Supercritical Drying of Aerogels Using scCO$_2$: Modeling and Drying Time Optimization

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Aerogels are nanoporous materials with open pore structures and large specific surface areas. Wet gels turn to aerogels by using a suitable drying technology, usually the supercritical fluid-assisted drying process, able to avoid the pore collapse phenomenon in order to keep intact the nanoporous texture of the wet material. The engineering of aerogel materials requires a deep knowledge of the different materials processing steps. In this work, the influence of different gel formulation parameters (e.g., target density, initial gel solvent used, morphology) on the supercritical CO$_2$-assisted drying of aerogels was evaluated in terms of drying profile and kinetics. The contribution of diffusion in the supercritical drying and the use of the Fickian model for the description of the process mechanism was evaluated.

1. INTRODUCTION

Aerogel technology provides high added-value lightweight materials (densities as low as 0.004 g/cm^3) with outstanding surface area (up to 3000 m^2/g) and open porosity (95-99 %). Namely, current market demand for silica aerogels has increased for several industrial applications (space engineering, thermal insulation, solar-energy collectors, Cherenkov detector, waste treatment, drug delivery and targeting systems) [1].

The general processing steps followed for the production of aerogels are summarized in Fig. 1. Briefly, aerogel processing starts with the formation of a gel from an aqueous solution (*hydrogel*) or an organic solution in general (*lyogel*) (Step 1 in Fig. 1). Gel formation from the solution (*sol*) is induced by a chemical or physical cross-linking promoter. Then, the water or organic solvent present in the gel structure is usually replaced by an alcohol to lead to an alcogel (Step 2). Finally, the solvent (usually ethanol) is extracted from the gel by a proper drying method (Step 3), usually supercritical carbon dioxide scCO$_2$-assisted drying, in order to obtain the aerogel end material.
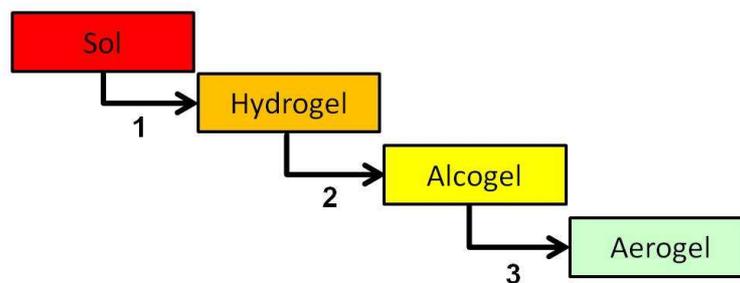
Fig. 1: Schematic depiction of the supercritical drying process for the preparation of aerogels: *1*: Gelation; *2*: Solvent exchange from water to ethanol; *3*: Supercritical CO$_2$-assisted drying of gels.

The engineering of aerogel materials requires a deep knowledge of the different processing steps depicted in Fig. 1. In this respect, the main challenge during the drying step (Step 3 in Fig. 1) is to eliminate the liquid solvent from the gel without collapsing the already existing nanoporous structure and thereby avoiding the subsequent shrinkage and cracking of the dried gel. Three main drying techniques are distinguished (Fig. 2): *(1) Ambient air drying* is not able to preserve the gel structure leading to *xerogels*. The liquid-vapor menisci existing in the pores of the gel recedes upon drying inferring a capillary pressure gradient in the pore walls of up to 100-200 MPa, able to collapse the pores. *(2) Freeze drying* lowers the temperature of the gel below the crystallization temperature of the solvent (Step 2.i in Fig. 2) and then the solvent is removed as a vapor by reduction of pressure (sublimation, Step 2.ii). This drying method needs slow sublimation rates and if the gel solvent volume increases upon crystallization, the obtained dried gel (*cryogel*) is cracked and usually in the form of small particles. *(3) Supercritical drying* of gels (Step 3.i: liquid solvent to supercritical solvent; Step 3.ii: supercritical to gaseous solvent) avoids the presence of any intermediate vapor-liquid transition and surface tensions in the gel pores, preventing the gel structure from the pore collapse phenomenon during solvent elimination. Hence, supercritical drying overcomes the problems encountered with the other drying methods to preserve the high open porosity and superior textural properties of the wet gel in a dry form.
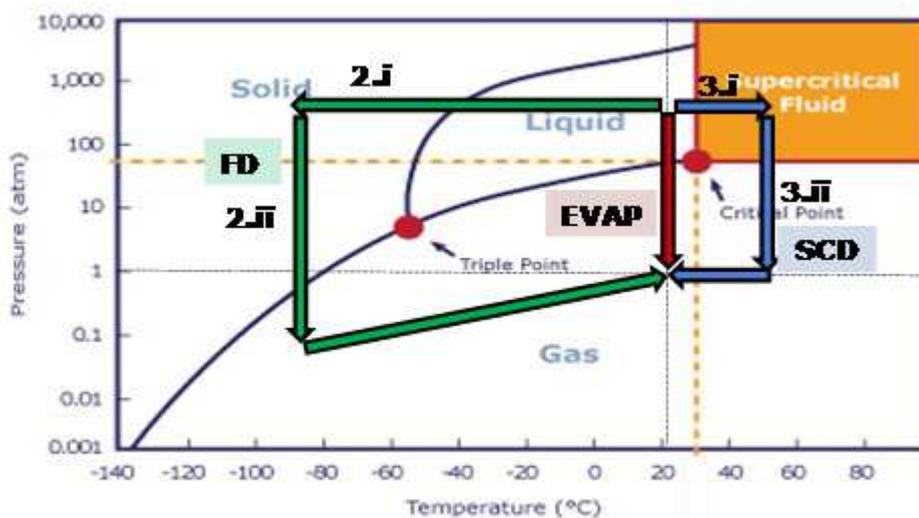
Fig. 2: Drying routes for the solvent (liquid CO_2 as an example) removal of a gel: Atmospheric drying (EVAP, red line), freeze drying/lyophilisation (FD, green lines) and supercritical drying (SCD, blue lines).

The study of the kinetics of the gel supercritical drying is regarded as a key aspect to be considered in the specific case of the design of high-performance aerogel-based materials. Materials engineers usually overestimate the drying time as an experimental approach to ensure that no remnant liquid is present in the dried gel, so that aerogels are formed. However, this praxis cannot be allowed in an industrial production scale, due to the resulting waste of resources (man-hours, energy, facilities…). The study of the gel drying will not only

provide fundamental information for the design of aerogel materials, but will also allow the optimization of the process from an economical point of view since it will reduce processing times and optimize the exploitation of resources.

In this work, the effect of different gel parameters (target density –0.08 or 0.15 g/cm^3–, initial gel solvent –ethanol or acetonitrile– and morphology –cylinders or microspheres–) on the supercritical drying of silica gels will be evaluated in terms of drying profile and material textural properties.

2. MATERIALS AND METHODS

2.1. REAGENTS

Tetramethoxysilane (TMOS, 98% purity) was purchased from Fluka Germany. Methanol 99.5%, hydrochloric acid 30% and ammonium hydroxide 25% were purchased from Merck Germany. Ethanol (99.8 % purity) and acetonitrile (chromatographic grade) were obtained from Omnilab and SigmaAldrich, respectively. Deionized water was used in all experiments. Domestic grade of canola oil was used for the preparation of the silica gel microspheres. CO_2 (>99.9 mol% purity) was supplied by AGA Gas GmbH. All chemicals were used as provided without any further processing.

2.2. PROCESSING

2.2.1. Gel preparation

Silica gel monoliths (L=3.0 cm, D=1.2 cm) were produced following the two step sol-gel process reported in literature [2] using TMOS as silica precursor and ethanol or acetonitrile as initial solvent to reach aerogel target densities of 0.08 g/cm^3 or 0.15 g/cm^3. The resulting aerogel samples were labeled as Si-X-Y, being X=0.08 or 0.15 depending on the aerogel target density (g/cm^3), and Y=EtOH, AcN as a function of the initial gel solvent used (ethanol and acetonitrile, respectively). After gelation, the resulting gels are aged in ethanol for a minimum period of one week.

Silica aerogel microspheres were prepared by coupling the sol-gel processing to the emulsion (ethanol-in-ethanol saturated oil, 1:1 volume ratio) technology [3]. The resulting gel-oil dispersion was left overnight for aging and then filtered. The resulting gel microspheres were soaked in ethanol for a minimum period of one week.

2.2.2. Supercritical drying

The gel was placed in a tubular autoclave (Column E1 in Fig. 3) of the equipment along with a known excess of ethanol. The temperature of the column was fixed at 318 K and the system was pressurized with CO_2 up to 11.0 MPa. Then, an outlet flow of CO_2 through the column of 2 NL/min was set. The gaseous CO_2 outlet stream was vented to the ambient and the ethanol-rich liquid stream was collected in glass vials. An alcoholmeter device (Dräger 6810) was coupled to the gaseous outlet of the setup to measure the amount of ethanol contained in the gaseous CO_2–rich stream at defined time intervals. The extraction was run for a certain period

of time and then depressurized to reach atmospheric pressure at 318 K and at a CO_2 flow of 2 NL/min. All experiments were performed in duplicate.
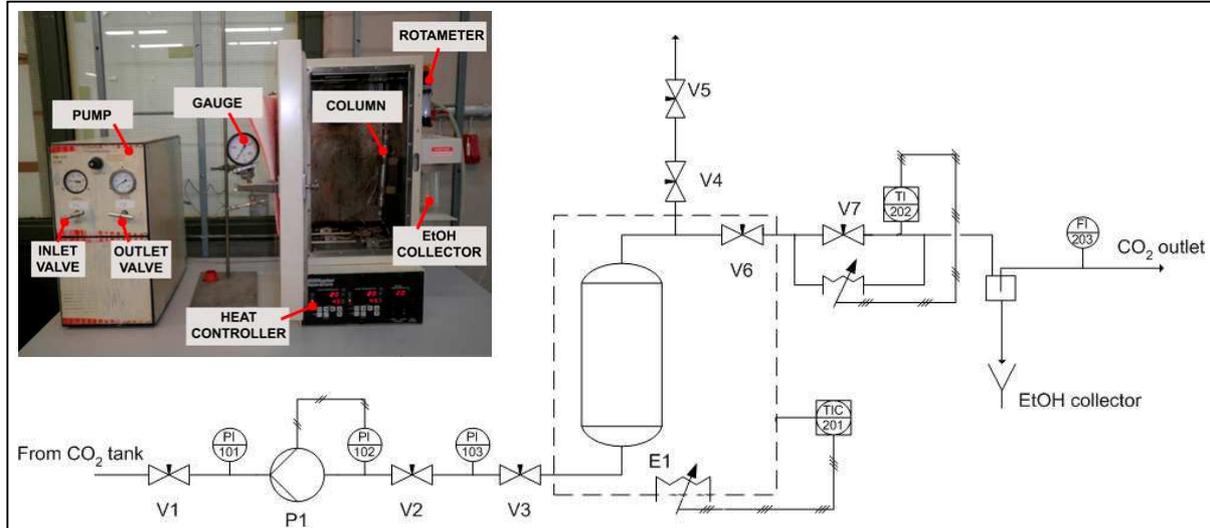
Fig. 3: Process flow diagram of the equipment used for the supercritical drying of gels (Top left: Picture of the equipment).

2.3. CHARACTERIZATION

Textural properties of the silica aerogels were determined by low-temperature N_2 adsorption-desorption analysis (Nova 3000e). Specific surface area (A_{BET}) was determined by the BET-method. Pore volume (V_p) and mean pore diameter (d_p) were estimated using the BJH-method. Micrographs of the samples were taken using a scanning electron microscope (SEM, Leo Zeiss 1530). All samples were gold-sputtered (10 nm thickness) prior to imaging.

3. RESULTS

The ethanol removal profile of the silica gels cylinders using a supercritical CO_2-assisted drying process showed a time-dependent behavior in all cases (Fig. 4). In a first step, more than 60 % of the solvent initially in the gel was removed after 10 min, and then the drying rate gradually slows down. The drying rate especially decreases for the removal of the last 5% of ethanol remaining in the gel. After 2 h of drying time, more than 98% of the ethanol initially in the gel was removed for all silica gel cylinders studied.
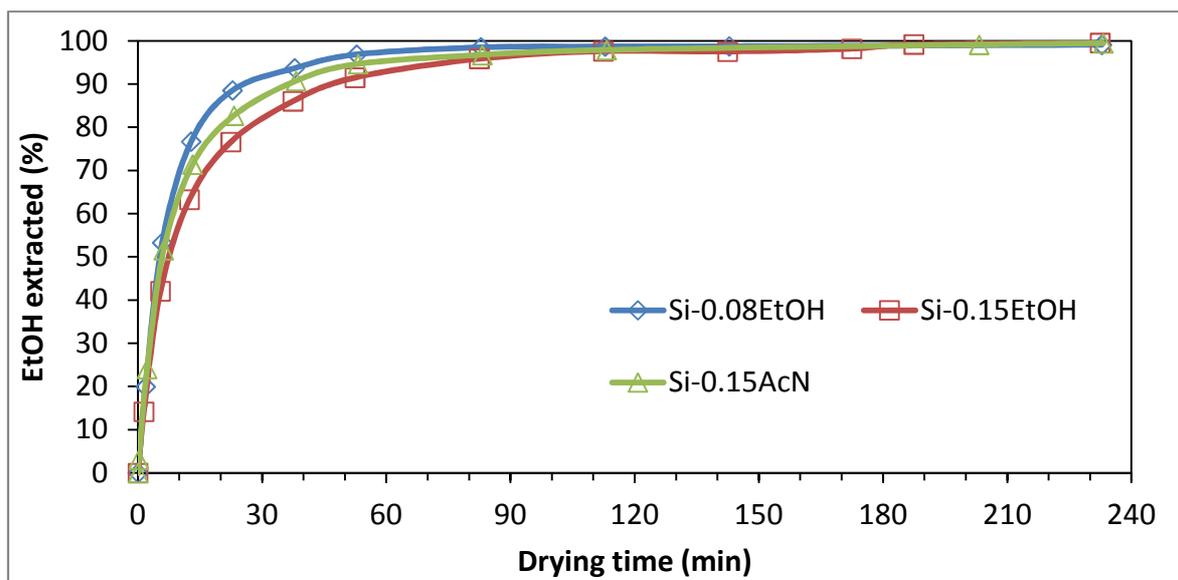
Fig. 4: Supercritical drying of silica aerogels: Ethanol extraction profile at 11.0 MPa and 318 K of gels with different densities (0.08 and 0.15 g/cm^3) and initial gel solvent (ethanol or acetonitrile).

The supercritical drying rate was influenced by the aerogel target density (0.08 g/cm^3 *Vs* 0.15 g/cm^3). Results showed that the solvent removal was faster for silica aerogels with lower density (Fig. 4). Despite having similar specific surface areas (Table 1), lighter silica aerogels exhibit higher mesopore volume and a higher porosity. In general, mass transfer controlled processes (e.g., supercritical extraction processes) are favoured with an increase in the material porosity. The same trend is expected and encountered for the supercritical drying of silica gels, i.e., supercritical extraction of ethanol from porous solid silica backbones, as the gel porosity increases.

Table 1: Textural properties of supercritically dried silica aerogel monoliths during

	A_{BET}, m^2/g	V_p, cm^3/g	d_p, nm
Si-0.08-EtOH	1000±50	3.08±0.15	17.4±0.9
Si-0.15-EtOH	1014±51	2.42±0.12	17.4±0.9
Si-0.15-AcN	756±38	2.91±0.14	17.3±0.9

The initial solvent used for the preparation of the silica gels also influenced the drying kinetics. Silica gels processed using acetonitrile (Si-0.15-AcN) were dried faster than those using ethanol as gel solvent (Si-0.15-EtOH). The broader pore size distribution observed for Si-0.15-AcN sample than that of Si-0.15-EtOH (not shown) may be the reason behind the differences between the drying profiles obtained for both samples.

The mass transfer mechanism involved in the supercritical drying of aerogels was described to be influenced by several phenomena (liquid swelling and spillage, convective flow, diffusion). The contribution of diffusion to the ethanol removal from silica gel cylinders was evaluated using the Fick´s second law [4]. Results showed in Fig. 5 discard the assumption of diffusion as the only mass transfer resistance in the supercritical drying of silica alcogels. The said model fails to predict the first drying rate step, whereas it fits well the removal of the last remnants (< 5-8 % ethanol left) of solvent from the gel. The last step of the supercritical drying of silica alcogels is thus supposed to be diffusion controlled. A diffusion coefficient value of 1.2×10^{-8} m^2/s was obtained for the case of Si-0.15-AcN sample showed in Fig. 5.
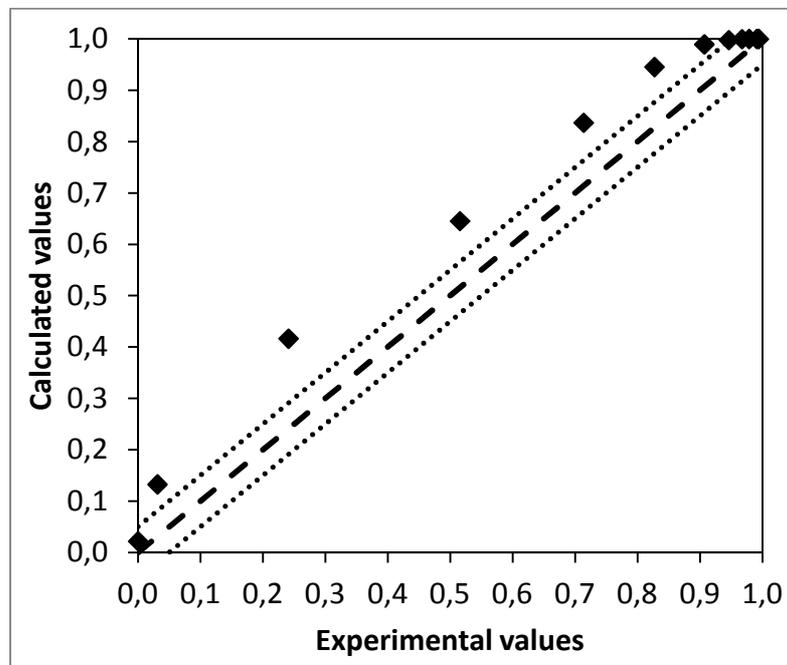
Fig. 5: Supercritical drying of silica aerogels: Normalized parity plot of experimental values of ethanol extracted from silica gel (target density: 0.15 g/cm^3, initial solvent: acetonitrile) by supercritical drying *Vs* calculated values considering Fickian diffusion mechanism (broken line: 45°-slope line; dotted lines: RMSE envelope +0.5σ –top– and -0.5σ –bottom–).

The drying profile of similar amounts of silica gel cylinders and silica gel microspheres of the same target density (0.08 g/cm^3) were compared. Silica aerogel microparticles showed a spherical shape with mean diameters of 100-160 µm (Fig. 6a) and the typical nanoporosity of silica aerogels (Fig. 6b). The drying rate for both cylinder and microspheres was very similar during the first stage of the drying process (0-60 % ethanol extracted) (Fig. 7). Afterwards, the supercritical drying of the silica aerogel microspheres is much faster than for the case of cylinders (Fig. 7) and shorter drying times (*ca.* 60 min) are needed to get a solvent removal of 98-99%. Diffusion in non-steady state mass transfer-controlled processes is mainly influenced

by the minimum dimension of the material. The reason behind the dissimilar drying profile for gel cylinder and microspheres may be the fact that the minimum diffusion path length of the microparticles is much lower than that of the silica monoliths (length >> diameter, cylinder radius = 0.58 cm). As a consequence, the drying rate will be faster for the silica microspheres than for the cylinder when the contribution of diffusion in drying is significant, as it is the case. Diffusion may be thus the main mass transfer driving force governing the final steps of the supercritical drying, confirming the hypothesis already stated by the modelling of the drying of gel cylinders.
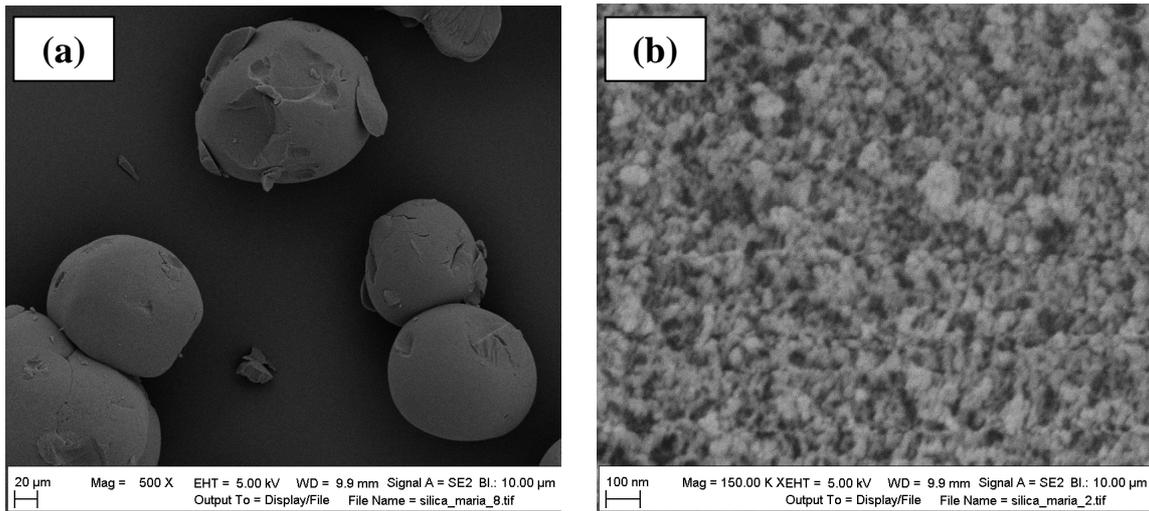
Fig. 6: SEM pictures of silica aerogel particles of 0.08 g/cm^3: a) morphology, and b) textural appearance.
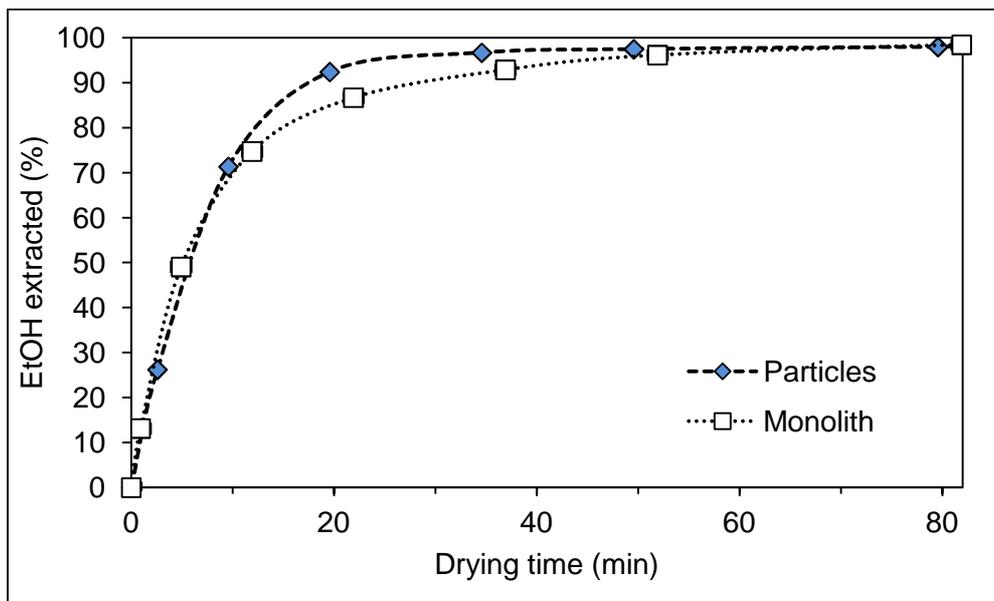
Fig. 7: Supercritical drying of silica aerogels: Effect of the morphology in silica gels of target density 0.08 g/cm^3 in the ethanol extraction profile at 11.0 MPa and 318 K.

4. CONCLUSION

Silica aerogel monoliths and microparticles with solvent removal of 98-99% can be produced at short drying times (2 h and 1 h, respectively). The profiles of the supercritical drying of gels showed a time-dependent behaviour, i.e., non-steady state process. Lower aerogel densities (0.08 Vs 0.15 g/cm^3) and smaller morphologies (cylinders Vs microspheres) accelerated the drying process. Several mass transfer phenomena are involved in the supercritical drying of silica gels, being diffusion the predominant one during the final stages of the drying process. Modeling of the drying profiles gave diffusion coefficient values in the range of 10^{-8} m^2/s for silica aerogels.

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