

# Hierarchically structured silica via combination of salt sintering process and phase separation

BJOERN REINHARDT<sup>1</sup>, DIRK ENKE<sup>1</sup>, GERHARD BIENHAUS<sup>2</sup>

<sup>1</sup>Institute of Chemical Technology, University of Leipzig,  
Linnéstraße 3, 04103 Leipzig, Germany

<sup>2</sup>Biosearch Technologies Inc., Tröbach 2, 96523 Steinach, Germany

\*Corresponding author: bjoern.reinhardt@uni-leipzig.de

Hierarchically structured, porous glass monoliths have been prepared successfully via combination of a salt sintering process and phase separation of a sodium borosilicate glass. The materials were characterized by N<sub>2</sub>-adsorption, Hg-intrusion and scanning electron microscopy. Secondary pore sizes were adjusted by the use of different grain fractions of the filler, different primary pore sizes could be obtained by a variation of the annealing conditions. Thus, both pore systems could be adjusted independently. The resulting monoliths consist of a system of secondary pores between 20 and 150 µm and primary pores within the walls of the open-pored sintered material between 1 and 70 nm. The hierarchical porous materials exhibit surface areas up to 420 m<sup>2</sup>g<sup>-1</sup> and total porosities up to 74%. Various shapes, *e.g.*, rods, plates and granules were obtained by using appropriate pressing tools.

Keywords: sintering, phase separation, borosilicate glass.

## 1. Introduction

Materials with a polymodal hierarchical pore structure have potentially a wide range of practical applications in various fields such as catalysis, separation processes, biomaterials and sensors. Controlled porous, hierarchical materials can be prepared via phase separation in a modified sol–gel process [1], via pseudomorphic transformation of porous glasses [2] or by an addition of soot particles to zeolite crystals [3]. But the pore sizes of these materials can be adjusted only in a small pore range and shaping is only possible to a minor extent. Therefore, during the last years there was a considerable effort to develop materials with hierarchical pore structures and flexible geometric shapes.

In this paper we report the preparation of porous, hierarchically structured materials by using a combination of a salt sintering process [4] and phase separation of a sodium

borosilicate glass [5]. Thereby, this process offers an opportunity to adjust pore sizes of both pore systems in a wide range in accordance with the textural properties of open-pored sintered glasses and porous glasses. The textural properties of the resulting materials were characterized by Hg-intrusion, N<sub>2</sub>-adsorption and environmental scanning electron microscopy (ESEM).

## 2. Experiment

### 2.1. Materials

Alkali borosilicate glass beads of the system Na<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> were used for the preparation of hierarchically structured glass monoliths. A typical composition of the initial glass beads was 6 wt% Na<sub>2</sub>O, 30 wt% B<sub>2</sub>O<sub>3</sub> and 63 wt% SiO<sub>2</sub>. Various additives lowered the softening point and the glass transition temperature ( $T_s \approx 920$  K,  $T_g \approx 740$  K) and, thus, facilitated the melting process. The particle size fraction of the glass beads was 50–80 μm. An inorganic salt was used as a pore-forming agent, which was removed after sintering and annealing. In this study, potassium sulfate (99.9% Acros) and sodium chloride were applied as a pore-forming agent (filler). Water was added as a binder to obtain mechanically stable green bodies.

### 2.2. Experimental procedure

The preparation follows the general scheme in Figure 1. The procedure represents the combination of the preparation of open-pored glasses via salt sintering and porous glasses according to the Vycor-process [6, 7].

The sodium borosilicate glass and the inorganic salt were fractionated for the preparation. Depending on the desired porosity, a mixture of both compounds was prepared and the binder was added dropwise until the mixture became slightly moist. The mixture was homogenized and uniaxially pressed at 100 MPa into cylindrical plates with dimensions of  $\varnothing 25$  mm×5 mm. The green body was dried to remove

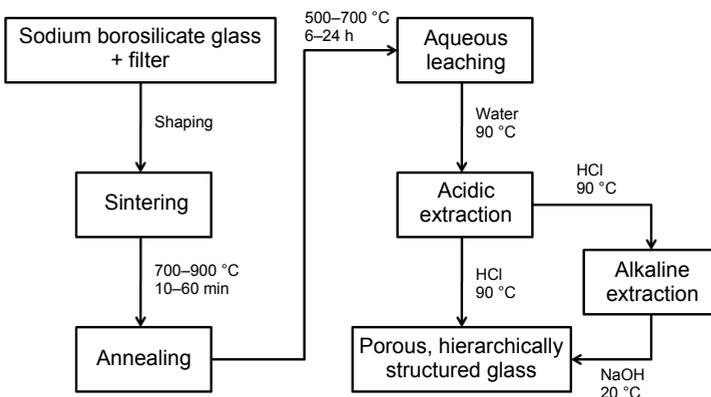


Fig. 1. General preparation scheme for porous, hierarchically structured glasses.

the water. In the next step the compacts were sintered for 30 min at 1043 K in air with a heating rate of 600 K/h. After sintering the composite was cooled down rapidly below the critical temperature of phase separation.

Then the phase separation was initiated by an additional thermal treatment which was performed at various temperatures depending on the desired primary pore size. The annealing temperature increased from sample *A* to sample *C*. The inorganic salt was extracted with water at 363 K for 2 h. Finally the resulting open-pored macroporous material was treated with hydrochloric acid (3 N, Acros) at 363 K for 8 h to remove the sodium-rich borate phase. Secondary silica species within the primary pore system were formed after acid extraction of the compacts which were phase separated at higher temperatures. The silica deposits were removed by treatment with NaOH (0.5 N, Acros) at room temperature for 2 h. Finally the porous glass material was washed with deionized water and dried in air.

### 2.3. Characterization

The pore size distribution and the pore volume were determined by mercury intrusion using the porosimeter POREMASTER 60 (Quantachrome). A contact angle of 141.3° was used for mercury. The pore diameter was calculated by applying the Washburn equation and a cylindrical pore model. The validity of this model for porous glasses has been demonstrated in many previous studies.

The specific surface areas were calculated from the nitrogen sorption using the ASAP 2010 (Micromeritics Instruments). The samples were heated at 523 K under vacuum to remove the adsorbed water. The pore diameter of microporous primary pores was calculated from the nitrogen adsorption using the model of Horvath–Kawazoe [8].

Environmental scanning electron microscopy (ESEM) was used for examinations of the microstructure of the resulting materials. The images were recorded on a device of the series ESEM XL 30 FEG (Philips). The samples were provided with a fresh fracture surface and investigated in a water vapor atmosphere at a pressure of 160 Pa.

## 3. Results and discussion

Hierarchically structured glasses of the systems macro/micro, macro/meso and macro/macro have been successfully prepared. Figure 2 shows the mercury pore size distributions and the corresponding nitrogen sorption isotherms of the primary pore system. The isotherms indicate a systematic transition from micro- (type I, sample *A*) via meso- (type IV, sample *B*) to macroporous materials (type II, sample *C*). Sample *B* exhibits no additional micropores.

An increasing annealing temperature of the initial glass compacts results in an increase of the primary pore diameter and therefore in a decrease of the specific surface areas. Primary pore sizes between 1 and 70 nm were obtained. The microporous sample *A* exhibits a high specific surface area of 420 m<sup>2</sup>g<sup>-1</sup> which decreases to 28 m<sup>2</sup>g<sup>-1</sup> for the macroporous sample *C*.

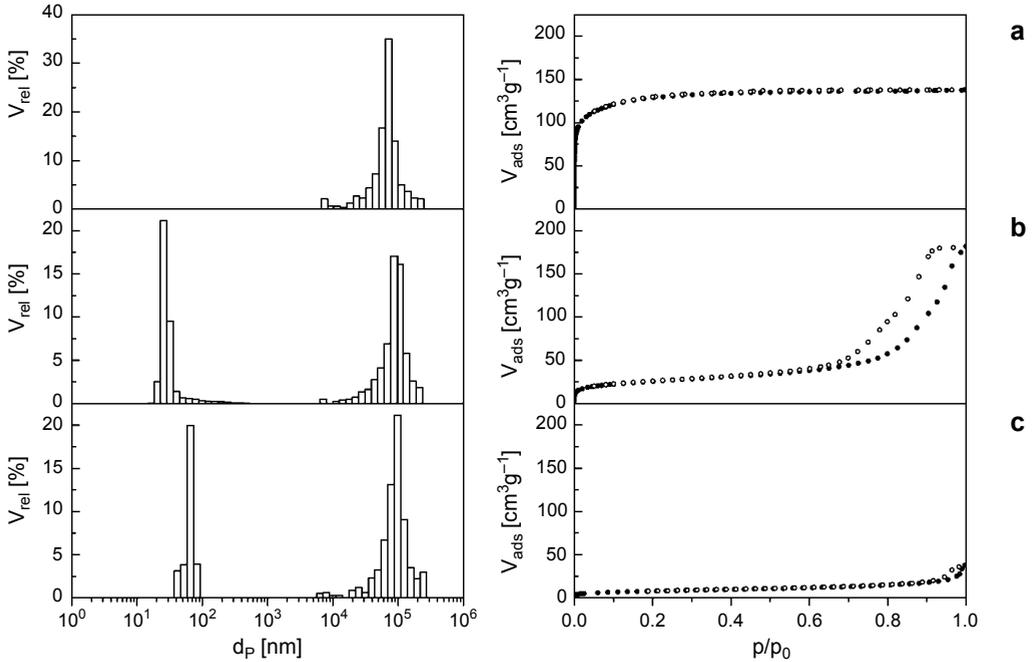


Fig. 2. Mercury pore size distributions and the corresponding nitrogen sorption isotherms of the prepared samples. The systems macro/micro (a), macro/meso (b) and macro/macro (c) were successfully realized.

The secondary pore sizes around 100  $\mu\text{m}$  and the total porosities of 60 to 70% remained almost unchanged during the thermal and leaching treatment. Those pore sizes can be adjusted by using different salt fractions as described elsewhere [4, 7]. Secondary pore sizes between 20 and 500  $\mu\text{m}$  were realized. The secondary pore system possesses an interconnected pore structure as shown in Fig. 3. The pore structure is comparable to those of porous glasses. This justifies the use of a cylindrical pore model for calculation of the pore size distribution via mercury intrusion.

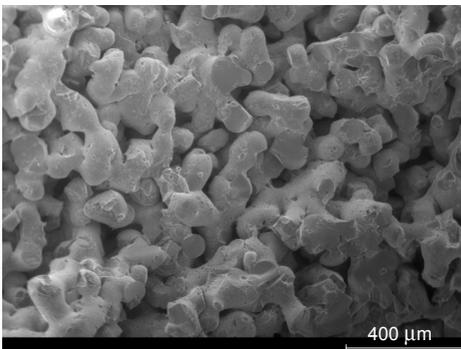


Fig. 3. ESEM-image of the secondary pore system after removal of the inorganic salt. The pore system possesses an interconnected sponge-like pore structure as known from porous glasses.

Table. Textural properties of the resulting porous, hierarchically structured glass monoliths.

Sample	$d_{P(\text{prim})}$ [nm]	$d_{P(\text{sec})}$ [ $\mu\text{m}$ ]	$V_{P(\text{prim})}$ [ $\text{cm}^3\text{g}^{-1}$ ]	$V_{P(\text{sec})}$ [ $\text{cm}^3\text{g}^{-1}$ ]	$O_s$ [ $\text{m}^2\text{g}^{-1}$ ]	$P_{\text{tot}}$ [%]
A	1 <sup>a</sup>	105	0.21 <sup>b</sup>	0.52	420 <sup>c</sup>	62
B	34	92	0.48	0.79	91 <sup>c</sup>	74
C	65	96	0.36	0.81	28 <sup>c</sup>	72

<sup>a</sup> Calculated from nitrogen adsorption according to Horvath–Kawazoe [8];

<sup>b</sup> Calculated by converting the adsorbed gaseous nitrogen into liquid nitrogen by  $V_{P(\text{prim})} = 0.001547 V_{\text{ads}}$ ;

<sup>c</sup> Calculated from nitrogen adsorption using Dubinin–Radushkevich method [9] for sample A and BET method [10] for samples B and C.



Fig. 4. The sintering process provides an alternative method to obtain monoliths with flexible geometric shape: tubes, rods, plates and granules could be prepared successfully.

The Table summarizes the textural properties of the hierarchically structured silica materials on the basis of porous glasses where  $d_{P(\text{prim})}$  is the primary pore diameter,  $d_{P(\text{sec})}$  the secondary pore diameter,  $V_{P(\text{prim})}$  is the primary pore volume,  $V_{P(\text{sec})}$  the secondary pore volume,  $O_s$  the specific surface area and  $P_{\text{tot}}$  the total porosity. Unless otherwise noted, the pore diameters and volumes were determined by mercury intrusion.

Various geometric shapes of the hierarchically structured silica, *e.g.*, plates, rods and tubes, were realized successfully by using appropriate pressing tools (Fig. 4).

## 4. Conclusions

Hierarchically structured, porous glass monoliths were successfully prepared via combination of sintering and phase separation. Secondary pores according to the filler principle were obtained after an aqueous leaching of the glass-salt-composite. Pore sizes and pore morphology depend on the used grain fraction and the process control of sintering. Hierarchical pore systems of the type macro/macro, macro/meso, macro/micro were realized. A primary micropore system within the walls of the sintered glass was obtained after an extraction with mineral acids. Meso- and macroporous

materials were prepared by an additional thermal treatment and a combined acidic-alkaline extraction. Additionally, we could demonstrate that the sintering process allows a very flexible geometric shaping.

With this paper, we show some basic principles for the design of new hierarchically structured materials.

## References

- [1] NAKANISHI K., TAKAHASHI R., NAGAKANE T., KITAYAMA K., KOHEIYA N., SHIKATA H., SOGA N., *Formation of hierarchical pore structure in silica gel*, Journal of Sol-Gel Science and Technology **17**(3), 2000, pp. 191–210.
- [2] RAUSCHER M., SELVAM T., SCHWIEGER W., FREUDE D., *Hydrothermal transformation of porous glass granules into ZSM-5 granules*, Microporous and Mesoporous Materials **75**(3), 2004, pp. 195–202.
- [3] HARTMANN M., *Hierarchical zeolites: A proven strategy to combine shape selectivity with efficient mass transport*, Angewandte Chemie International Edition **43**(44), 2004, pp. 5880–5882.
- [4] SIEBERS F.B., GREULICH N., KIEFER W., *Manufacture, properties and application of open-pore sintered glasses and open-pore sintered glass-ceramics*, Glastechnischer Bericht **62**, 1989, pp. 63–73.
- [5] JANOWSKI F., HEYER W., *Poröse Gläser – Herstellung, Eigenschaften und Anwendung*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1982.
- [6] NORDBERG M.E., *Properties of some Vycor-brand glasses*, Journal of the American Ceramic Society **27**(10), 1944, pp. 299–305.
- [7] KIEFER W., *Method of manufacturing porous sintered inorganic bodies with large open pore volume*, United States Patent US458854, 1984.
- [8] HORVATH G., KAWAZOE K., *Method for the calculation of effective pore size distribution in molecular sieve carbon*, Journal of Chemical Engineering of Japan **16**(6), 1983, pp. 470–475.
- [9] DUBININ M., *A study of the porous structure of active carbons using a variety of methods*, Quarterly Reviews, Chemical Society **9**(2), 1955, pp. 101–114.
- [10] BRUNAUER S., EMMETT P.H., TELLER E., *Adsorption of gases in multimolecular layers*, Journal of the American Chemical Society **60**(2), 1938, pp. 309–319.

*Received August 29, 2011  
in revised form February 13, 2012*