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Short Communication

Attempts to design porous carbon monoliths using porous concrete as a template

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ABSTRACT

The preparation of carbon monoliths with defined shape and hierarchical pore system has been investigated. A template assisted route was applied using porous concrete as the template. The synthesis route was combined with a one pot chemical activation using phosphoric acid and zinc chloride, respectively, as the activating agents. As the template caused the formation of primary macropores the activation created a secondary system of micropores which resulted in a significant increase of the specific surface area up to about 1400 $m^2 g^{-1}$. The material was characterized by means of mercury intrusion, helium pycnometry, and nitrogen adsorption at 77 K.

1. Introduction

Porous carbons have been used as adsorbents, catalysts or electrode material for a long time [1–3]. Besides this there is a growing interest to develop carbon based material for novel applications in energy storage and energy conversion such as fuel cells, super capacitors or hydrogen storage systems [4]. Despite the broad diversity of applications the requirements on the carbons can be reduced to a few features at which the pore size distribution plays a dominating role. Micropores cause both a high specific surface of the material and a strong interaction between molecules and the material as well. On the other hand macropores are beneficial for mass transport and that's why an optimal balance between micropores and macropores which are hierarchically arranged is often essential for an application of the carbon material. Furthermore, a defined geometric shape of the material is often crucial to integrate it in technical devices. Powders are undesirable because they give rise to pressure drop in flow systems or can be released under operation conditions. In summary, there is a long standing interest in preparing porous carbon monoliths with hierarchical pore systems and defined geometrical shape.

During the last 15 years template assisted routes have been established as a suitable tool to prepare porous carbons with tailored properties [5–9]. The basic principle of those routes is quite simple and consists in the filling of the pores of an inorganic template (e.g. zeolites, silica) with a carbon precursor followed by a carbonization step and finalized by the dissolving of the template to obtain a negative carbon replica of the template. Such methods can be applied to prepare porous carbon monoliths [10–16].

Recently, we reported about the template assisted preparation of porous carbons using porous concrete as the template [17,18]. Porous concrete is a low cost material which can easily be shaped. The synthesis procedure starts with the pore filling of the porous concrete with an aqueous sucrose solution. After carbonization of the sucrose within the template pores and the removal of the template by dissolving in hydrofluoric acid a negative carbon replica of the porous concrete was obtained. The resulting carbons possess mainly macropores which are created by the removal of the template pore walls. Besides this, a small amount of rather narrow mesopores and micropores could be detected probably formed by a partial carbon gasification due to the reaction with the concrete silanol groups [17]. Defined shaped monoliths could be obtained by modifying the template loading procedure [18]. However, as mentioned above the materials obtained so far are mainly macroporous and that's why their specific surface is quite low. It was therefore the idea to add an activating agent like phosphoric acid or zinc chloride to the precursor solution to perform the carbonization under conditions close to those known for the production of activated carbons. Such agents will catalyse the carbonization and reduce the carbon release due to the thermal decomposition. The resulting materials have a significant amount of micro- and mesopores. Therefore it was expected that narrow pores should be formed in the pore walls of the primary macropores which are obtained by the template effect of the porous concrete. In such

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a way, a hierarchical pore system should be created in the carbon replica.

2. Experimental

2.1. Synthesis procedure

A technical product of porous concrete (Ytong DIN 4166, *Xella GmbH*) delivered as panels has been used as the template raw material. From the panels particles and monoliths of different size were obtained by crushing (jaw crusher, sieving, sieve fractions of 4.0–5.0 mm) and drilling (cylinders 10 mm diameter). The template samples were treated by hydrochloric acid which dissolves the calcium and aluminium containing concrete phases. After washing with ethanol and drying at 473 K a mass loss of 35% was observed. As a consequence the BET surface area was increased from about 60 up to 130 $m^2 g^{-1}$ whereas the total pore volume (estimated by ethanol infiltration) was increased from 0.84 up to 1.3 $cm^3 g^{-1}$ [17]. The pore sizes of the concrete template were broad distributed from mesopores to macropores (Fig. 2 and [17]). The template particles and monoliths were then impregnated in a vacuum desiccator with an aqueous solution of sucrose and the activating agent H_3PO_4 and $ZnCl_2$, respectively. The applied infiltration procedure was very close to an incipient wetness infiltration because it has been finished when the outer surface of the template grains was slightly wetted by the precursor solution. To prepare the precursor solutions several facts like the concentration of the sucrose and the activating agents, the density of the solution (which is affected by the interaction of the compounds with each other) and the viscosity had to be considered. Starting from a 68-wt.% sucrose solution a part of the sucrose was replaced by the activating agent to establish zinc-to-sucrose and phosphor-to-sucrose mass ratios of 0.15, 0.3 and 0.45, respectively. Blank samples, i.e. solutions without activating agent but corresponding sucrose concentration were prepared. The composition of the precursor solutions is given in Table 1.

The impregnated template samples were then calcined in a nitrogen stream in a two-step procedure. First, the samples were treated at 873 K to carbonize the sucrose. In case of the phosphoric acid activated samples the carbon-template-composites were then loaded again with the precursor solution. It turned out to be impossible to repeat the loading cycles with zinc chloride containing solutions because the viscosity of these solutions was too high.

After dissolving the template in hydrofluoric acid the samples were thoroughly rinsed in water to remove all rests of the activating agents. Finally, the samples were treated again in a nitrogen stream at now 1173 K to strengthen the carbon structure. To avoid the formation of elemental phosphor the treatment at 1173 K was performed after the rinsing i.e. after the removal of all phosphorus residues.

The notation of the samples is demonstrated on the following example: Bl 0.71 means a blank sample which is prepared using sucrose solution with 0.71 g sucrose per cm^3 of solution. Bl 0.71(2) is the notation of a sample which is prepared using sucrose solution with 0.71 g sucrose per cm^3 of solution but the template has been loaded twice (see above). The twice loaded blank samples are attributed to the phosphoric acid activated carbons because these materials were obtained from twice loaded templates, too. P 0.57–0.3(2) means a carbon which is synthesized using phosphoric acid as the activating agents at a phosphor-to-sucrose mass ratio of 0.3 and a sucrose concentration of 0.57 g per cm^3 of solution whereas the template was twice loaded as it is described above.

Blanks samples are attributed to activated samples prepared by solutions with nearly equal sucrose concentration and equal number of loading steps, e.g. Bl 0.71 to Zn 0.71-0.45 or Bl 0.59(2) to P 0.57-0.3(2), respectively.

2.2. Characterization

Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 volumetric adsorption system. The total surface area and micropore volumes were determined using the BET equation and the method of Dubinin-Radushkevich (DR), respectively. The pore size distribution was obtained from the adsorption branch of the nitrogen isotherm using the density functional theory (DFT, slit pores) [19].

The skeleton density of the carbons was measured by helium pycnometry on a Porotec Pycnomatic ATC equipment.

The macropore system of the carbons was investigated by mercury intrusion in the device Poremaster from Quantachrome.

The total pore volume has been estimated by an infiltration of n-octane and subsequent weighing of the infiltrated samples. N-octane has been chosen because it is non polar and therefore suitable to infiltrate the hydrophobic carbons. It is not too volatile and so experimental errors due to an evaporation could be limited. On selected samples (cylinders) the total volume has been calculated by the difference between the geometrical volume and the skeleton volume estimated by helium pycnometry.

3. Results

The activated materials are only slightly contaminated by the activating agents. As the zinc chloride activated carbons are almost free from zinc residues (<0.05 wt.%.) values of about 1 wt.% were found for the phosphoric acid activated carbons. The phosphoric residues are obviously embedded into the carbon matrix otherwise they had been removed by the washing with hydrofluoric acid and water.

Fig. 1 shows the photograph of grains and monoliths from the template and the carbon replica, respectively. Independently of the used activating agent all replicas were stable and inherited the template shape. The blank samples can bear a compressive stress of about 300 kPa. For the characterization experiments which will be described below carbon grains were used. It has been proven that their textural properties are very similar to those obtained from cylinders (s. Table 2).

Table 1
Composition of the precursor solutions.

	Mass H_2O [g]	Mass sucrose [g]	Mass $ZnCl_2$ [g]	Mass H_3PO_4 [g]	Conc. sucrose [g cm^{-3}]
Bl 0.90	32	68	–	–	0.90
Bl 0.71	43.9	56.1	–	–	0.71
Bl 0.59	50.7	49.3	–	–	0.59
Zn 0.85-0.15	32	68	21.3		0.85
Zn 0.71-0.45	32	68	63.8		0.71
P 0.71-0.15(2)	32	68	–	38	0.71
P 0.57-0.30(2)	32	68	–	76	0.57