Preparation of CaCO₃ and CaO Replicas Retaining the Hierarchical Structure of Spruce Wood

Somruedee Klaithong[a], Daniel Van Opdenbosch[b], Cordt Zollfrank[b], and Johann Plank[a]

[a] Lehrstuhl für Bauchemie, Technische Universität München, 85747 Garching, Lichtenbergstraße 4, Germany

[b] Fachgebiet Biogene Polymere, Technische Universität München, 94315 Straubing, Schulgasse 16, Germany

Reprint requests to Prof. Dr. Johann Plank. Fax: +49-89-289-13152.
E-mail: sekretariat@bauchemie.ch.tum.de

Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The principal structural characteristics of softwood (spruce) were replicated in CaCO₃ and CaO on various levels of hierarchy from the macroscopic to the submicron scale. Positive replicas were obtained by infiltrating pretreated softwood templates with a Ca(OCOOCH₃)₂ precursor solution which hydrolyzed into CaCO₃ nanoparticles. They reproduce the hierarchical porous structure of the wood template. Calcination at temperatures from 350 to 900 °C yields calcite as the main polymorph. Mechanical stability of the replica is optimized when the specimen is calcined at 900 °C.

Key words: Wood Template, Calcium Carbonate, Submicron Particles, Hierarchical

Introduction

Hierarchically structured inorganic materials have been recognized as attractive compounds and materials in applications such as catalysis, sensoring, pharmaceuticals, building materials, *etc.* [1]. For similar purposes, nano- and mesoporous materials are utilized as well. Some well documented examples include mesoporous silica (*e. g.* MCM-41), prepared with quaternary ammonium surfactants ("quats") as templating agents [2, 3], or nanoporous silica aerogels which are fabricated *via* sol-gel processess utilizing alkoxysilane precursors [4, 5]. Among those materials, aerogels stand out because of their unsurpassed heat insulating properties which derive from their nanoporosity and the Knudsen effect [6]. In spite of their many advantages, these porous materials exhibit a homogeneous porosity across the matrix which in many cases is undesirable. In specific applications, those materials require a three-dimensional hierarchy in addition to an anisotropic porosity. More recently, a number of hierarchically structured inorganic materials have been synthesized by using biological templates originating from plants (*e. g.* wood, seed, reed, bamboo) or animals (*e. g.* shell, nacre, tooth, bone) [7]. Replication of these structures was achieved by infiltrating the biotemplates with inorganic precursors and subsequent removal of the organic matrix *via* chemical or thermal treatment [8]. Wood has been identified as a versatile template. Contrary to *e. g.* aerogels, it combines an uniaxial porosity with high stiffness [7]. For example, spruce wood consists of parallel tube-like wood cells, the tracheid fibers, with a diameter in the range of 20 microns. In the cell wall of the tracheid fibers, cellulose fibrils are embedded in a hemicellulose and lignin matrix [9]. The cellulose fibrils are partly crystalline and they spiral the lumen at the characteristic microfibril angle [10]. Consequently, this structure is hierarchical at the nanometer level which was proven by SAXS analysis [11, 12]. Wood templates useful for the synthesis of porous materials can be prepared according to different methods. One process includes acid extraction followed by partial delignification with sodium chlorite [13]. This approach not only removes inorganic impurities, but also opens up the pore structure in order to create accessibility for the precursor molecules [14]. Furthermore, functionalization of the template with maleic acid anhydride was found to be

advantageous to stabilize the fibrillar structure and to reduce the shrinkage of the template [15 – 17]. Several attempts to replicate the hierarchical structure of wood from the micrometer to the nanometer scale were successful. For example, a hierarchically porous ceramic silica material was obtained by *in situ* mineralization of wood cellular structures infiltrated with a surfactant-templated sol-gel solution [18]. A hierarchically structured iron oxide possessing a tunable porous structure was synthesized from different wood templates [19]. Also, a highly crystalline porous oxide material was produced by infiltrating a $Ce_{0.5}Zr_{0.5}O_2$ sol into the tissue of wood [20]. Furthermore, a nanoscopic replication of the cellulose fibril was successfully fabricated by infiltrating TEOS into delignified and functionalized spruce wood templates [15]. Using tailor-made precursor sols and salt solutions, hierarchically structured phosphor materials based on softwood could be fabricated [21 – 23]. Very recently calcium carbonate aerogels have been considered as a potential replacement for polystyrene foam contained in heat insulating renders and panels used by the construction industry [24]. The preparation of $CaCO_3$ aerogels utilizes calcium di(methylcarbonate) as precursor and subsequent hydrolysis to calcium carbonate particles [25]. However, their poor mechanical strength currently restricts their use as insulating material in cement mixtures. Further, their purely nanometer-scale porosity does not allow reaction with microcrystalline cement hydrates and influences bonding to the cementitious matrix.
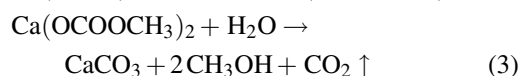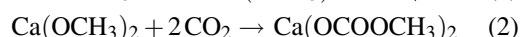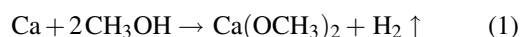
In this study, we investigated the fabrication of hierarchically structured $CaCO_3$ by using calcium di(methylcarbonate) as calcium precursor [25] and subsequent hydrolysis into a $CaCO_3$ sol. After infiltrating spruce wood templates with the precursor, their cellulose matrix was removed by calcination at temperatures varying between 350 and 900 °C. Calcination temperature and duration was varied in order to study their effect on the type of $CaCO_3$ polymorph formed, on the $CaCO_3$ particle size, the quality of replication, and the mechanical stability of the replica.

Results and Discussion

Calcium carbonate precursor

The concept of wood replication with $CaCO_3$ is based on the hydrolysis of calcium di(methylcarbonate) as precursor [25]. First, calcium dimethylate

is prepared by reacting calcium metal with methanol (Eq. 1). Subsequent bubbling of gaseous CO_2 through this solution results in calcium di(methylcarbonate) (Eq. 2) which partly precipitates from the solution as several μm long needles which are removed by centrifugation. The clear solution (solid content 0.4 wt.-%) is used in the following infiltration process. Through hydrolysis of the calcium precursor with residual moisture present in the wood cells, $CaCO_3$ is eventually formed (Eq. 3) and successfully replicates the hierarchical structure of the wood. However, depending on the number of infiltration steps and the calcination conditions, different materials are obtained.

$$Ca + 2\,CH_3OH \rightarrow Ca(OCH_3)_2 + H_2 \uparrow \qquad (1)$$

$$Ca(OCH_3)_2 + 2\,CO_2 \rightarrow Ca(OCOOCH_3)_2 \quad (2)$$

$$Ca(OCOOCH_3)_2 + H_2O \rightarrow$$
$$CaCO_3 + 2\,CH_3OH + CO_2 \uparrow \qquad (3)$$

Low-temperature treatment

Here, the pre-treated wood samples were infiltrated only once and treated thermally at 350 °C over a period of 48 h to decompose the wood template very slowly. This method produced large specimens which exceptionally precisely replicated the hierarchical structure as is shown in Fig. 1. Functional elements of the original wood samples such as pit holes were exactly replicated (Fig. 1a). Additionally, the tracheids of the wood are clearly reproduced in detail (Fig. 1b). Surprisingly, this product was found to consist of the meta-stable $CaCO_3$ polymorph vaterite as evidenced by XRD analysis (Fig. 2). Even a sample stored for 4 months still contained only vaterite, according to the XRD pattern (Fig. 2b). This demonstrates the exceptional stability of this polymorph under the given conditions.

Preparation of calcined replicas

A replica of the wood sample was produced by infiltrating a pretreated spruce wood template once with $Ca(OCOOCH_3)_2$ solution, followed by calcination at 500 °C for 2 h to completely remove the cellulose and other biopolymers. The resulting product consisted of a quite fragile positive $CaCO_3$ replica of the original wood template whereby the hierarchical structure was precisely reproduced by individual submicron $CaCO_3$ particles, as was evidenced by SEM imaging (Fig. 1c,
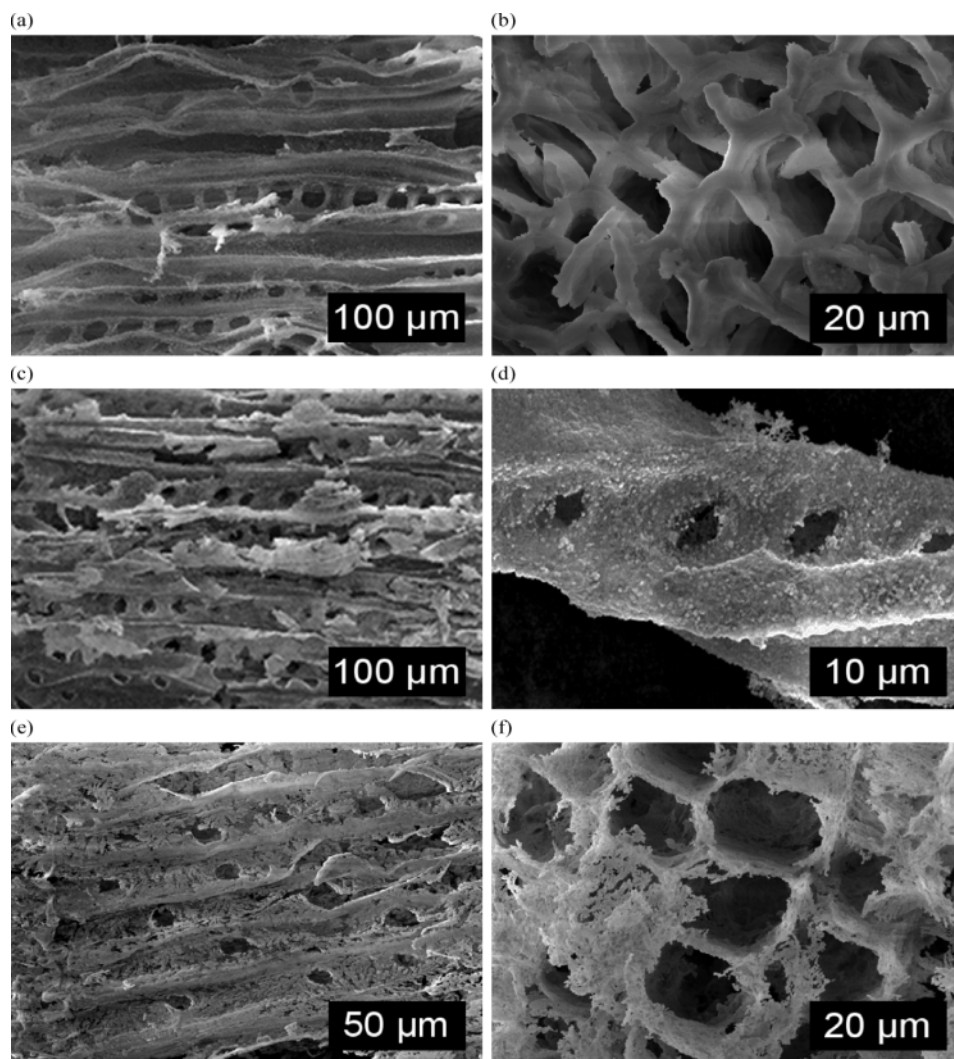
Fig. 1. SEM images of the CaCO₃-replicated wood samples: a, b) one infiltration and calcination at 350 °C for 48 h, resulting in a structure made of vaterite polymorph; c, d) one infiltration and calcination at 500 °C for 2 h leading to calcite and e, f) five infiltrations and calcination at 900 °C, producing CaO.

d). Spherical $CaCO_3$ particles with diameters of between 200 and 500 nm are visible which are assembled such as to replicate the structural features of the original wood, particularly the pit holes and tracheid fibers. This appearance differs significantly from previous silica replicas of wood where initially formed SiO_2 nanoparticles coalesced into an annealed monolith. As a result of the particulate structure, the $CaCO_3$ replica forms a fragile body with an extremely poor mechanical stability. XRD analysis revealed that the $CaCO_3$-replicated wood sample consisted only of the polymorph calcite (Fig. 2c).

Effect of multiple infiltration steps

In order to improve the mechanical stability of the replica, two parameters were considered: The amount of precursor infiltrated and the calcination conditions. At first, repeated infiltration steps were probed with the aim to obtain a more dense assembly of the $CaCO_3$
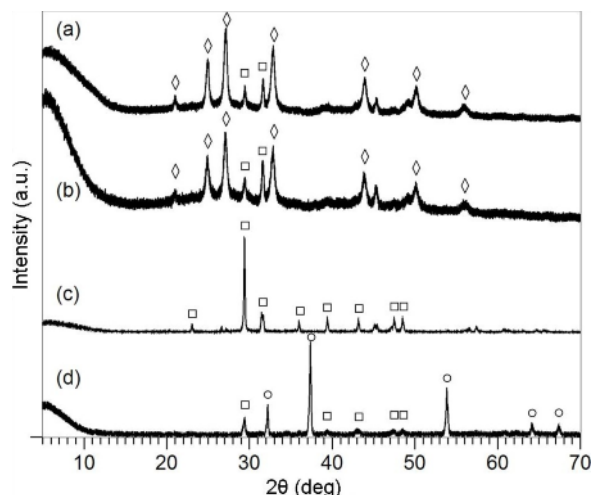
Fig. 2. XRD patterns of the CaCO$_3$-replicated wood samples: a, b) after thermal treatment at 350 °C (vaterite: JCPDS 25-127), c) after calcination at 500 °C for 2 h (calcite: JCPDS 05-586) and d) formation of CaO (JCPDS 37-1497) after calcination at 900 °C; $\diamondsuit$ = vaterite, $\square$ = calcite, $\bigcirc$ = CaO.

nanoparticles. These new samples were prepared by infiltrating them for 2 or 5 times and subsequent calcination at 500 °C for 2 h. After the first infiltration step, these samples were kept at 80 °C for 5 h before the second infiltration was conducted and subsequent calcination was performed. The twice infiltrated product was still fragile, but its stability had improved compared to the sample from one infiltration only. This effect can be attributed to larger and more compactly arranged submicron CaCO$_3$ particles ($d = 200$ nm to $1\,\mu$m). The number of infiltration steps was subsequently increased to 5. However, the stability of the replicas improved only slightly, and the material was still very brittle, thus limiting its applicability. SEM micrographs revealed that in spite of this multiple infiltration, a similar size and arrangement of the calcite particles like after two infiltrations was observed. From these results it was concluded that several infiltration steps do not lead to replicas possessing sufficient mechanical stability.

Effect of calcination temperature

Next, samples infiltrated once were calcined at 750 and 900 °C. The product obtained at 750 °C was similarly fragile as the sample calcined at 500 °C. However, calcination at 900 °C led to replicas consisting of

CaO (as evidenced by XRD, see Fig. 2d) with again only slightly annealed particles, and thus with limited mechanical stability. Apparently, increasing the calcination temperature did not improve the mechanical stability of the replicas. It should be noted that when stored in air the CaO replica is hygroscopic and will be carbonated slowly over time.

Combination of multiple infiltrations and high calcination temperature

Furthermore, various combinations of multiple infiltration and high calcination temperature were probed. Samples infiltrated five times were calcined at 750 or 900 °C for 2 h. The product obtained at 750 °C exhibited higher stability compared to the product calcined at 500 °C only, but it still was much inferior to silica replicas [3]. However, the product calcined at 900 °C constituted an almost monolithic wood replica with reasonable stability. At this temperature, CaCO$_3$ decomposes into CaO and CO$_2$, the CaO (as evidence by XRD, diagram not shown here) being more annealed as observed by SEM (Fig. 1e, f). There, the well replicated honey comb structures of the cell wall as well as strongly annealed CaO particles are visible. From these experiments it was concluded that the ionic character of CaCO$_3$ prevents it from sintering into mechanically stable monoliths such as in SiO$_2$ replicas where covalent bonds are formed between the primary particles.

Specific surface area

Using the BET method, a specific surface area of $8.0\,\mathrm{m^2\,g^{-1}}$ was found for the sample obtained from five infiltrations and calcination at 500 °C. This value is significantly lower than that reported for aerogels which lie between 45 and 200 m^2 g^{-1} [3, 24]. The result suggests that the CaCO$_3$ replicas produced here might be useful as carriers for drugs, catalysts or sensors. However, with respect to their thermal insulation properties they appear to be inferior to aerogels.

Conclusion

Our experiments have demonstrated that a CaCO$_3$ replica of hierarchically structured spruce wood can be obtained by infiltrating pretreated wood specimens with a solution of calcium di(methylcarbonate) in methanol which hydrolyses with residual moisture from the wood into a CaCO$_3$ sol. Upon calci-

nation, the sol produces CaCO$_3$ nanoparticles which precisely reproduce the mesoporous structure of the wood template. Heating to 900 °C transforms the CaCO$_3$ into a more robust CaO replica. The CaCO$_3$ replicas exhibit relatively poor mechanical stability and normally consist of the CaCO$_3$ polymorph calcite. Under mild, but extended calcination conditions (350 °C 48 h), the meta-stable CaCO$_3$ polymorph vaterite is formed. The specific surface area of the replicas is similar to that of mesoporous silica. In further experiments, the results obtained with other earth alkaline di(methylcarbonates), particularly of Mg(OCOOCH$_3$)$_2$, will be studied whereby a focus lies on the preparation of mechanically more stable replicas.

Experimental Section

Preparation of the template

The spruce wood samples (either cubes with side lengths of 1 cm or radial thin sections of 300 μm in thickness) were cut from the sapwood of spruce trees, weighed and subjected to a series of chemical treatments. In a first step, 150 g of wood was washed by extraction with 500 mL of a 2 : 1 by weight mixture of toluene and ethanol and then with the same volume of pure ethanol for 6 h each using a Soxhlet apparatus. All samples were stored in ethanol between the process steps to prevent drying. For preparation of the templates, 1 g of this wood was placed in an oxidizing solution containing 1.4 g of sodium chlorite (NaClO$_2$) and 0.5 g of acetic acid in 23.1 g of deionized water. Delignification was carried out twice at 70 °C for 3 h, the delignification solution being renewed after the initial 3 h. Afterwards, a mild vacuum from a water-jet pump was applied for half an hour. Following the delignification treatment, the templates were immediately extracted with ethanol to remove any residual solution [13].

Infiltration and calcination

Calcium metal in the amount of 1.5 g (0.0374 mol) was suspended in 250 mL absolute methanol (dried and stored over molecular sieve, 3 nm) and heated to 65 °C to produce a solution of Ca(OCH$_3$)$_2$. After 90 min of stirring at room temperature, carbon dioxide gas was bubbled through the Ca(OCH$_3$)$_2$ solution. After 90 min of reaction time, a turbid solution of Ca(OCOOCH$_3$)$_2$ had formed which was centrifuged. The clear solution (containing $\sim$ 13 g of the salt) was rinsed into a vial which contained the spruce wood template. Infiltration of the wood cells occurred during the drying process at 70 °C. The infiltrated wood template was then kept in an oven at 80 °C for 7 h and subsequently calcined *e. g.* at 500 °C for 2 h at a heating rate of 1 K min^{-1}. Additional calcination experiments were performed at 200, 330 and 470 °C for 0.5 h. Immediately after infiltration, hydrolysis of Ca(OCOOCH$_3$)$_2$ with residual moisture from the wood template occurred and a CaCO$_3$ sol was formed. SEM images of the product obtained from calcination were taken using an XL30 ESEM FEG instrument (FEI Company, Eindhoven/The Netherlands). The calcium carbonate polymorph contained in the replicas was indentified *via* X-ray diffraction (D8 advance, Bruker AXS instrument, Bruker, Karlsruhe/Germany). The specific surface area (BET method, N$_2$) was measured on a Nova 4000e, Quantachrome instruments (Boynton Beach, FL/USA) utilizing a sample degassed for 2 h at 200 °C.

[1] C. E. Byrne, D. C. Nagle, *Carbon* **1997**, *352*, 259 – 266.
[2] C. Y. Mou, H. P. Lin, *Pure Appl. Chem.* **2000**, *72*, 137 – 146.
[3] H. Zheng, C. Gao, S. Che, *Micropor. Mesopor. Mater.* **2008**, *116*, 299 – 307.
[4] S. S. Kistler, *Nature* **1931**, *127*, 741 – 741.
[5] S. S. Kistler, *J. Phys. Chem.* **1932**, *36*, 52 – 64.
[6] K. Raed, U. Gross, *Int. J. Thermophys.* **2009**, *30*, 1343 – 1356.
[7] P. Fratzl, R. Weinkamer, *Pro. Mater. Sci.* **2007**, *52*, 1263 – 1334.
[8] O. Paris, I. Burgert, P. Fratzl, *MRS Bull.* **2010**, *35*, 219 – 225.
[9] D. Fengel, G. Wegener, A. Greune, *Wood Sci. Technol.* **1989**, *23*, 123 – 130.
[10] H. F. Jacob, D. Fengel, S. E. Tschegg, P. Fratzl, *Macromol.* **1995**, *28*, 8782 – 8787.
[11] A. Gourrier, W. Wagermaier, M. Burghammer, D. Lammie, H. S. Gupta, P. Fratzl, C. Riekel, T. J. Wess, O. Paris, *Appl. Crystallogr.* **2007**, *40*, s78–s82.
[12] O. Paris, *Biointerphases* **2008**, *3*, fb16 – fb26.
[13] P. A. Ahlgren, W. Q. Yean, D. A. I. Goring, *Tappi.* **1971**, *5*, 737.
[14] L. Sapei, R. Nöske, P. Strauch, O. Paris, *Chem. Mater.* **2008**, *20*, 2020 – 2025.

[15] D. Van Opdenbosch, G. Fritz-Popovski, O. Paris, C. Zollfrank, *J. Mater. Res.* **2011**, *26*, 1193 – 1202.

[16] C. Zollfrank, R. Kladny, H. Sieber, P. Greil, *J. Europ. Ceram. Soc.* **2004**, *24*, 479 – 487.

[17] G. Fritz-Popovski, D. Van Opdenbosch, C. Zollfrank, B. Aichmayer, O. Paris, *Adv. Funct. Mater.* **2013**, *23*, 1265 – 1272.

[18] Y. S. Shin, J. Liu, J. H. Chang, Z. M. Nie, G. Exarhos, *Adv. Mater.* **2001**, *13*, 728 – 732.

[19] Z. T. Liu, T. X. Fan, W. Zhang, D. Zhang, *Micropor. Mesopor. Mater.* **2005**, *85*, 82 – 88.

[20] A. Deshpande, I. Burgert, O. Paris, *Small* **2006**, *2*, 994 – 998.

[21] D. Van Opdenbosch, M. H. Kostova, S. Gruber, S. Krolikowski, P. Greil, C. Zollfrank, *Wood Sci. Technol.* **2010**, *44*, 547 – 560.

[22] M. H. Kostova, M. Batentschuk, F. Goetz-Neunhoeffer, S. Gruber, A. Winnacker, P. Greil, C. Zollfrank, *Mater. Chem. Phys.* **2010**, *123*, 166 – 171.

[23] M. H. Kostova, C. Zollfrank, M. Batentschuk, F. Goetz-Neunhoeffer, A. Winnacker, P. Greil, *Adv. Funct Mater.* **2009**, *19*, 599 – 603.

[24] T. Kornprobst, J. Plank, *GDCh-Monographie: Tagung Bauchemie* **2010**, *42*, 121 – 128.

[25] J. Plank, H. Hoffmann, J. Schölkopf, W. Seidl, I. Zeitler, Z. Zhang, *Res. Lett. Mater. Sci.* **2009**, 1 – 3.