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Supercritical drying of aerogel: *In situ* analysis of concentration profiles inside the gel and derivation of the effective binary diffusion coefficient using Raman spectroscopy

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ABSTRACT

We here experimentally visualize *in situ* temporally and spatially resolved composition and concentration fields developing inside silica aerogels during the supercritical drying process. For the extraction of the pore liquid ethanol we used supercritical carbon dioxide. The evolution of the composition profiles inside the gel was measured *via* one-dimensional Raman spectroscopy. The composition profiles were converted into concentration profiles using an equation of state. The evolution of the concentration fields shows that ethanol is continuously transported out of the gel. On the contrary CO_2 is first transported into and at later drying times (before the depressurization) out of the gel structure. The binary diffusion coefficient was derived as a function of the composition and found to vary by two orders of magnitude for different stages of the drying process.

1. Introduction

Aerogels are a diverse class of ultralight solid materials known for their combination of remarkable properties such as very low thermal conductivity [1–4], ultra-low dielectric constant [5], high optical transmission [4], low index of refraction [6], and very low sound speed or acoustic impedance [6,7], making them attractive for wide areas of application. These tunable properties have been attributed mainly to their porous structures, which result in an extremely low density and large specific surface area of aerogels. Aerogels are products resulting from a transformation of a wet gel into its dried form while preserving most of its primitive porous backbone. With respect to silica gels, the gel is first synthesized *via* the sol–gel technology that tailors its molecular composition. After an aging and washing processes the porous silica structure of the wet gel is strengthened and the pores of the gels remain solely filled with the pore liquid, typically an organic solvent. In our case the pore liquid is ethanol. If the wet gel is dried under circumstances where capillary forces cause the partial collapse of the porous silica structure [6,8] the dry and then usually wrinkled gels are referred to as xerogels or cryogels. Thus, in order to preserve the porous structure of the gel, the gel can be dried according to the supercritical drying approach where no capillary forces emerge [9–11]. First the organic solvent is extracted from the gel using compressed CO_2 at operational conditions above the mixture critical point of the mixture of pore liquid and CO_2. This ensures the extraction in a single-phase mixing process where no liquid–gas interfaces and thus no capillary forces can emerge. After the complete substitution of the organic solvent with CO_2, the CO_2 can be released also in a single-phase process during slow depressurization at operational conditions above its critical temperature. What remains is a dried gel, whose pores are directly after the drying process filled with CO_2. When the dry gel is exposed to air the CO_2 is exchanged by air and the gel is referred to as aerogel.

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In fact, the price of drying an aerogel plate increases exponentially with its thickness [12]. Thus, for the optimization, design, and scale-up of aerogel drying in large-scale application, the knowledge of the mass transport mechanisms is extremely useful, for instance, to maximize yield while keeping the production and operational cost low. Although there have been experimental investigations to estimate the effective diffusion or mass transport coefficients during aerogel drying [9–11,13,14], there are no measurement data available directly revealing the mass transport mechanisms taking place inside the porous structure of the gel. Therefore in this paper, we utilize a one-dimensional Raman spectroscopy technique for the *in situ* quantification of temporally resolved local concentration profiles inside the silica gel during the drying process. A very similar technique was previously applied by others in order to derive the binary diffusion coefficients from the measured composition profiles of miscible liquids at ambient conditions [15–18] and by our group for the quantification of the diffusion coefficients in binary system of pendant drops at elevated pressures in cases of both, steady-state and unsteady-state conditions [19,20]. Nuclear magnetic resonance has recently been applied in order to measure the self-diffusion of methanol and ethanol in silica gels and in order to image the pore liquid density (methanol) at different drying times [21]. When the gel was dried in CO_2 at 5.8 MPa and 293 K, Behr et al. [21] derived from the decay of the amount of methanol contained in the gel structure an effective diffusion coefficient which they called transport diffusion coefficient of $(2.4 \pm 0.2) \times 10^{-9}\ m^2\ s^{-1}$.

Fig. 1 provides an overview of the measurement and evaluation strategy applied for the analysis of the mass transport mechanisms during supercritical aerogel drying. The structure of the manuscript also follows the structure shown in Fig. 1. Ethanol, which is the pore liquid, is extracted from the silica gel using compressed CO_2 at a pressure of 9.0 MPa and a temperature of 318.15 K. Using a one-dimensional Raman technique, Raman spectra from many different measurement locations aligned along one line (one-dimensional probe volume in Fig. 1) are measured during the drying process and recorded as one image. Therefore in the stack of Raman spectra arrays (images) in the top of Fig. 1 each image represents one time instance at which a profile along the probe volume is measured (Details follow in the experimental section). The Raman spectra are – after a calibration of the Raman spectra vs. the composition of the mixture ethanol + CO_2 – converted into composition profiles x_{CO_2}. Applying a concentration optimized Soave–Redlich–Kwong equation of state, the composition profiles x_{CO_2} are converted into concentration profiles. From the evolution of the concentration profiles the mass transport of CO_2 and ethanol into and out of the gel is analyzed.

2. Experiment

2.1. Materials

Silica gels were manufactured by KEEY Aerogel S.A.S. from Polyethoxydisiloxane (PEDS) precursor, a pre-polymerized sol

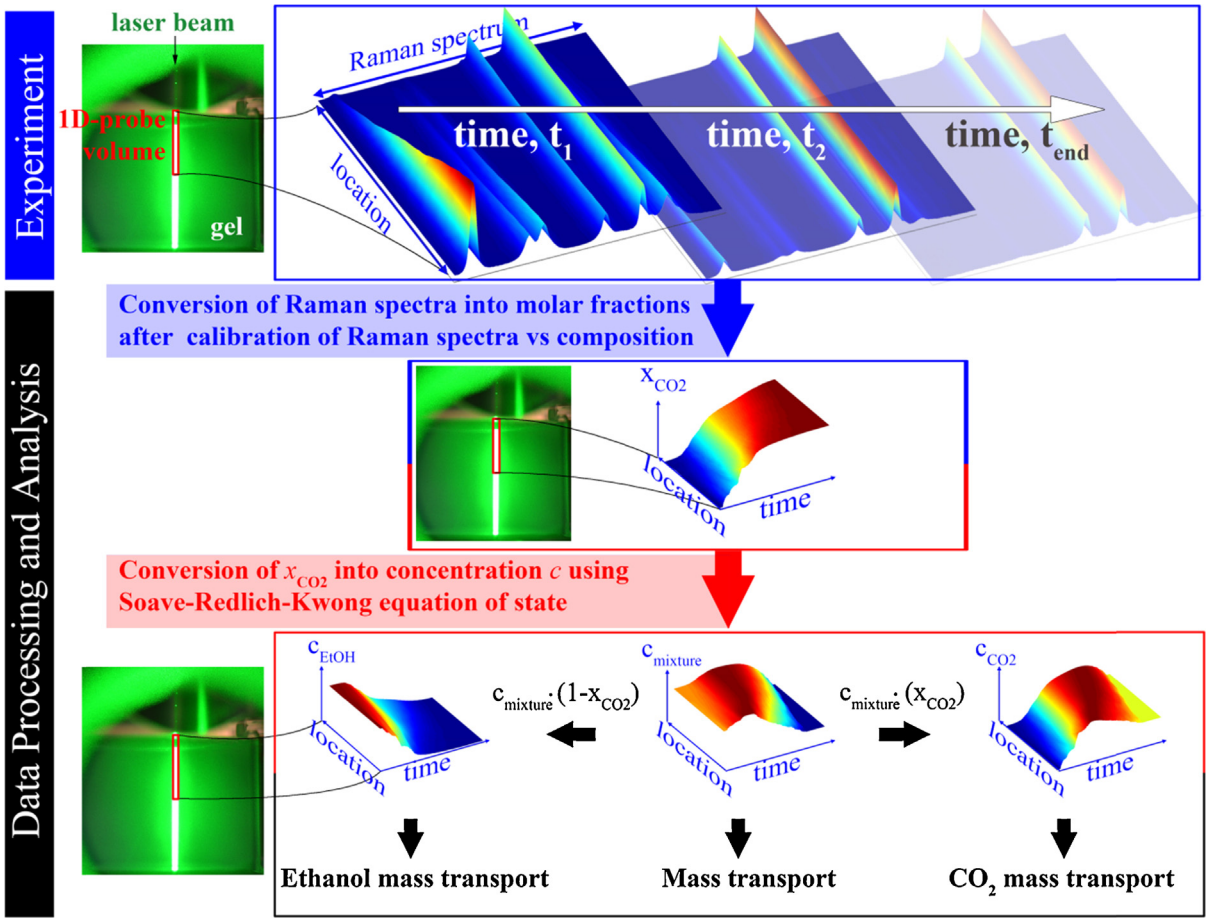

Fig. 1. Sketch of the measurement and evaluation strategy for the *in situ* analysis of the mass transport mechanism during the aerogel drying process. First Raman spectra are recorded locally resolved along the one-dimensional probe volume. Then the composition profile is computed as molar fractions x_{CO_2} from the many Raman spectra after a calibration. Then the molar fractions are converted into concentrations of the mixture $c_{mixture}$, ethanol c_{EtOH} and CO_2 c_{CO_2} using the Soave–Redlich–Kwong equation of state. Finally mass transport mechanisms can be deduced from the evolution of the concentration profiles.