



Subcritically dried resorcinol–formaldehyde aerogels from a base–acid catalyzed synthesis route



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ARTICLE INFO

Article history:

Received 21 March 2014

Received in revised form 25 June 2014

Accepted 28 June 2014

Available online 8 July 2014

Keywords:

Sol–gel

Resorcinol–formaldehyde aerogel

Base–acid catalyzed

Subcritical drying

ABSTRACT

Resorcinol–formaldehyde (RF) aerogels are prepared from a newly developed base–acid catalyzed sol–gel synthesis route. RF-gels synthesized are nanostructured and can be dried under ambient conditions without significant shrinkage. The sol–gel reaction of resorcinol (R) and formaldehyde (F) in water (W) (R/F = 0.7, R/W = 0.04) is initially catalyzed by Na₂CO₃ with a molar ratio of resorcinol to catalyst (R/C) of 100. After a specified time after starting the reaction (1–3 h), citric acid (1 M, 4–20 vol.%) is added which initiates the acid catalyzed step and causes a spontaneous gelation. The time of change in pH value by adding acid is of great importance and influences the structure and properties of the material. RF-aerogels consisting of small particles much smaller than 100 nm are prepared by applying a long base catalyzed step. Particle size, density, thermal conductivity and surface area are basically independent of the amount of citric acid, but this parameter influences the mechanical resistance. A theoretical model is used to describe the time dependence of catalyst change in the sol–gel process.

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1. Introduction

Nanoporous materials, such as aerogels, are increasingly important in various fields of technology due to their attractive properties. The characteristic properties of aerogels are high porosity of more than 80%, high surface area (up to 1000 m² g⁻¹), low envelope density (0.03–0.5 g/cm³) and low thermal conductivity (as low as 0.012 W/m K) [1,2]. These properties lead to applications such as thermal or acoustic insulation materials [3]. Moreover carbon aerogels are used as supercapacitors, battery electrodes or as adsorbents due to a high electrical conductivity, high surface area and a controllable pore structure [4–6]. Carbon aerogels are synthesized via the pyrolysis of organic aerogels. One of these organic aerogels is resorcinol–formaldehyde (RF) which was first published by Pekala [7] in 1989. They are produced by a sol–gel reaction of resorcinol (1,3-dihydroxybenzene) and formaldehyde in an aqueous solution [8,9]. The molecules undergo an electrophilic aromatic substitution to hydroxymethyl resorcinol derivatives (–CH₂OH) via one, two or three times of substitution on the same aromatic resorcinol. The derivatives react in a condensation reaction and form methylene (–CH₂–) and methylene ether (–CH₂OCH₂–) bridged compounds. It was discovered, that the pH-value catalyzes the

electrophilic aromatic substitution by activating resorcinol (base catalyzed) or formaldehyde molecules (acid catalyzed) [8]. A deprotonation of resorcinol in the base catalyzed route causes a higher electron donating ability and enhances the reactivity. In contrast, the acid catalyst induces a higher electrophilicity of formaldehyde by protonation. Meanwhile, different bases and acids were tested adjusting the pH-value, e.g. Na₂CO₃ [7,10], (NH₄)₂CO₃ [11], acetic acid [12] or hydrochloric acid [13]. The catalyst influences strongly the time of gelation and the structure formed, but not exclusively. Likewise the molar ratios of resorcinol to formaldehyde (R/F), resorcinol to water (R/W) and resorcinol to the catalyst (R/C) and the reaction conditions such as the temperature design the reaction and the latter properties of the aerogel [14]. Usually, RF-aerogels were dried using a supercritical fluid like CO₂. For this, all substances in the pores of the gel, i.e. all unreacted educts and not polymerized molecules, need to be removed and replaced by a solvent which is miscible with CO₂. In an autoclave supercritical CO₂ extracts the solvent without cracks or a collapse of the three-dimensional network. In 1997 Fischer et al. [5] first published ambient pressure (subcritically) dried RF-aerogels by employing a different recipe than Pekala had practiced. They changed the molar ratios of R/C from a high base catalyst concentration (R/C ≤ 300) to a very low concentration (R/C = 1000–1500). In a RF-solution with a low base catalyst concentration less particles but bigger ones are formed with a size about a few hundred nanometers up to a few microns. The walls of the network are then

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strong enough to withstand the capillary forces during subcritical drying, i.e. evaporation of the solvent. In contrast to supercritically dried and nanostructured RF-aerogels, subcritically dried ones have higher thermal conductivity, lower surface area and are more dense due to the structure [15,16].

The present paper describes the synthesis and the characteristics of subcritically dried RF-aerogels from a base–acid catalyzed synthesis route which combines the conventional base and acid catalyzed methods. Properties were considered under the aspect of density, surface area and thermal conductivity and the structure is analyzed by SEM examination.

2. Experimental

2.1. Materials

The chemicals used are resorcinol (>98%) and sodium carbonate Na_2CO_3 ($\geq 99.8\%$) which are purchased from Sigma Aldrich. The 24% formaldehyde solution (not buffered) used is from VWR, citric acid ($\geq 99\%$) from Merck and ethanol (denatured, 96%) from Walter CMP GmbH & Co. KG. All chemicals were used as received.

2.2. Synthesis

13.76 g of resorcinol are dissolved in 43.77 g deionized water and the base catalyst Na_2CO_3 (0.133 g) is added while stirring. After homogenisation, 21.23 g of a 24% formaldehyde solution is added to start the sol–gel reaction. The recipe used contains the molar ratios resorcinol to formaldehyde (R/F) of 0.7, resorcinol to water (R/W) of 0.04 and resorcinol to catalyst (R/C) of 100. The moment of adding the formaldehyde solution is taken as the zero-point in time. After 10 min of stirring, 60 mL are taken from the solution and filled in a separate vessel which is heated by a water bath to 40 °C. After a specified time after the zero-point, citric acid (1 M) is added initiating the acid catalyzed step. Times chosen are between 1 and 3 h with a time distance of 0.5 h and the volume percentage of citric acid is 4, 8, 14 or 20 vol.%. The final gelation and 6 days of aging is then performed at 40 °C supplemented by the washing procedure with ethanol and the subcritical drying at 40 °C until the weight of the sample is stable.

2.3. Methods

The density was determined with the envelope density analyzer GeoPyc[®] 1360 from Micromeritics and a compression test was performed with a testing instrument from Lutzke implemented with a pressure gauge realizing a maximal force of 100 N. The thermal conductivity was measured by the Hot Disc method with the thermal constants analyzer type TPS 2500. The specific surface area S_{BET} was obtained using nitrogen adsorption with the analyzer TriStar II 3020 from Micromeritics and was calculated using the Brunauer–Emmett–Teller (BET) model [17]. Finally, the microstructure was examined with a field emission scanning electron microscope (FE-SEM) Merlin[®] from Carl Zeiss after sputtering the sample with gold.

3. Results

3.1. Formation of base–acid catalyzed RF-aerogels

A photograph of a base–acid catalyzed aerogel is shown in Fig. 1. The aerogels prepared appear in a color between ocher, orange and brown. A freshly prepared RF-solution is yellow colored and changes to a dark-red color during base-catalyzed sol–gel process. When citric acid is added, a formation of particles is noticeable



Fig. 1. Photograph of a subcritically dried base–acid catalyzed resorcinol–formaldehyde (RF) aerogel synthesized.

which causes a bright-red cloudy and milky dispersion. The viscosity increases rapidly until the gel point is reached what takes 2–5 min after the addition of acid. An aerogel such as pictured in Fig. 1 is then obtained after aging and drying.

The catalysts influence the pH value of the RF-solution which affects directly the gel formation. The graph in Fig. 2 illustrates the change of pH value of the RF-solution during a base catalyzed (R/C = 100) and during a base–acid catalyzed (R/C = 100, 14 vol.% citric acid) route. The pH is plotted against the time wherein the zero-point in time is the moment the last component formaldehyde was added to the resorcinol solution and the sol–gel reaction was started. In both cases the reaction starts at pH = 7.3. When only the base catalyst is present, the pH value decreases slowly and reaches 5.8 near the gel point. Between 10 and 80 min the negative slope is strong and nearly linear and then decreases gradually and finds an almost constant value at 5.8. After 2 h and later on an

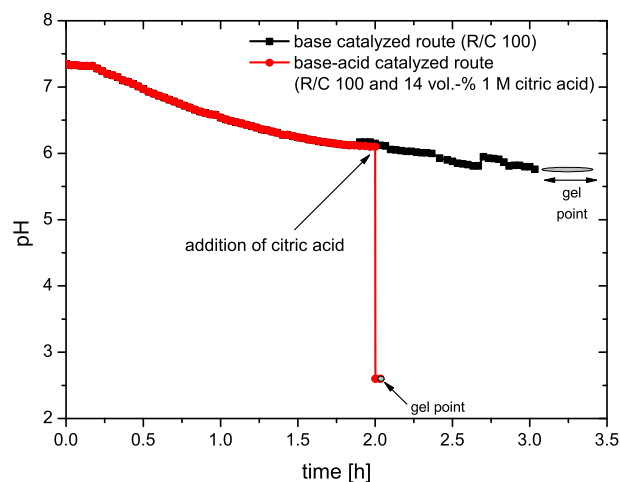


Fig. 2. Change in pH value during the sol–gel reaction of a base catalyzed resorcinol–formaldehyde (RF) solution at 40 °C (base catalyst: Na_2CO_3 , R/C = 100) and of a base–acid catalyzed RF-solution (base catalyst: Na_2CO_3 , R/C = 100; acid catalyst: 1 M citric acid, 14 vol.%, time of addition: 2 h). The zero-point is the moment the last component formaldehyde was added to the RF-solution.

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