



## Transformation of porous glasses into MCM-41 containing geometric bodies



Hans Uhlig<sup>a,\*</sup>, Marie-Luise Gimpel<sup>a</sup>, Alexandra Inayat<sup>b</sup>, Roger Gläser<sup>a</sup>, Wilhelm Schwieger<sup>b</sup>, Wolf-Dietrich Einicke<sup>a</sup>, Dirk Enke<sup>a</sup>

<sup>a</sup>University of Leipzig, Institute of Chemical Technology, Linnéstr. 3, 04103 Leipzig, Germany

<sup>b</sup>University of Erlangen-Nuremberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany

### ARTICLE INFO

#### Article history:

Received 13 March 2013

Received in revised form 22 August 2013

Accepted 23 August 2013

Available online 4 September 2013

#### Keywords:

Pseudomorphic transformation

Controlled pore glass

Porous glass

Hierarchy

MCM-41

### ABSTRACT

This contribution presents the transformation of Controlled Pore Glass (CPG) granules into MCM-41 material. Porous glasses with pore diameters between 34 and 390 nm and varying pore volumes were used as starting materials. In dependence on the textural properties of the starting porous glasses and the synthesis conditions a pseudomorphic transformation of porous glass granules into hierarchically structured MCM-41 granules was accomplished. Such MCM-41 granules exhibit not only the original macroscopic shape but also the pore morphology of the starting porous glass. Based on systematic variations of alkalinity, glass pore volume and glass pore diameter the requirements for a pseudomorphic transformation are defined.

Materials with a hierarchical pore system (meso- or macropores of the porous glass, ordered mesopores inside the former glass walls) could be generated via the variation of the molar ratio between cetyltrimethylammonium hydroxide and total cetyltrimethylammonium template amount (CTAOH/CTAOH + CTAB). The transformation products were characterized by nitrogen adsorption, mercury intrusion, X-ray diffraction, scanning electron and light microscopy.

During the transformation the primary pore walls were found to swell into the initial pore space, which is caused by bulk density differences between the non-porous glass walls and the template containing MCM-41 material. A pore volume above 1.0 cm<sup>3</sup>/g and pore diameters above 60 nm were found to be pre-requirements for a pseudomorphic transformation of the porous glasses into MCM-41. Furthermore, a complete transformation was only possible for glasses exhibiting sufficiently high surface area, which was not the case for very large pore diameters of around 390 nm.

© 2013 Elsevier Inc. All rights reserved.

### 1. Introduction

The introduction of hierarchy into various porous solids, e.g., catalyst supports or drug delivery systems, is currently a field of intense research [1]. On the other hand, macroscopic shaping of such “advanced” materials is still an important but academically neglected aspect in the transfer to technical applications. In this regards, the pseudomorphic transformation is a powerful tool not only to introduce hierarchy into porous materials, but also to provide them with a certain macroscopic shape without the need for chemical binders or mechanical pressing [2,3]. The characteristic of a pseudomorphic transformation is at least the maintenance of the geometrical shape of the starting material and also of its original pore morphology [4]. In this way, a hierarchical pore system is created when only the pore walls of the starting material are transformed into a porous structure. The hierarchical pore system

consists of the starting pores which then lead into the pores of the newly built structure [3].

The pseudomorphic transformation of amorphous silica gels into micellar templated silicas (MTS) was first introduced by Galarneau et al. [5–9]. This method enables the control of the textural properties of porous silica on the basis of a dissolution–reconstruction mechanism. The shape retention makes it possible to synthesize monoliths with e.g., MTS pore structure, whereas the classical syntheses lead to powders. The relevant publications show a wide range of amorphous silica starting materials for pseudomorphic or at least shape-preserving transformations, like silica gel beads, granules [7] or sol–gel monoliths with hierarchical pore system [10], which were converted into MCM-41 or MCM-48 monoliths. Additionally, a roughening of the silica gel surface to increase the surface area for HPLC applications was achieved by partial pseudomorphic transformation [11].

Although the synthesis of silica gels is explored sufficiently and they are widely available, their pore size distribution is usually broader compared to CPGs and pore sizes above 50 nm are difficult

\* Corresponding author.

E-mail address: [hans.uhlig@uni-leipzig.de](mailto:hans.uhlig@uni-leipzig.de) (H. Uhlig).

to achieve. Phase separated sol–gel monoliths can cover a macropore range of 100–10,000 nm, but compared to CPGs their synthesis is difficult because of the sensitive silica network that tends to shrink and break during the drying phase. Thus, for systematic studies involving pore size dependencies from the micro up to the large macropore range, porous glasses might be better starting systems since their textural properties can be finely tailored during the preparation process [12]. Furthermore, CPG is one of the few porous silica materials that can be obtained isoporous, i.e., with same pore diameter at different pore volumes and different pore wall thicknesses. Porous glass can be prepared in many different geometric shapes (monoliths) [3] and shrinkage does not occur. It consists of amorphous silica with a controllable pore size in the range between 1 and 1000 nm, a specific surface area of up to 500 m<sup>2</sup>/g and a pore volume between 0.1 and 1.5 cm<sup>3</sup>/g [12]. Additionally, these materials exhibit high mechanical, thermal and chemical stability. Porous glasses were already successfully applied as starting systems for pseudomorphic transformations into zeolitic monoliths [13].

Until now there are no systematic studies regarding the influence of the textural parameters (pore size, pore volume, wall thickness) of the starting material on the course of the pseudomorphic transformation, i.e., degree of transformation, generation of a hierarchical pore structure, preservation of the original pore structure. Additionally, a pseudomorphic transformation of porous glasses into MTS structures was not facilitated up to now. In comparison to other starting materials for pseudomorphic transformation like silica beads or silica monoliths with hierarchical pore structure, porous glasses are characterized by a completely different preparation process and thus by a different microstructure. This might result in a different dissolution rate during pseudomorphic transformation.

A typical solution for pseudomorphic transformations of silica materials into MTS structures contains a mixture of NaOH and a surfactant like cetyltrimethylammonium bromide (CTAB). The alkaline OH<sup>-</sup> dissolves silica species from the starting material, which then self-assemble around the micelles formed by the surfactant. However, NaOH influences the surface charge of the silica species, mobilizes silica species very easily and can thus decrease the quality of the transformation products. Besides, sodium free MCM-41 is hydrothermally more stable [14]. To avoid the use of NaOH we introduced a modified approach where the bromide anion of the CTAB surfactant was replaced with hydroxide anions [15]. In this way, the dissolution of the silica walls and subsequent templating of the MTS material were combined in one molecule. With this bifunctional CTAOH template, dealuminated zeolite Y extrudates have already been successfully transformed into MCM-41 geometric bodies [15].

Here, we report for the first time about the synthesis of MTS monoliths by pseudomorphic transformation of porous glass monoliths. Furthermore, the present study is the first systematic investigation of the influence of different pore sizes and pore volumes of the starting material on the resulting pore system of the MTS monoliths and the feasibility of a pseudomorphic transformation.

## 2. Experimental

Porous glass beads (PGB) of particle size fraction 100–200 μm were produced according to a procedure published elsewhere [16]. Porous glass granules (PGG) of the same particle size were produced by Biosearch Technologies, Steinach, Germany. These starting materials were characterized by graded pore diameters of 34, 62, 150, 274 and 390 nm. The pore volumes varied between 0.4 and 1.4 cm<sup>3</sup>/g.

Cetyltrimethylammonium hydroxide (CTAOH) was prepared by ion exchange of cetyltrimethylammonium bromide (CTAB (Fluka,

96%)) over the anion exchanger Ambersep<sup>®</sup> 900(OH) (Alfa Aesar) for 24 h at room temperature. The transformation of the porous glass particles into MCM-41 took place in 50 ml Teflon autoclaves at 120 °C for 72 h. For complete transformation a solution of 0.08 mol/l CTAOH was used. For partial transformations the alkalinity of the surfactant solution was altered by mixing different portions of CTAOH with CTAB (with  $c_{\text{CTAOH}} + c_{\text{CTAB}} = 0.08$  mol/l) in order to prevent falling below the critical micelle concentration. The glass samples were treated with surfactant solutions of four different CTAOH/(CTAOH + CTAB) molar fractions (0.33, 0.50, 0.66 and 1.00) for 72 h at 120 °C. All experiments are summarized in Table 1.

After the synthesis the products were filtered, washed three times with distilled water and dried at 50 °C for 24 h. After drying the products were calcined in air in a muffle furnace using the following temperature program: heating rate 10 K/min to 550 °C with isothermal steps at 150 °C for 1 h, 400 °C for 1 h, 550 °C for 4 h.

A standard MCM-41 reference material was synthesized from LiChrosphere<sup>®</sup> 60. The mesopore volume was 1.05 cm<sup>3</sup>/g and defined as 100% MCM-41.

Nitrogen physisorption isotherms were measured with a Micromeritics<sup>®</sup> ASAP2010 and Quantachrome<sup>®</sup> Autosorb iQ after sample pretreatment in vacuum for 10 h at 250 °C. Specific surface areas were calculated using the B.E.T. method, the total pore volume was obtained at  $p/p_0$  0.99. Pore size distribution curves were calculated from the adsorption branch of the isotherm on the basis of the NLDFT method. Only for the samples assigned to the starting glass with 34 nm pore diameter the B.J.H. method (adsorption branch) was used for pore size determination because NLDFT was not able to properly visualize the pore size distribution in this case. The mesopore volume of the MCM-41 phase was determined by the  $t$ -plot method in the range of 0.6–0.9  $p/p_0$ . For the meso/macro porous transformation products, the total pore volume was calculated as the sum of the cumulative pore volume from mercury intrusion (for pores down to 40 nm) and the mesopore volume of the MCM-41 phase (pores with diameter around 4 nm). The primary pore volume ( $V_{\text{Prim}}$ ) is defined as the volume of the glass pores before transformation or the volume of the remaining initial (primary) pores after transformation.

Mercury intrusion measurements were performed on a Quantachrome<sup>®</sup> POREMASTER using a contact angle for mercury of 141°. The total pore volumes from the mercury intrusion curves were calculated as the cumulative pore volume of all non-interparticle pores with pore diameters down to 40 nm. The pore volume of pores with diameter below 40 nm was obtained from nitrogen adsorption.

Powder XRD patterns were recorded with a Philips X'pert Pro diffractometer operated at 40 kV, using Cu K<sub>α</sub> radiation in steps of 0.005° with a sampling time of 7 s per step. Before measurement, the samples were intensively powdered in a mortar.

As optical microscope, a Carl Zeiss Jena Amplitiv Microscope was used with a 150× magnification.

Scanning electron microscopy images were recorded with the electron microscope ULTRA55 (Carl Zeiss MST AG) at 1.5 kV and SE2 detector. Before the measurement, samples were slightly broken with a pestle in order to facilitate measurements of the interior of the particles and fixed on a conducting carbon pad.

## 3. Results and discussion

### 3.1. Transformation of porous glasses with pore volumes below 1 cm<sup>3</sup>/g and different pore diameter

The first series of transformation experiments was performed with the porous glass beads (PGB-50, PGB-75, PGB-100, PGB-125,

Download English Version:

<https://daneshyari.com/en/article/73414>

Download Persian Version:

<https://daneshyari.com/article/73414>

[Daneshyari.com](https://daneshyari.com)