydrocarbons, nitrogen) vacuum sorption apparatuses. Samples of porous glasses* were heated before adsorption in vacuum to 100 or 200°.

In addition to CH_3OH and C_4H_9OH, the sorption of C_2H_5OH was also investigated. The corresponding isotherms are not given in Figs. 1-3, since, owing to the extremely slow uptake of C_2H_5OH, the experimental points cannot be considered fully equilibrated. For the same reason, some points of the butanol sorption isotherm on glass No. 2 may be nonequilibrium.

The amount of ethanol absorbed at $p/p_s = 0.2$** by porous glasses Nos. 1, 2, and 3 is approximately: 0.042, 0.120, and 0.032 cm^3/g, respectively. As is evident from the figures and from these data, water and methyl alcohol, whose molecules have the smallest dimensions among the substances studied, are sorbed by the porous glasses to a considerably greater extent than the larger molecules C_2H_5OH, hydrocarbons, and especially C_4H_9OH. It follows from this that the selective sorption observed on these porous glasses is due to the presence in them of very fine pores, the diameters of which are comparable with the sizes of simple molecules. An estimate of the pore sizes of porous glasses Nos. 1 and 3 can be made from the data on the sorption of water and nitrogen

Fig. 1. Selective sorption on porous glass No. 2, obtained from potassium silicate glass.

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on them. These porous glasses, like Linde 4 Å molecular sieve, absorb water well and sorb almost no nitrogen (at −196°). Evidently, these porous glasses, as well as the porous crystals—zeolites, must be characterized by very uniform pores with an extremely narrow distribution curve of their diameters.

* The greater part of the porous glasses was obtained and kindly made available to us by Yu. A. Shmidt. The authors express their gratitude to him.

** Expressed in cubic centimeters of liquid of normal density.

Since the diameter of an H_2O molecule is about 2.8 Å, and the diameter of an N_2 molecule about 4 Å, the pore diameters of these porous glasses must lie within the range 2.8 Å-4 Å. Porous glass No. 2 has pores of somewhat larger size, but even in this case they are so fine that the greater part of their volume remains inaccessible to the comparatively small molecules C_4H_9OH ($d = 5.8$ Å[3]) and the hydrocarbons C_5.

The question arises: how can the formation of such uniform pores of such small dimensions in porous glasses be explained? Cavities and channels of molecular dimensions found in zeolite crystals are voids in the crystal lattice between the silicon- and aluminum-oxygen tetrahedral structural elements that form it and are combined in a definite way but packed insufficiently densely, as well as their groups. The cations of alkali and alkaline-earth metals, which compensate the negative charge of the aluminosilicate tetrahedral elements and are located in these voids, do not occupy their entire volume, and a considerable part of it remains free and is filled with water molecules. Removal of water upon heating the zeolite leads to the liberation of cavities, but is not accompanied by any changes in its crystal structure.

Fig. 1. Selective sorption on porous glass No. 2, obtained from potassium silicate glass.

The structure of alkali silicate glasses is also formed by silicon-oxygen tetrahedral elements bonded to one another, in the voids between which cations of alkali metals are located. However, the packing density of oxygen in glasses is so great that not only the sites occupied by alkali cations, but also the free voids of the silicon-oxygen network of the glass remain inaccessible for the sorption of even such small molecules as water molecules. These glasses become porous and acquire the ability to absorb only after they have been leached by treatment with acid solutions. The leaching process begins with exchange of the alkali cations of the glass for protons of the acid. For example, for sodium silicate glass this process may be represented by the scheme:

Fig. 2

Figure 2: Fig. 2

$$\begin{array}{c} | \\ -\mathrm{Si}-\mathrm{O}^{-}\mathrm{Na}^{+} + \mathrm{H}^{+} \longrightarrow -\mathrm{Si}-\mathrm{OH} + \mathrm{Na}^{+} \\ | \quad \text{glass} \quad \text{solution} \quad | \quad \text{glass} \quad \text{solution} \end{array}$$

At a sufficiently high content of SiO_2 in the glass, leaching by treatment of the glass with acid solutions should not be accompanied by destruction of the Si–O–Si bonds in the silicon-oxygen network of the glass. A number of sufficiently well-founded considerations may be advanced in support of these views ([2,4,5]). One of the most convincing confirmations is the production, as a result of leaching, of crystalline sodium disilicate ($Na_2Si_2O_5$) and of the likewise crystalline hydrate of silica–disilicic acid ($H_2Si_2O_5$).

Therefore, the formation of extremely fine channels in the silicon-oxygen network of the glass as a result of leaching cannot be attributed to ruptures

bonds Si–O–Si and their rearrangement. The appearance of such channels in glass could be the direct result of the extraction from the glass, during leaching, of large alkali ions and their replacement, according to the scheme given above, by incomparably smaller protons. In this case one should expect an increase in the pore volume with an increase in the content of alkali oxide in the glass and with an increase in the ionic radius of the alkali cation. Indeed, both dependences can be traced in porous glasses obtained as a result of leaching lithium-, sodium-, and potassium-silicate glasses of different compositions.

Fig. 2. Selective sorption on porous glass No. 3, obtained from potassium silicate glass. 1 –H_2O; 2 –CH_3OH; 3 –C_4H_9OH; 4 –N_2; 5 –*n*-C_5H_{12}; 6 –*iso*-C_8H_{18}

Thus, increasing the content of Na_2O in the glass from 20 to 25 and 33% leads to an increase in the total pore volume of the leaching products, determined from the limiting value of water sorption, respectively from 0.062 to 0.076 and 0.157 cm^3/g. The pore volumes of porous glasses obtained from potassium silicate glasses of analogous compositions are, respectively: 0.120; 0.140 and 0.210 cm^3/g. From lithium glass containing 33% Li_2O, a porous glass with a pore volume of 0.068 cm^3/g is obtained, i.e., considerably smaller than that of the corresponding sodium and especially potassium glass.

However, the pore volumes determined from the water sorption isotherms in all cases prove to be 2-3 times greater than the total volume of the cations extracted from the glass during leaching. This circumstance is due not only to the fact that the volume of the cavity released in the glass after the alkali cation passes into solution must in all cases be greater than the intrinsic volume of the cation. Of much greater importance here is the secondary process of water synthesis

Fig. 3

Figure 3: Fig. 3

from closely situated hydroxyls formed in the glass after the replacement of randomly distributed alkali cations by protons. The water formed in this way at low temperatures remains in the glass, but when the porous glass is evacuated it is released already at room temperature, freeing some additional pore volume as a result of the partial removal, together with the water molecules, of oxygen from the glass that had entered into their composition. The representation—

Fig. 3. Selective sorption on porous glass No. 1, obtained from sodium silicate glass. Separately (*a*) are shown the sorption isotherms of water and nitrogen on another sample of porous glass No. 1.

information on the low-temperature dehydration of porous glasses obtained by leaching sodium-silicate glasses follows from analysis of the curves of their dehydration in vacuum ([2]).

Thus, the appearance of extremely fine channels of molecular dimensions in alkali-silicate glasses as a result of their treatment with acid solutions is due to the extraction from the glass of alkali cations located in the voids of the silica-oxygen network, and to the subsequent removal, together with water, of part of the oxygen that had been a constituent of the glass. Porous glasses capable of selective sorption are inferior to porous crystals (zeolites) in the volume of their sorption space; however, owing to the specific features of porous glasses and the possibility of deliberately controlling their structure, the latter can supplement and expand the existing set of molecular sieves—porous crystals—and may prove suitable for those cases of mixture separation in which porous crystals cannot be used.

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