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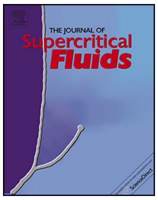

View cell investigation of silica aerogels during supercritical drying: Analysis of size variation and mass transfer mechanisms

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ABSTRACT

We report the synthesis and supercritical drying of silica aerogels made via a sol–gel process. Tetramethylortosilicate has been used as precursor. Hydrolysis and poly-condensation steps were followed by carbon dioxide supercritical drying ($T = 45\,^\circ$C; $P = 10.5$ MPa). The complete supercritical drying step was video recorded in order to study the evolution of the size of the gels, concluding that a noticeable shrinkage only takes place during the decompression of CO_2 at the end of the drying process, being the total shrinkage of 3–4%. The mass transfer mechanisms during drying have also been studied through analysis of the evolution transparency of the aerogels along the supercritical drying process. The mass transfer processing during drying was observed to be dominated by convection in the earliest stages, where a direct relationship between drying rate and CO_2 flow were found. In the later stages, diffusion of the remaining organic solvent through the alcogel determined the mass transfer process.

1. Introduction

Aerogels are micro-mesoporous materials with typical pore sizes of 10–100 nm, high surface areas (400–1500 m^2/g), low densities (typically 0.25–0.5 g/cm^3, although densities as low as 0.003 g/cm^3 can be achieved) and high porosities (92–98%) [1]. This unique combination of characteristics, that confers very interesting properties to aerogels like a low thermal conductivity, ultra-low dielectric constant or low index of refraction, has given rise to a wide range of practical applications. The most developed application of aerogels, already in a commercial stage, is as high performance thermal insulating materials, which is favored by the low thermal conductivity of the material as well as by its low cost, low weight and high transparency to visible light [2]. Aerogels are also widely used as carrier materials, as their very high pore volumes (up to 4 cm^3/g) allow for loading capacities significantly above those of alternative porous materials, while their pore size characteristics provide favorable mass transfer conditions, with gas diffusion coefficients of the order of 0.1 cm^2/s, a similar order of magnitude as bulk gas diffusion coefficients [3]. Active compounds successfully loaded into aerogels include pharmaceuticals [4] and inorganic compounds [5]. The high thermal stability of silica aerogels, with melting temperatures above 1200 °C, makes them suitable for applications as catalyst supports in reactions performed at high temperatures, as for example hydrogenation reactions using palladium catalysts supported in aerogels [6]. Their surface activity, inferred by the abundance of hydroxyl groups, that can be used as active sites for the incorporation of different functionalization agents [7], makes them useful as filters for volatile organics or for other applications in which an active surface is needed [8].

Aerogels are obtained through a two-step process: a sol–gel intertwining reaction, yielding a solid gel structure immersed in an alcohol solvent medium known as alcogel, and the removal of this solvent from the pores of this gel to produce a dry aerogel. The key process step that infers the unique textural properties of aerogels (high surface area, pore volume, pore size distribution...) is the solvent removal. This step can be difficult due to the surface tension of the liquid contained in the gel nanopores that infers a capillary pressure gradient during the formation of aerogels by drying of gels. Several techniques have been used in order to dry the aerogels like atmospheric drying and freeze drying [9], but the most successful results have been obtained employing a supercritical drying technique [1,10], either with supercritical carbon dioxide or supercritical alcohol, that allows removing the solvent without formation of gas–liquid interfaces thus reducing the possible collapse of the pore structure of the aerogel during drying.

Even employing supercritical drying methods, certain shrinkage of aerogels due to a partial collapse of their pore structure or other

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morphological variations is frequently observed after drying. This makes it difficult to obtain dry aerogels of a controlled, specified size. The effects of the aging and drying conditions on the properties of silica aerogels using supercritical alcohol drying have been studied by L. Kocon et al. [11] and Juncal Estella et al. [12] concluding that these conditions strongly influence the porous structure of silica gels, and that shrinkage during supercritical alcohol drying is mainly due to the re-structuring of clusters. Using supercritical carbon dioxide for the drying, the impact of depressurizing rate on the porosity of resorcinol-formaldehyde gels has been investigated by G. Amaral-Labat et al. [13] and Orsolya Czakkel et al. [14], concluding that shrinkage always increased with increasing depressurizing rates. The results show that during the pressurization stage, the overall structure of the network remains unaffected by the rate of increase of pressure; on the other hand, depressurizing rate of the autoclave after drying has a significant influence on the final shrinkage, and hence on the resultant bulk density, surface area and pore volumes. Another point to consider is that if the diffusion time is not long enough, residual contents of solvent inside the aerogel could form a liquid phase during depressurization. Indeed, Zoran Novak et al. [15] claimed that cracks are caused by entering the two-phase region during the depressurization of the autoclave.

On the other hand, the precise characterization of the mass transfer mechanisms of aerogel drying is important for the evaluation of the minimum drying time required to achieve the desired solvent residual content, which strongly influences the textural properties of the aerogel as concluded by García-González et al. [16]. Most modeling studies of aerogel drying assume that drying is governed by the diffusion of organic solvent through aerogel pores. García-González et al. [16] and P. Wawrzyniak et al. [17] studied the kinetic profile of the extraction curves of ethanol from silica aerogel, and correlated the results using the Fick's law in cylindrical coordinates. Novak et al. [15] concluded that the diffusion coefficient was uniform throughout cylindrical aerogel samples. These authors observed significant discrepancies between model and experimental results during the first stages of drying, while a good agreement was attained in the latter stages. Based on these results, García-González et al. [16] hypothesized that the process is governed by a mass transfer mechanism based on a combination of convection and diffusion, with an initial preponderance of convection and an increased contribution of diffusion to the process as drying time progresses and less solvent remains in the gels.

In this work, tetramethylortosilicate (TMOS) has been used as precursor of a sol–gel reaction forming gel monoliths of different sizes in methanol solvent media, and solvent from these alcogels has been removed by extraction with supercritical carbon dioxide thus producing dry aerogel monoliths. The drying process has been carried out in a high pressure view cell. It has been video recorded in order to follow the evolution of the aerogels during the drying with supercritical carbon dioxide, paying special attention to the size variation and the advective transport during the first stages of the drying. With this, direct information regarding the mass transfer mechanisms and the drying steps in which variations of the dimensions of the aerogel occur has been obtained.

2. Experimental methods

2.1. Reagents

Tetramethoxysilane (98% purity), and NH_4OH (28.0–30.0%) were purchased from Sigma–Aldrich (Spain). Methanol (99.8% purity) was obtained from Panreac (Spain). CO_2 (>99.95 purity) was supplied by Carburos Metálicos S.A. (Spain) Deionized water was used in all experiments.

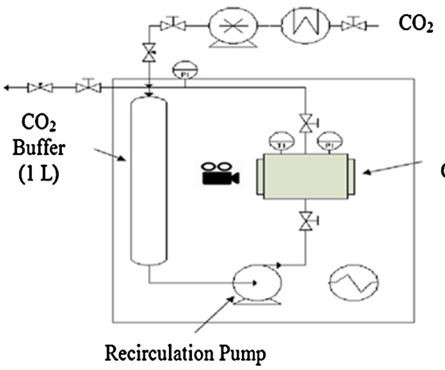

Fig. 1. Equipment used for supercritical drying of aerogels.

2.2. Processing

2.2.1. Preparation of silica gel cylindrical monoliths

Hydrophilic silica alcogels were produced following the sol–gel process used by other authors such as Suzana Štandeker et al. [18] or Carlos Folgar et al. [19], following the molar ratio: TMOS:CH_3OH:H_2O:NH_4OH, 1:3:4:5 × 10^{-3}. Methanol and TMOS were mixed together and the solution of ammonium hydroxide–water was added to the mixture drop by drop. After a few seconds the stirrer was stopped and the mixture was poured into cylindrical molds of different diameters (~8.9 mm and ~14.2 mm) for gelation. Straightaway, gels were immersed in methanol for aging during a period of at least 7 days. During this time methanol was renewed twice in order to completely remove water from the solution before initiating the supercritical CO_2 drying of the gels.

2.2.2. Supercritical drying of gels

The equipment schematized in Fig. 1 was used for supercritical drying of alcogels. The main components were a 1 L CO_2 buffer, a 25 mL extractor (view chamber) and a recirculation gear pump whose frequency of rotation could be modified thus varying the CO_2 flowrate through the view cell. The entire equipment was placed inside a hot air circulating oven that kept the temperature constant during drying.

After the aging period described in Section 2.2.1, alcogels were placed on a metallic tray in the extractor. Straightaway, the rest of the container was filled up with methanol in order to avoid the formation of cracks in the alcogel while the supercritical conditions were reached. Then the complete equipment was heated and CO_2 was pumped into the circuit. Once the operation conditions were reached (10.5 MPa, 45 °C), the recirculation pump was activated and extraction of methanol began. In order to increase the efficiency of drying, CO_2 in the closed circuit was renewed several times during each experiment. During CO_2 renewal, the extractor was isolated from the rest of the circuit by closing the valves in the inlet and outlet of the extractor, which allowed to renew the CO_2 of the rest of the circuit without decompressing the view chamber, thus minimizing the damage in the aerogel structure due to pressure variations during CO_2 renewal. Three loads of fresh CO_2 were required in order to remove methanol from the alcogels. These loads were renewed after extraction times of 30 min in the first cycle, 45 min in the second cycle, and 45 additional minutes in the third cycle. Adding the time spent between the cycles (when reloads took place), the total drying time was about 3 h, in good agreement with the times proposed by different authors including M.J. van Bommel et al. [20]. Finally the equipment was slowly in order to avoid formation of cracks in aerogels. Different decompression rates of the order of ~0.3 bar/min were tested.