

THE INFLUENCE OF LONG ADDITIONAL THERMAL TREATMENT OF CONTROLLED POROUS GLASSES ON THE STRUCTURALIZATION OF THEIR SILICA NETWORK

A. L. Dawidowicz and S. Pikus

INSTITUTE OF CHEMISTRY, MARIA CURIE-SKŁODOWSKA UNIVERSITY,
SQ. MARIA CURIE-SKŁODOWSKA 3, 20-031 LUBLIN, POLAND

(Received January 20, 1986)

The materials used as sorbents in gas and liquid chromatography include controlled porosity glasses (CPG). The heating of CPG in the temperature range 400–800 °C leads not only to dehydroxylation of their surface, but also to a diffusion of the boron atoms (and a smaller amount of sodium atoms) remaining in the silica network of the CPG towards the glass surface. Simultaneously, crystallization of the silica network of the CPG takes place.

The present paper deals with the changes of the crystallographic structures in thermally treated glasses which differ in their mean pore diameters. The results show not only the existence of cristobalite in the siliceous lattice of the heated glasses, but also the presence of α -quartz, the very symmetrical structure of SiO_2 .

Materials very often applied as sorbents, supports, catalysts or column packings for chromatography are controlled porous glasses (CPG). Their usefulness results from their chemical, mechanical and thermal resistance [1, 2].

CPG are usually obtained by appropriate thermal treatment and the leaching of Vycor-type glass ($\text{R}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, where $\text{R}_2\text{O} = \text{Li}_2\text{O}$ or Na_2O or K_2O) [1, 2].

During thermal treatment, phase separation takes place in Vycor glass. In the continuous silica structure, the continuous alkali metal borate phase is formed. The latter can be removed from the thermally treated Vycor glass by means of a leaching process [1, 2]. As a consequence of this procedure, porous materials (CPG) are obtained. The pore diameter in the CPG depends on the composition of the initial glass, the duration and temperature of thermal treatment (i.e. the prehistory of the liquification process), and the leaching procedure of the Vycor glass [1, 2]. The porous networks of CPG are composed mainly of SiO_2 (ca. 94–98%) and residual amounts of R_2O (ca. 0.1–0.5%) and B_2O_3 (1–6%). Additionally, their porous structure is completely different from that of silica gels [1]. The two materials also differ in thermal behaviour. During the thermal treatment of the CPG (in the

temperature range 400–800°), sodium and boron atoms remaining in the porous structure of the CPG diffuse from the bulk to the surface [1–5].

It appears [1, 6, 7] that the heating of porous glasses at above 500° leads not only to the enrichment of the CPG surface in boron and sodium atoms, but also to the formation of cristobalite in the siliceous structure of the CPG. This is a result of the mentioned diffusion process. The diffusion of sodium and boron atoms causes the structuralization of the silica lattice constituting the porous structure of the CPG. Certain published data suggest that the amounts of α and β -cristobalite formed depend on the duration and temperature of heating.

The present paper deals with the changes in the crystallographic structures in the lattices of CPG (with different pore diameters) during their thermal treatment.

Experimental

Materials

Three porous glasses with different mean pore diameters (resulting from various processes of liquification and phase separation [1, 2]) were employed in the investigation. These materials were obtained by heating Vycor glass (7% Na₂O; 23% B₂O₃; 70% SiO₂) at 600° for 12, 16 or 30 hr (glasses 12/600, 16/600 and 30/600), respectively. The heated glasses were leached according to the previously described procedure [8, 9]. The physicochemical properties of the porous glasses obtained are presented in Table 1.

Table 1 Specific surface areas, mean pore diameters and sodium oxide and boron oxide residue in porous skeleton

| Glass | Specific surface area, m ² /g | Mean pore diameters | Boron oxide and sodium oxide residue, % wt |
|--------|---|------------------------|---|
| 12/600 | 87 | 22 nm | 1.96 B ₂ O ₃ , 0.32 Na ₂ O |
| 16/600 | 59 | 32 nm | 2.34 B ₂ O ₃ , 0.41 Na ₂ O |
| 30/600 | 45 | 46 nm | 3.78 B ₂ O ₃ , 0.43 Na ₂ O |

In order to induce the crystallization process in the prepared porous glasses, portions of the individual glasses were heated at 700° over various periods of time.

Methods

X-ray patterns of the investigated glasses were obtained on a DRON-3 diffractometer using a CuK _{α} radiation lamp with a Ni filter. For identification of the

crystallographic phases, the interplanar d spacings were calculated from the diffractograms obtained. The intensities of selected peaks were also measured.

Specific surface areas were calculated from the BET data obtained with a Carlo Erba nitrogen Sorptomatic 1806 (Milan, Italy).

The mean pore diameters of the prepared sorbents were taken from the porosimetric data. Porosimetric measurements were made with a Carlo Erba type 1500 mercury porosimeter (Milan, Italy).

Boron amounts were estimated with a Carl Zeiss type PGS-2 spectrograph (Jena, GDR). A set of glasses with known, controlled quality and quantity composition was used as standards.

The concentrations of sodium atoms in the investigated samples were measured with a Hilger and Watts atomic absorption spectrophotometer (London, G.B.), applying a hollow cathode lamp.

Results and discussion

The physicochemical properties of the individual initial porous glasses are compared in Table 1. Table 1 shows that an increase of the duration of thermal treatment of the Vycor glass (crude glass used for preparation of the CPG) causes an increase of the pore diameter in the CPG. Simultaneously, the specific surface area decreases with the increase of the mean pore diameter. These processes have been discussed many times [10, 11]. The quantitative composition of the initial porous glasses reveals the increase of the sodium and boron residues in the porous skeleton of the CPG with the increase of the heating time of the Vycor glass during preparation of the CPG. This can be explained as a result of the better solubility of Na_2O and B_2O_3 in the SiO_2 network of the CPG with the prolongation of the liquification process [1].

In order to induce the crystallization process in the initial glasses, individual samples of the materials obtained were heated at 700° over an increasingly longer period of time. Figures 1, 2 and 3 present parts of the diffractograms corresponding to the initial glasses 12/600, 16/600 and 30/600, and to the same glasses heated for progressively longer periods. Figure 1 additionally contains the X-ray pattern for silica gel heated at 700° for 100 hr. Figures 1, 2 and 3 yield evidence that the heating performed on the porous glasses causes partial crystallization of the CPG. This is manifested by the appearance of peaks in the diffractograms. The general conclusion is that the increase of the heating time leads to a gradually higher crystallization of the glass in the form of α -cristobalite. This is confirmed by the growth of the peak height corresponding to this phase.

A precise comparison of all the Figures reveals large differences between the

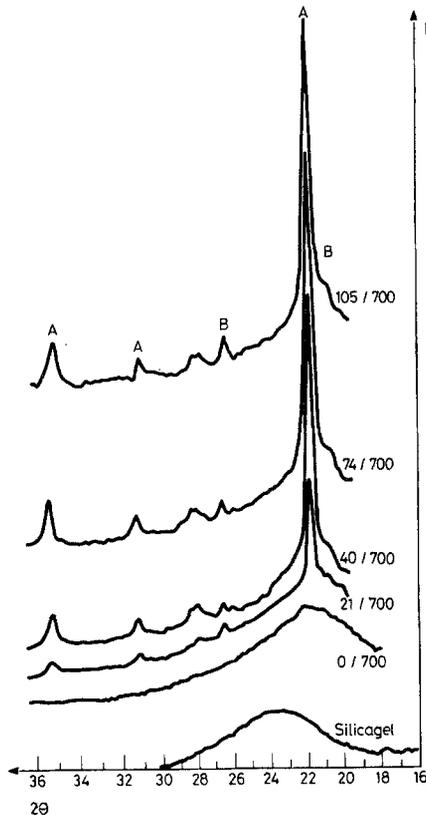


Fig. 1 X-ray patterns for 12/600 glasses heated over different period of time at 700 °C and silica gel heated for 100 hrs at 700 °C. (A) peaks means α -cristobalite, (B) peaks means α -quartz

individual glasses (series 12/600, 16/600 and 30/600) not only in the amounts of cristobalite formed. The formation of α -cristobalite in porous glasses has been described previously [1, 6, 7]. This process is characteristic for CPG and does not occur in silica gel (under the employed conditions), as confirmed by the X-ray pattern for heated silica gel (Fig. 1). It has already been stated [1, 6, 7] that the crystallization process in CPG is connected with the migration of boron and sodium atoms in the siliceous structure of the porous glass. Consequently, structuralization takes place in the silica lattice of the CPG. On analysis of the X-ray patterns of the initial glasses (curves 0/700, Figs 1, 2 and 3), a small amount of α -cristobalite is found only in CPG 30/600. It should be remembered that this porous glass was obtained in the longest liquification process [2, 8], during 30 hr. It is known from the literature [1] that, during the long heating of Vycor glass, crystallization can take

place in the silica phase formed (non-soluble silica network) when phase separation is still continuing.

When the crystallization rate of α -cristobalite is compared with the amount of Na and B atoms remaining in the porous structure of the CPG after the etching process, their mutual dependence is evident (see Figs 1–3 and Table 1). The more Na and B

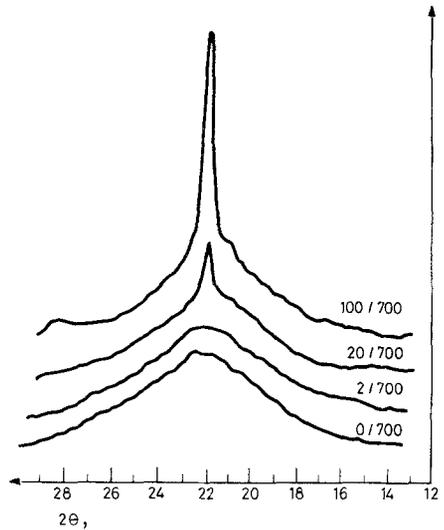


Fig. 2 X-ray patterns for 16/600 glasses heated during 0, 2, 20, 100 hrs at 700 °C. Visible peak belong to α -cristobalite

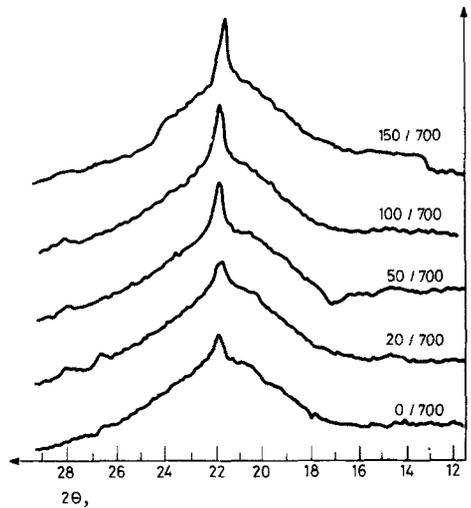


Fig. 3 X-ray patterns for 30/600 glasses heated during 0, 20, 50, 100, 150 hrs at 700 °C. Visible peak is originated from α -cristobalite

left in the siliceous skeleton of the CPG after its preparation procedure, the less α -cristobalite is formed in unit heating time. This is especially clear if glasses 12/600 and 30/600 (Figs 1 and 3, respectively) are compared. In spite of the presence of α -cristobalite in the initial porous glass 30/600, its amount in this glass after 150 hr of heating is lower than in CPG 12/600 additionally heated for only 21 hr.

The X-ray patterns for the series of glasses 12/600 (Fig. 1) are especially interesting. They show the presence of α -quartz ($d = 4.24 \text{ \AA}$; 3.34 \AA) in glass 12/600 after only 21 hr of additional heating at 700° . The amount of this highly symmetrical phase increases with increase of the duration of additional heating, at the cost of a decrease in the amount of α -cristobalite (compare X-ray patterns 40/700, 74/700 and 105/700, Fig. 1).

The different relationships between the crystallization rate vs. sodium and boron residue in the various porous glasses may be a result of the different self-purification rates of the CPG silica skeleton. When the amount of sodium and boron atoms in the CPG structure is smaller, i.e. when the duration of self-purification of the CPG porous structure is higher, the crystallization of the siliceous CPG skeleton may be higher too, and, apart from α -cristobalite, the most symmetrical structure of SiO_2 (α -quartz) can also be formed. α -Quartz formation deserves special notice, as it has previously not been discussed in the literature in relation to thermally treated CPG.

The shape of the diffractogram peaks should also be taken into account. They are high, distinct and narrow. This is especially well seen for the 12/600 series. It proves that the surface area of the crystalline phase involves dimensions considerably larger than 50 nm.

Conclusions

1. These investigations confirmed earlier data [6, 7] concerning the crystallization of thermally treated glasses.
2. The presented data and the results of previous investigations [5, 10] indicate that the crystallization process in CPG does not lead to substantial changes in their porosity.
3. During crystallization, mainly α -cristobalite is formed. The rate of its formation depends not only on the duration and temperature of the thermal treatment [6, 7], but also on the amount of sodium and boron atoms remaining in the CPG.
4. The observed rate of α -cristobalite formation was especially high for glass with low Na_2O and B_2O_3 contents. Moreover, the simultaneous formation of α -quartz was observed in this glass. The presence of α -quartz in thermally treated porous glasses has not previously been discussed.

References

- 1 F. Janowski and W. Heyer, Poröse Gläser, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1982.
- 2 M. B. Volf, Technical Glasses, Pitman and Sons LTD., London 1961, p. 176.
- 3 V. M. Kirutenko, A. V. Kiselev, V. J. Lygin and K. L. Shchepalin, Kinetika i Kataliz, 15 (1974) 1584.
- 4 M. J. D. Low and N. Ramasubramanian, J. Phys. Chem., 71 (1967) 3077.
- 5 A. L. Dawidowicz and S. Pikus, Appl. Surface Sci., 17 (1983) 45.
- 6 W. Heyer, F. Wolf and B. Kluge, Chemische Technik, 30 (1978) 96.
- 7 W. Heyer and F. Wolf, Z. Chem., 18 (1978) 111.
- 8 W. J. Haller, J. Chem. Phys., 42 (1965) 686.
- 9 A. L. Dawidowicz, A. Waksmundzki and A. Deryło, Chem. Anal., 24 (1979) 811.
- 10 A. L. Dawidowicz and J. Choma, Materials Chemistry and Physics, 8 (1983) 323.
- 11 A. L. Dawidowicz, J. Rayss and Z. Supryniewicz, Chromatographia, 17 (1983) 157.

Zusammenfassung — Gläser kontrollierter Porosität (CPG) gehören zu den in der Gas- und Flüssigkeitschromatographie verwendeten Sorbenten. Erhitzen von CPG auf 400–800 °C führt nicht nur zur Dehydroxylierung ihrer Oberflächen, sondern auch zur Diffusion der im Siliciumdioxidgitter des CPG verbleibenden Boratome (und in geringerem Maße auch von Natriumatomen) zur Glasoberfläche. Gleichzeitig erfolgt die Kristallisation des Siliciumdioxidgitters der CPG. Im vorliegenden Artikel werden die Veränderungen der kristallographischen Strukturen in thermisch behandelten, sich im mittleren Porendurchmesser unterscheidenden Gläsern untersucht. Es wird gezeigt, daß im Siliciumdioxidgitter der hitzebehandelten Gläser nicht nur Cristobalit, sondern auch die hochsymmetrische SiO₂-Struktur des α -Quarzes vorliegt.

Резюме — Материалы, используемые в качестве сорбентов в газовой и жидкостной хроматографии, включают стекла с регулируемой пористостью. Нагревание таких стекол в интервале температур 400–800 °C вызывает не только дегидроксилирование их поверхности, но и диффузию оставшихся в сетчатой структуре силикатов атомов бора (в меньшей степени атомов натрия) к поверхности стекла. Одновременно с этим в стеклах происходит кристаллизация силикатного остова. Настоящая работа касается изменений кристаллографических структур в термически обработанных стеклах, отличающихся средним диаметром пор. Результаты исследования показали наличие в решетке силикатов термически обработанных стекол не только кристобалита, но также α -кварца и высоко симметричной структуры двуокиси кремния.