Journal of Thermal Analysis, Vol. 30 (1985) 793–801

THE INVESTIGATION OF THERMALLY TREATED GLASSES OF CONTROLLED POROSITY BY MEANS OF DIFFERENTIAL THERMAL ANALYSIS

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(Received July 30, 1984; in revised form February 14, 1985)

Some of the materials used as chromatography packings, adsorbents or catalyst supports are glasses of controlled porosity (CPGs). The chemical structure of these materials can easily be changed by heating the porous glass. Such thermal modification leads to the enrichment of the CPG surface in boron atoms. The long exposure of CPGs to thermal treatment can even cause the formation of borate crystals in the pores of the glasses. This paper considers the application of thermal analysis to the investigation of porous glasses heated for different periods of time.

Controlled porous glasses (CPGs) are among the most interesting packings used in gas and liquid chromatographic columns. These materials are characterized by strong chemical and thermal resistance. Further, almost any porous structure with a narrow pore size distribution in porous glasses can be obtained [1, 2]. Chemical analysis of the porous skeleton of the glass shows the contents to be SiO_2 ($\sim$97%), B_2O_3 ($\sim$3%) and Na_2O ($\sim$0.5%) [2, 3]. Infrared spectroscopic studies of dehydration and hydration of porous glass surfaces have provided evidence of the existence of B atoms, B—OH groupings and silanol structures on the porous glass surface [2, 3]. It has been found that, if surface hydroxyls play an active role in determining the characteristics of the surface, the existence of B—OH groups is of particular interest, as the reactivity of the silica surface is affected by their presence [4–8]. The characteristic feature of CPGs is the possibility of changing the surface B concentration. This can be accomplished by appropriate thermal treatment of the porous glass [7–9]. During the heating of CPGs in the temperature range 400–800°, the B atoms remaining in the silica network diffuse from the bulk to the surface. The surface is enriched in B atoms. The concentration of surface B atoms is proportional to the time and temperature of heating [7]. It is known [7–9] that long treatment leads even to the formation of B_2O_3 crystals on the CPG surface. The analyses of CPGs subjected to long thermal treatment carried out in our laboratory suggest

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that their surfaces do not contain pure B_2O_3 crystals, but rather a mixture of B_2O_3 and $Na_2O.yB_2O_3$ (borate crystals $xNa_2O.yB_2O_3$).

This paper presents the results of investigations of CPGs by means of thermal analysis. In order to resolve the above question, the measurements were carried out using a series of CPGs with surfaces differently enriched in B atoms, and the results were compared with those for glasses after the removal of borate crystals and for material consisting of silica gel containing a known amount of $Na_2[B_4O_5(OH)_4].8H_2O$ on its surface. Additionally, ASSA and spectrophotometric investigations have been performed to confirm the presence of Na and B atoms on the surface of glasses after long thermal treatment.

Experimental

1. Materials

All types of glass (see Table 1) were obtained from sodium borosilicate Vycor glass [1, 2]. This material was transformed to porous form by appropriate thermal treatment and leaching [1, 10] (glass I).

In order to obtain CPGs with various amounts off B atoms on their surfaces, portions of glass I were additionally separately heated at 700 ± 1° during 13, 38 and 100 hr (glasses II, III and IV, respectively). The specific surface areas of the thermally modified glasses are presented in Table 1.

For comparison of the obtained CPGs with the artificial system composed of silica gel with $Na_2O.B_3O_3$ on its surface, a portion of hydrothermally treated [11] silica gel Si-100 (Merck, Darmstadt) was impregnated with $Na_2B_4O_7$ solution in

Table 1 The specific surface areas and the oxides contents for investigated materials

Materials	Specific surface areas, m^2/g	The amount of Na_2O and B_2O_3 extracted from surface of glass		The amount of Na_2O and B_2O_3 in glass before extraction of surface		The amount of Na_2O and B_2O_3 in glass after extraction of surface	
		Na_2O, μg/m²	B_2O_3, μg/m²	Na_2O, wtg %	B_2O_3, wtg %	Na_2O, wtg %	B_2O_3, wtg %
Glass I	74.5	0.038	0.11	0.53	2.76	0.54	2.77
						2.75*	0.53*
Glass II	60.8	6.97	19.32	—	—	—	—
Glass III	53.6	41.42	158.7	—	—	—	—
Glass IV	42.7	58.12	292.9	0.52	2.73	0.28*	1.68*
Silica gel	122.1	—	—	—	—	—	—

* After extraction of the glass surface by NaOH.

water (0.5 wt %). After evaporation of the water, the silica gel was heated at 700 ± 1° for 50 hr (to dehydroxylate the surface of the silica gel and $Na_2B_4O_7 . 10H_2O$). Under these conditions, the sintering of $Na_2O . B_2O_3$ with the SiO_2 surface can occur, but the same temperature was employed as in the case of the thermal treatment of the CPGs. The amount of $Na_2O . 2B_2O_3$ deposited on 1 m^2 of silica gel surface was 4.1×10^{-2} mg.

2. *Methods*

Specific surface areas were investigated by means of the equipment described in [12]. The measurements were based on the BET method.

The average pore diameters of the obtained materials were measured by means of Carlo Erba (Milan, Italy) 1500 mercury porosimeter.

In order to estimate the presence of sodium borate on the CPG surface, the obtained glasses were extracted with hot 3*n* H_2SO_4 for 10 hr. In one case, in order to remove both borate clusters and a thin layer of silica wall from the CPG surface, portions of glass IV (where the borate crystals are the largest [7, 13]) and glass I were extracted with 0.5*n* NaOH at room temperature for 2 hr. The last operation was performed for the thorough removal of borate crystals from the surface, even crystals sintered with the silica surface.

The B_2O_3 contents were estimated in two porous glasses and in the acidic extraction solutions from the surface of all investigated porous glasses. The separation of B atoms from SiO_2 was carried out as described in [14]. The B content was determined from spectrophotometric measurements (at 550 nm), employing the reaction with curcumin [15].

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

Differential thermal analyse were carried out with a Q–1500 D derivatograph (MOM, Hungary). The heating rate was 0.6 deg/min and 2.5 deg/min in the temperature ranges 20–250° and 250–750°, respectively. The changes in T, DTA and TG were measured. The samples of investigated glasses and gels were placed in corundum crucibles. The atmosphere was air. The mass of sample analysed was 1 g. It should be stressed that all obtained samples had been heated at 700° during their preparation procedure. Consequently, their surfaces were partly dehydroxylated. The DTA results for such thermally treated glasses and silica gels did not differ significantly from the others. For this reason, all materials analyzed by DTA were wetted with a constand amount of water.

Results and discussion

The quantitative and qualitative analysis of the amount of B and various compounds on the surface of CPG after long thermal treatment is a very difficult problem. This results from:

a) the complexity of the triple system SiO_2—B_2O_3—Na_2O,
b) the porous structure of a CPG,
c) the different forms in which B atoms occur (3- and 4-coordinate) [16],
d) the low amount of B atoms in relation to SiO_2 on the CPG surface,
e) the low atomic weight of B.

As mentioned above, some information concerning the presence of B atoms and B—OH groups on the CPG surface is provided by the infrared spectroscopy of pure CPG surfaces and the same surfaces with adsorbed molecules. These results were confirmed by measurements on artificial systems composed of silica gel and B_2O_3 ([17]. There was no possibility to determine the presence of Na atoms by means of spectroscopy.

Figures 1 and 2 present DTA curves obtained for differently thermally treated CPGs containing a constant amount of adsorbed water. Figure 1 shows DTA curves in the temperature range 20–100° recorded at a heating rate of 0.6 degree/min. Although the measurements were carried out up to 250°, there were no significant changes in the investigated parameters, and the range above 100° is not shown in Figs 1 and 2. The DTA curves in Fig. 2 correspond to a heating rate of

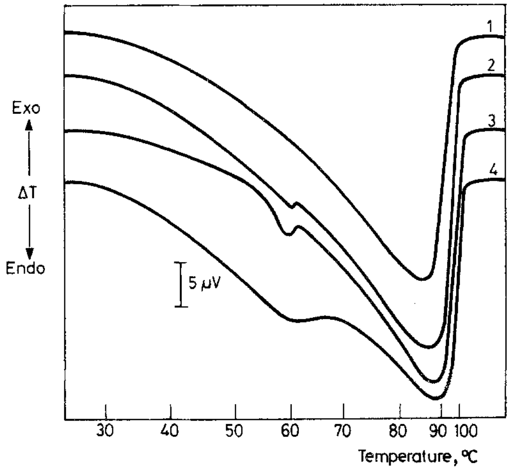

Fig. 1 DTA curves in the temperature range 20–100°C for glasses: I — curve 1, II — curve 2, III — curve 3 and IV — curve 4 wetted with 60 wtg % of water

2.5 degree/min in the temperature range 250–750°. A slow temperature increase was applied at the beginning of the thermal analysis in order to show more explicitly the heat effects in that region. A large endotherm at ~90° for all investigated samples I–IV (see Fig. 1) is connected with the evaporation of water from the surface of the CPG (this is confirmed by a similar DTA curve obtained for silica gel with deposited water—Fig. 3, curve 1).

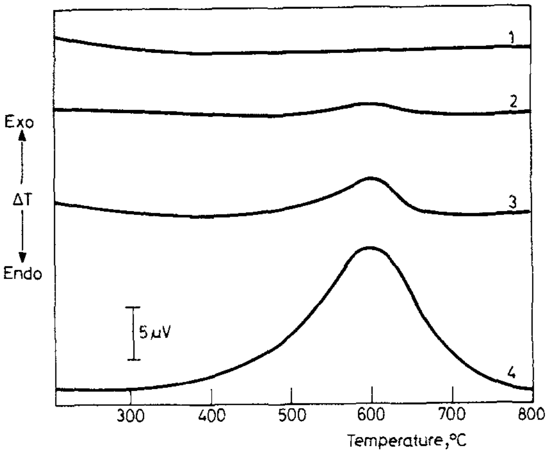

Fig. 2 DTA curves for glasses I, II, III and IV in the temperature range 250–750°C (numbers of curves—see Fig. 1 and text)

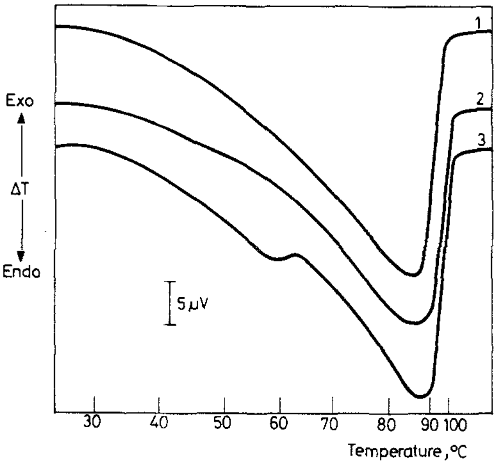

Fig. 3 DTA curves in the temperature range 20–100°C for investigated materials wetted with constant amount of water (60 wtg %): curve 1 — silica gel, curve 2 — glass IV after leaching in 0.5*n* NaOH solution (where borate clusters were removed), curve 3 — silica gel with deposited $Na_2O.2B_2O_3.10H_2O$.

As Fig. 1 shows, there is another endotherm at ~60° in DTA curves 2–4. The magnitude of this heat effect increases with the increase of the duration of thermal treatment of the CPG. The same conclusion can be arrived at from Fig. 2. The DTA exotherm with max at ~600° (Fig. 2, curves 2, 3, 4) increases with the increase of thermal exposure. This exotherm does not exist in curve 1 in Fig. 2 corresponding to initial glass I.

As mentioned before, the silica network of CPG contains a certain amount of Na_2O and B_2O_3. The presented curves suggest that, during the heating of glass with B_2O_3 [7, 9], Na_2O diffuses to the CPG surface, too. The $xNa_2O+yB_2O_3$ system can form many different and complex compounds [18, 19], which are very difficult to investigate, especially in the presence of SiO_2. The characteristic feature of $xNa_2O.yB_2O_3$ is the existence of many heat effects in the $Na_2O.B_2O_3.H_2O$ system [20–22]. For this reason, water was added to the surface of the thermally treated materials (see Experimental). Especially two effects are very strong:

1. Exothermal effects in the range 600–640°.
2. Endothermal effects in the range 59–64°.

The former may be connected with the phase transition in kernite, $Na_2[B_4O_6(OH)_2].3H_2O$, or with the crystallization of $3B_2O_3.Na_2O$ from ameghinite, $3B_2O_3.Na_2O.4H_2O$ [21]. The endothermal effects are characteristic of the changes in hydration of $xNa_2O.yB_2O_3$ [20].

In order to prove that the heat effects presented in Figs 1 and 2 correspond to the $Na_2O.B_2O_3.H_2O$ system, two types of investigation were made:

a) a quantitative analysis of Na_2O and B_2O_3 in the CPG and in the acidic extration solution from the CPG surface;

b) a thermal analysis of the artificial system.

Table 1 shows the specific surface areas, the amounts of Na_2O and B_2O_3 extracted from the CPG surface, calculated per 1 m^2 of the surface, and the Na_2O and B_2O_3 concentrations in the CPG before and after extration. Table 1 reveals that Na atoms exist on the surface of the thermally treated CPG. They are almost absent from the surface of the initial glass I, which confirms the good wash-out of the surface of glass I during its preparation. It appears from the presented data that the increase of the duration of thermal treatment of glass I (see glasses II, III and IV) causes the increase in the amounts of Na and B extracted from the surface. Thus, it can be said that, in parallel with the known effect of the diffusion of B atoms, Na atoms too diffuse to the surface during the thermal treatment of CPG. The analysis of the Na_2O and B_2O_3 contents in glasses I and IV before and after the extraction of the surface confirms the above finding. After the surface extraction, glass IV possesses a lower concentration of the discussed oxides than before the long thermal treatment.

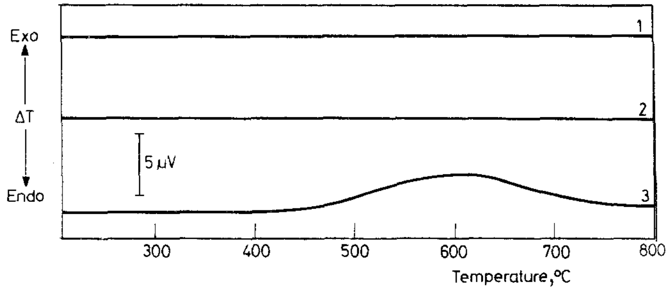

Fig. 4 DTA curves in the temperature range 250–750°C for the same materials as in Fig. 3

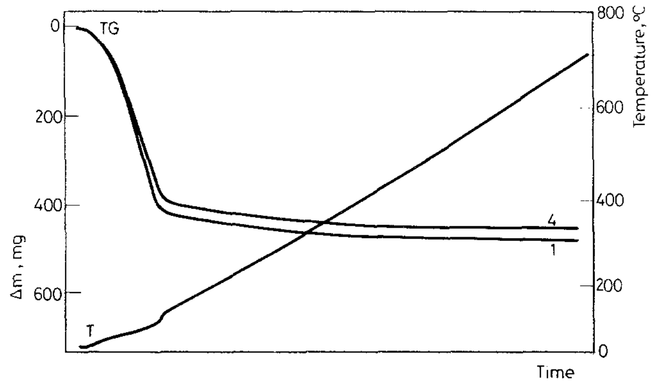

Fig. 5 TG curves of water thermodesorption characteristic for material I – curve 1 and material IV curve 4.

If the heat effects presented in Figs 1 and 2 are connected with the presence of B atoms on the CPG surface, they also should be seen for the silica gel system with deposited $Na_2O.B_2O_3$, but not in the case of pure silica, or CPG with the surface extracted (where borate crystals were removed). The DTA curves for these systems are shown in Figs 3 and 4. The DTA curves in Figs 3 and 4 in the case of silica gel (curve 1) suggest that the heat effects at ~60 and ~600° do not occur. This is also the case for glass IV after its leaching in 0.5*n* NaOH solution where borate clusters were removed (see curve 2 in Figs 3 and 4). Neither endothermal nor exothermal effects are seen at the discussed temperatures. Curves 3 (Figs 3 and 4), corresponding to the artificial system, reveal the presence of both heat effects. The investigations illustrated by Figs 3 and 4 evidently confirm that the discussed DTA peaks for thermally treated glasses result from the formation of the $xNa_2O.yB_2O_3$ system (probably polyborates) on the CPG surface.

In Fig. 5, the TG curves for wetted glasses I and IV are presented (curves 1 and 4, respectively). Although in this paper the borate crystals on the CPG surface have been investigated by means of a derivatograph, it must be stressed that DTA data give more information on the composition of borate surface clusters than do TG data. Since the TG curves for all the investigated glasses are of the same shape, these relationships are presented only for materials I and IV (initial glass I and glass IV, where B is enriched to the maximum degree). The differences in the TG curves for other materials not presented here vary in their sharpness. This probably results from the amount of borate surface crystals and differences in the specific surface areas (see Table 1).

Conclusions

1. The results of the presented investigations show the possibility of employing DTA measurements for the study of CPG surfaces. The complexity of the investigated systems makes DTA measurements more useful than other methods. Combining DTA and TG curves does not give substantial information about the glasses.
2. The DTA results and qualitative analysis prove the presence of the $x\mathrm{Na_2O}.y\mathrm{B_2O_3}$ system on the surface of thermally treated CPG.
3. An increase in the thermal exposure of the CPG leads to an increase in the sodium borate content on the CPG surface, as confirmed by the increase in the relevant DTA peaks and by quantitative analysis.

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Zusammenfassung — Einige der als chromatographische Säulenpackungen, Adsorbenten oder Katalysatorträger verwendeten Materialien sind Gläser mit definierter Porosität (CPGs). Die chemische Struktur dieser Materialien kann leicht durch Erhitzen verändert werden. Eine solche thermische Modifizierung führt zu einer Anreicherung von Bor in der Oberflächenschicht. Eine langdauernde Erhitzung der CPGs kann sogar zur Bildung von Boratkristallen in den Poren der Gläser führen. Im vorliegenden Artikel wird die Anwendung der thermischen Analyse zur Untersuchung von porösen Gläsern in Abhängigkeit von der Erhitzungsdauer behandelt.

Резюме — Некоторые материалы, используемые в качестве набивок хроматографических колонок, адсорбентов или носителей катализатора, являются стеклами с регулируемой пористостью. Химическая структура таких пористых материалов может быть легко изменена путем их нагрева. Такая термическая обработка приводит к обогащению поверхности стекол атомами бора. Длительная термическая обработка стекол с регулируемой пористостью может вызвать даже образование боратных кристаллов в порах стекла. В статье рассматривается применение термического анализа для исследования пористых стекол, подвергнутых различным временам нагрева.