Research Letter

Preparation and Characterization of a Calcium Carbonate Aerogel

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We report on a facile method for the preparation of a calcium carbonate aerogel consisting of aggregated secondary vaterite particles with an approximate average diameter of 50 nm. It was synthesized via a sol-gel process by reacting calcium oxide with carbon dioxide in methanol and subsequent supercritical drying of the alcogel with carbon dioxide. The resulting monolith was opaque, brittle and had overall dimensions of $6 \times 2 \times 1$ cm. It was characterized by X-ray powder diffraction, nitrogen adsorption method (BET), and scanning electron microscopy.

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1. Introduction

The preparation of an aerogel was first described by Kistler in the 1930s. He synthesized a silica-based aerogel via a wet chemical sol-gel process and subsequent supercritical solvent extraction [1, 2]. The aerogel showed unique material properties such as high optical transparency or opacity, heat insulation capability, and high absorption capacity [3, 4]. These properties led to the use of silica aerogels in ion exchange materials, adsorbents, semipermeable membranes, pharmaceuticals, cosmetics, optical and acoustical devices, coating materials, and heat insulation applications for buildings [5–7]. Since then, various types of aerogels based on carbon [8], alumina [9, 10], transition metal oxides [11], or main-group metal oxides [12] were synthesized.

In 2007, Horga et al. reported on the preparation of a calcium carbonate aerogel for the first time [13]. Their process involves the ionotropic gelling of alginate in a calcium salt solution, followed by an exchange of the solvent water against ethanol, and supercritical drying of the calcium alginate alcogel. Calcination of the calcium alginate aerogel finally leads to a calcium carbonate aerogel. Obviously, this process requires many consecutive steps. In this communication we report on a more facile way to prepare a calcium

carbonate aerogel resulting from the condensation of vaterite nanoparticles. These were prepared by controlled hydrolysis of calciumdi(methylcarbonate) which was obtained by the reaction of carbon dioxide with calcium oxide in absolute methanol. The resulting CaCO_3 alcogel was subjected to supercritical drying with CO_2 to produce the CaCO_3 aerogel.

2. Experimental Section

2.1. Preparation of CaCO_3 Sol. Buzagh's method was used to prepare the CaCO_3 sol [14]. Thus, 54.0 g (0.963 mol) calcium oxide (calcined for 24 h at 950°C) were suspended in 800 mL absolute methanol (dried and stored over molecular sieve, 3 nm) and heated to 40°C . After 90-minute stirring, carbon dioxide was bubbled through the reaction vessel for one hour at a flow rate of 1 L/min. The carbon dioxide was fed into the reaction vessel through a metal tube close to a stirrer (1000 rpm) to ensure a fast reaction in the methanolic suspension. When all the calcium oxide was dissolved and converted into a sol, the flow of carbon dioxide was stopped. The resulting sol contained nanoparticles with particle sizes ranging from 5 to 20 nm (dynamic light scattering measurements, Zetasizer Nano-ZS, Malvern Instruments Ltd.).

SCHEME 1: Reaction steps involved in the formation of the CaCO_3 sol from calcium oxide and gaseous carbon dioxide in methanol.

FIGURE 1: X-ray powder diffraction pattern of the CaCO_3 aerogel. Vertical dotted lines correspond to JCPDS entry 33-0268 (vaterite).

The particle size distribution curve showed a maximum at approximately 11 nm.

2.2. Sol-Gel Conversion. The sol turns into a translucent alcogel when stored for a short time (<1 hour). The gelation time depends on the amount of water present in the reaction vessel and the temperature. When more water was present during the synthesis (e.g., because of not using absolute methanol), gelation already took place in the reaction vessel. Higher temperature also leads to faster sol-gel conversion. The alcogels obtained were stable for days when stored under refrigeration. In air and at room temperature, they dried to an opaque powder which, when being freshly prepared, consisted of pure vaterite particles.

2.3. Preparation of CaCO_3 Aerogel. A part of the calcium carbonate alcogel was subjected to supercritical drying with carbon dioxide. The supercritical drying was carried out in a 1 L pressure autoclave (Parr Company, Germany). Approximately 18 g of alcogel were placed in the autoclave, and absolute methanol was added until the gel was completely immersed in the solvent. The autoclave was then sealed, pressurized slowly with carbon dioxide to 6.0 MPa and brought to a temperature of 281 K. When equilibrium was achieved between the methanol in the gel and the carbon dioxide surrounding the gel, the pressure was reduced to 4.0 MPa and then repressurized with carbon dioxide to 6.0 MPa. This procedure was repeated several times until the methanol was completely removed from the system. Subsequently, the autoclave was heated to 316 K which is above the critical temperature of carbon dioxide and kept there for at least one hour. After slow depressurization to atmospheric pressure, an opaque and brittle aerogel with

FIGURE 2: SEM pictures of the CaCO_3 aerogel; magnifications: 50,000 $\times$ (large picture) and 100,000 $\times$ (insert).

FIGURE 3: Schematic drawing of the reaction steps involved in the formation of the CaCO_3 gel.

dimensions of $6 \times 2 \times 1$ cm was obtained. The size of the aerogel was limited by the dimensions of the autoclave.

3. Results and Discussion

The sequence of reactions involved in the formation of the CaCO_3 alcogel which is the precursor for the preparation of the CaCO_3 aerogel is shown in Scheme 1. The aerogel was obtained by displacing methanol present in the alcogel with CO_2 .

The phase composition of the aerogel was determined by X-ray powder diffraction (Figure 1). The XRD pattern observed was identical with vaterite, a polymorph of calcium carbonate which is metastable at ambient temperature. The relatively large half width and the low intensity of the Bragg reflections indicate small particle sizes and only a moderate crystallinity.

A specific surface area (BET) of $45 \text{ m}^2/\text{g}$ was found for the calcium carbonate aerogel by nitrogen absorption. This value corresponds to an average particle diameter of approximately 50 nm, provided the particles in the aerogel are discrete, monosized, and spherical.

In Figure 2, SEM pictures of the aerogel are shown. The secondary vaterite particles in the aerogel exhibit a spherical and/or fibre-like shape with an average diameter of approximately 50 nm. This value corresponds quite well

with the diameter calculated from the nitrogen adsorption measurement. As can be seen in the SEM pictures, the individual particles are not strongly connected with each other. In fact, they are merely aggregated, which explains the brittle character of the calcium carbonate aerogel when mechanical stress is applied.

The formation of the calcium carbonate aerogel occurs in a three-step process which is illustrated in Figure 3. First, calcium di(methylcarbonate) is hydrolyzed by water to form an intermediate sol containing primary CaCO_3 nanoparticles showing a size of approximately 5 to 20 nm. Existence of these primary particles was also confirmed by TEM pictures (not shown here). In a second step, the primary particles grow to spherical or fibre-like secondary particles which were observed under the SEM. In a third step, these secondary particles finally aggregate to the gel.

Because water is the starting reagent for seed formation in this system, the amount of water present during the reaction greatly influences the number, morphology, and size of the primary and secondary particles and therefore also the bulk properties of the aerogel.

4. Conclusion

Through the simple synthesis described here, calcium carbonate aerogels are readily available from inexpensive starting materials. Aerogels with different surface areas, specific densities, and pore sizes are accessible. Our process allows to produce monoliths with a volume of 20–30 cm³. Potential applications include heat insulating materials and fillers for plastics.

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