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Porous carbon monoliths with pore sizes adjustable between 10 nm and 2 μm prepared by phase separation – New insights in the relation between synthesis composition and resulting structure

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ABSTRACT

Porous carbon monoliths with tunable porosity are promising materials for a variety of applications like energy storage and adsorption. But the synthesis of carbons with monolithic shape and controlled porosity is often time-consuming and expensive. Here, micro-/macroporous and micro-/mesoporous carbon monoliths were synthesized via a simple process of polymerization induced phase separation of resorcinol and formaldehyde followed by drying at ambient pressure and carbonization. The carbon monoliths are mechanically stable and exhibit specific surface areas between 390 and 1100 $m^2 \cdot g^{-1}$. The size of the macro- and mesopores can be tailored over a wide range from approximately 10 nm to 2 μm by simply altering the solvent composition during the synthesis of the organic monoliths. The influence of solvent composition and resorcinol concentration on the pore size in the carbon monoliths was investigated with a focus on the smaller pore sizes and an exponential relation was observed. Finally, selected monoliths were activated in a stream of CO_2 to produce hierarchically porous monoliths with specific surface areas between 1000 and 2400 $m^2 \cdot g^{-1}$. The activated monoliths were characterized in terms of their CO_2 adsorption and showed adsorption capacities of up to 3.10 $mmol \cdot g^{-1}$ at 298 K.

1. Introduction

In the past years, the interest in the synthesis of porous carbons has been growing because they are promising materials for various applications including energy storage [1–3], adsorption [4–6], separation media [7,8] and catalysis [9–11]. This is due to properties like high surface areas and high pore volumes as well as electrical conductivity and chemical stability. Compared to other porous materials considerable for these applications, like metal-organic frameworks (MOFs) or zeolites, carbons are easier to synthesize from cheaper starting materials and are more stable against external influences. Especially, in terms of mass transport and diffusion it is important that the porosity is well designed and microporosity (generated in carbon materials during the carbonization process) is combined with meso- or macroporosity. Such hierarchical pore systems are difficult to obtain for MOFs and zeolites, making porous carbons the material of choice for many of the aforementioned applications.

Mesoporosity in carbons is mostly generated either by hard templating with inorganic porous templates [12–14] or by soft templating through self-assembly of carbon precursors with surfactants [15–18]. Macroporous carbons are usually generated through hard templating with silica or polymer spheres [19], colloidal crystals [20–22] or monoliths [23–26]. These synthesis methods have led to numerous different porous carbons but they also show several drawbacks. The multi-step hard templating route is time-consuming and involves the removal of the inorganic template, which is mostly carried out by hazardous chemicals like hydrofluoric acid or concentrated sodium hydroxide solution. The soft templating route, however, although being more versatile than the hard templating one, is quite expensive because of the employment of block copolymers and limited to pores sizes between 2 and 8 nm. Moreover, regular shaped monoliths, which are favored especially for application as electrodes [27,28], are difficult to obtain from these routes.

And although a few reports exist on the synthesis of monolithic carbons by soft templating methods [29,30], in general, carbon aerogels prepared by pyrolysis of organic aerogels are employed when monolithic materials are required. These materials have first

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been described by Pekala et al. [31,32] and are usually synthesized by reaction of resorcinol and formaldehyde in presence of a catalyst. Their pore size can be easily adjusted by the amount of catalyst and the concentration of monomers [33–35]. However, the preparation of carbon aerogels usually involves long synthesis times and expensive supercritical drying of the organic gels.

A versatile alternative is the synthesis of organic monoliths via phase separation followed by carbonization. This method has been widely used for the synthesis of macroporous carbon monoliths [36–39]. Phase separation in polymeric systems can be induced thermally and chemically. In systems with an upper critical solution temperature thermally induced phase separation can be realized by cooling until the binodal or spinodal line is reached. Chemically induced phase separation (CIPS), however, is more complex and is initiated through the polymerization of the components. Thus, it is also called polymerization induced phase separation. In principal, CIPS is based upon the solubility of the polymer, which decreases with proceeding polymerization until it is no longer miscible with the solvent and phase separation occurs [40,41]. When a sol-gel reaction of the precursors is taking place in parallel to the phase separation the process can be regarded as freezing of the current structure of phase separation. As a result, the onset of phase separation and thus the structure and pore size of the resulting material can be controlled by careful selection of the solvent or solvent mixture. Depending on the actual composition of the system the phase separation can proceed via a nucleation-growth mechanism in the composition range between binodal and spinodal line or via spinodal decomposition in the range within the spinodal line [40,41].

Nakanishi and co-workers have shown that employing a resorcinol/formaldehyde system in a solvent mixture of water and ethanol catalyzed by iron(III) chloride is suitable for the production of macroporous carbon monoliths by a CIPS mechanism [39]. By varying the amounts of ethanol and iron(III) chloride they could synthesize carbons with macropore sizes ranging from approximately 200 nm to 3.5 μm. The same group also produced macroporous carbon monoliths with pores in the same order of magnitude with hydrochloric acid instead of iron(III) chloride [3].

Alonso-Buenaposada et al. found that the porosity of resorcinol-formaldehyde and carbon xerogels strongly depends on the methanol content of the formaldehyde solution applied [42–44]. For higher amounts of methanol they obtained xerogels with smaller pores. This behavior was attributed to an increased stabilization of formaldehyde through higher amounts of methanol that leads to a lower reaction rate. But from the information given it is as well possible that the changes in porosity are caused by a delay of phase separation due to the higher methanol content.

Moreover, Zhu et al. have shown that phase separation is also a suitable tool for the synthesis of carbon nanospheres [45]. They polymerized resorcinol and formaldehyde in a mixture of hydrochloric acid and ethanol in presence of F127. Varying the amounts of hydrochloric acid, ethanol and F127 mainly lead to aggregated spherical particles but for certain compositions monodisperse nanospheres were obtained.

These different aspects of phase separation show that a closer investigation is necessary which synthesis conditions yield which type of product. Thus, in this work, we carried out a detailed investigation of the phase separation of the resorcinol/formaldehyde sol-gel system in water and ethanol with hydrochloric acid as catalyst. By varying the ratio of water to ethanol, we obtained porous carbon monoliths (PCMs) with a wide range of pore sizes from small mesopores to large macropores. To the best of our knowledge, this is the first time that such a wide range of pore sizes has been covered by a single synthesis route. And while the synthesis of macroporous monoliths by phase separation is well explored [3,39], the synthesis of mesoporous monoliths has not been investigated in detail, so far. Moreover, we activated selected carbon monoliths in a stream of CO_2 at 900 and 950 °C, which lead to increased microporosity and high surface areas. As these factors are favorable for gas adsorption, the activated monoliths were investigated in terms of their CO_2 adsorption capacity.

2. Experimental details

2.1. Chemicals

The chemicals used for the synthesis of porous carbon monoliths were resorcinol (Sigma Aldrich, 99%), formaldehyde (Grüssing, 37 wt.% in water, stabilized with 15% methanol) hydrochloric acid (VWR Chemicals, 37 wt.% in water) and ethanol (Acros Organics, 99.5%).

2.2. Synthesis of porous carbon monoliths

The synthesis of porous carbon monoliths is based on a synthesis of Hasegawa et al. [3,39] with slight modifications.

For the synthesis of polymeric monoliths, 2.20 g of resorcinol were dissolved in 0.01 M hydrochloric acid and ethanol. The solution was cooled in an ice-bath for 30 min before the addition of 3.0 mL of formaldehyde (37 wt.% aqueous solution), which yields a molar ratio of formaldehyde to resorcinol of 2.02. The solution was stirred in the ice-bath for ten more minutes and was then quickly transferred to a centrifuge tube. The tube was placed in a water bath at 40 °C for polymerization for 24 h. After the polymerization, the samples were dried at 60 °C in air for five days. Carbonization was carried out in a tubular furnace under argon atmosphere at 1000 °C for 5 h (heating rate: $4\ K \cdot min^{-1}$).

The amount of hydrochloric acid and ethanol was varied from 4.9 mL of hydrochloric acid and 0.1 mL of ethanol to 3.0 mL of hydrochloric acid and 2.0 mL of ethanol. Hence, samples are denoted as PCM-*x*-*y*, in which *x* specifies the volume of hydrochloric acid and *y* the volume of ethanol. Table S1 in the supplementary data presents a detailed synthesis composition for each sample.

2.3. Activation procedure

Before activation, the samples were evacuated for 60 min. The monoliths were then heated to 900 °C or 950 °C with a heating rate of $10\ K \cdot min^{-1}$ in a constant flow of CO_2 (flow rate: $10\ mL \cdot min^{-1}$). The samples were held at the activation temperature under the flow of CO_2 between one and 4 h. After activation the monoliths were cooled to room temperature in a flow of nitrogen (flow rate: $50\ mL \cdot min^{-1}$).

2.4. Characterization methods

X-ray diffraction patterns were recorded with a PANalytical X'Pert Pro MPD using Cu Kα radiation ($\lambda = 1.5406$ Å, 45 kV, 40 mA).

Raman spectra were measured on a Bruker Senterra Raman microscope ($\lambda = 532$ nm, $P = 5$ mW).

Scanning electron microscopy images were taken on a Zeiss Leo 1525 and on a FEI Quanta 3D FEG microscope operated at 5 kV.

Nitrogen physisorption measurements were performed on a Quantachrome Quadrasorb-SI-MP and an Autosorb-6-MP instrument at 77.4 K. Pore size distributions were calculated from the adsorption and desorption branch by a quenched solid density functional theory (QSDFT) model assuming slit pores for pores smaller than 2 nm and cylindrical pores for pores larger than 2 nm with a moving point average of 3. The specific surface area was