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The content of the adsorption centers of high-silica porous glasses

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Abstract. Changes in the specific surface, pore size and content of Lewis (siloxane) and Brønsted (silanol) surface groups for high-silica nanoporous glass with a sponge-corpuscular structure depending on their thickness and storage time are studied and interpreted in terms of porous structure features, hydration and aging effects.

Keywords: two-phase alkaline borosilicate glass, porous silica glass, siloxane and silanol groups, Brønsted centers, Lewis centers, indicator method

1. Introduction

High porous silica glass is a product of chemical etching of two-phase alkaline borosilicate (ABS) glass. Due to its structure, porous glass (PG) is a unique nanoporous material, widely used as adsorbents for various purposes and matrices for the synthesis of composites with desired properties [1-3]. PGs have a highly developed surface formed by liquation channels of a chemically unstable phase extracted by acid treatment of the original glass, and colloidal particles of the “secondary” silica inside the pore space. The presence of active centers on the surface of PG, particularly including siloxane and silanol groups, can be used for the modification and adjustment of PG surface composition and properties.

The study of PG surface composition and its effect upon the target properties is particularly important for such applications as membrane filters, including the effect of storage time in aqueous media.

2. Materials and methods

In this study, PG NFF of the composition (mol.%) $0.17\text{Na}_2\text{O} \cdot 5.96\text{B}_2\text{O}_3 \cdot 93.75\text{SiO}_2 \cdot 0.07\text{P}_2\text{O}_5 \cdot 0.05\text{F}$ was obtained by acid (HNO_3 solution) etching of the original two-phase alkali borosilicate glasses of the composition (mol.%) $6.8\text{Na}_2\text{O} \cdot 22.1\text{B}_2\text{O}_3 \cdot 70.4\text{SiO}_2 \cdot 0.19\text{P}_2\text{O}_5 \cdot 0.52\text{F}$ (thermal treatment $550^\circ\text{C}/40$ hrs) [4], kept in water for a long time. Then the measurements of the specific surface were taken and the PG samples were examined for the presence of active centers on the surface formed by siloxane Lewis base centers (LBC) and silanol groups (Brønsted acid centers (BAC)). The specific surface was measured by the method of thermal desorption of nitrogen on a



specific surface analyzer “Sorbto-meter-M” with subsequent calculation according to BET method. The pores size in the studied PGs was measured using the Barrett–Joyner–Halenda method.

The study of surface active centers of various acidic forces was carried out using the indicator method [5] based on the selective adsorption of acid-base indicators from aqueous solutions on the surface of solids. For the studied PG samples, this technique was used to determine the content of LBC with pKa -0.3 (indicator *o*-nitroaniline), corresponding to oxygen atoms in the siloxane bridging groups $\equiv\text{Si}-\text{O}-\text{Si}\equiv$, and BAC with pKa 2.5 (indicator *m*-nitroaniline), corresponding to acidic hydroxyl (silanol) groups $\equiv\text{Si}-\text{OH}$.

The amount of indicator adsorbed from the solution on the surface of the PG NFF (composition indicated above) was determined by the change in the optical density of the solution using an SF-56 spectrophotometer (LOMO, St. Petersburg) in quartz cells relating to distilled water as a blank solution. The content of the studied centers was calculated on the basis of the measured changes in optical density of the corresponding indicator solution as:

$$q(\text{pK}_a) = \left| \frac{A_0 - A_1}{m_1} \pm \frac{A_0 - A_2}{m_2} \right| \cdot C_{\text{ind}} \cdot V_{\text{ind}} / A_0$$

where C_{ind} is the concentration of the indicator solution ($\text{mmol} \cdot \text{l}^{-1}$), V_{ind} is the volume of the indicator solution (ml), A_0 is the optical density of the initial solution of the indicator (blank), A_1 is the optical density of the indicator solution after contact with the immersed PG sample (change in A due to the adsorption of the indicator on the sample surface and the change in the pH of the medium when PG sample comes in contact with water), A_2 is the optical density of the indicator solution added to water decanted after contact with the PG sample (the change in A is only due to the change in pH when PG contact with water, which allows to exclude the influence of this factor in the calculation).

3. Results and discussion

The obtained data summarized in Table 1 indicate that the studied characteristics significantly depend on the sample thickness and storage time in water.

Table 1. Characteristics of PGs depending on their thickness and storage time in water.

Time of water storage	Thickness	S, m ² /g	Pore size r, nm	Q				Q _{2.5} /Q _{-0.3}
				pK _a = -0,3		pK _a = 2,5		
				nmol/g	nmol/ m ²	nmol/ g	nmol/ m ²	
5 days	1 mm	52.4	5.4	690	13,2	1810	34,5	2,6
5 days	2 mm	61	5.1	990	16,5	1240	20,3	1,25
3.5 months	2 mm	40.3	5.1	500	12,4	1170	29,0	2,3

Generally, for all the samples LBC content is higher compared with BAC. The increase of PG plate thickness (comparison of the samples stored for 2 days) results in almost 3-fold increase of the pore size, reduction of LBC (silanol) content and growth of LBC (siloxane) amount, suggesting that deep and probably more tortuous pores in the thicker sample are initially less hydroxylated compared with those in the thinner glass. However, the subsequent storage (3.5 months) of 2 mm thick sample results a significant decrease in its specific surface and content of both LBC and BAC, with a relative growth of BAC, probably due to recondensation of colloidal silica inside the pore space and a gradual

hydration. The obtained results are consistent with the phenomenon of "aging" known in silica chemistry [6–11], particularly relating to microporous glasses in respect of dissolution-deposition of secondary SiO₂ in their pores, which are filled with capillary-condensed water absorbed from air due to a considerable solubility of SiO₂ in water even at room temperature [8].

4. Conclusions

It was found that prolonged water treatment of high-silica porous glasses leads to a decrease in surface area of porous glasses and a change in the ratio of silanol and siloxane groups. The obtained data make it possible to assess the prospects for the use of composite materials based on PG for selective filtration.

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