Drying of silica gels with supercritical carbon dioxide

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Results of drying experiments of aerogels with supercritical carbon dioxide are reported. In addition to the results of experiments with a pilot extracting apparatus, a preliminary design is also given of a large-scale supercritical carbon dioxide extraction plant to be used for drying of aerogels. From the experiments it was found that crack-free aerogels could be obtained when drying with carbon dioxide under supercritical conditions. The lowest temperature and pressure at which crack-free aerogel samples were obtained was at 35 °C and 85 bar, respectively. The temperature had a minor influence on the drying time. It was also found that the diffusion of ethanol into the aerogel pores limits the drying time. This limitation implies that the thickness of the aerogel tiles will have a large influence on the cost of drying of an aerogel.

1. Introduction
Silica, as well as other metal oxide aerogels, can be produced as monoliths with extremely high porosities and very high specific surface areas [1–3]. As a result of the high porosity, silica aerogels are very good thermal insulators. They are, depending on their structure, also able to withstand temperatures up to 1000 °C and can be highly transparent for visible light [1–3]. For application as insulating material, it is necessary to produce aerogel tiles or plates of considerable size (> 0.1 m²), thickness (> 1 cm) and strength.

Silica aerogels can be prepared from ethoxysilanes by a two-step sol–gel process [1,4], resulting in a silica gel skeleton immersed in ethanol. Monolithic silica aerogels can then only be produced when the ethanol is removed in the absence of capillary forces in the gel pores, because even small capillary forces will result in a collapse of the gel skeleton and will crack the gels [1–3]. This removal can be achieved by placing the wet gel in an autoclave and heating the autoclave above the critical temperature of ethanol (Tc = 243 °C) [1–3,5–7]. At this temperature, ethanol is slowly removed by releasing the pressure (depending on the degree of filling of the autoclave, typically 80–120 bar after heating to temperatures between 250 and 300 °C) to 1 bar and the monolithic silica aerogel is obtained. It is clear that this is a very tedious procedure because the autoclave has to be heated to temperatures above 250 °C. Another way to produce a monolithic silica aerogel is by replacing the ethanol by carbon dioxide [1–3,8–11]. Most of the literature reports procedures in which the alcohol is replaced by liquid carbon dioxide. Monolithic silica aerogels are obtained by slowly raising the temperature of the carbon dioxide-filled gels until supercritical conditions are obtained and then slowly releasing the carbon dioxide pressure to 1 bar.

In this paper a procedure is described in which the complete alcohol–carbon dioxide exchange is carried out under supercritical conditions. Compared to the high-temperature autoclave drying procedure, the carbon dioxide drying procedure has the advantage that only relatively low temperatures (35 °C) are necessary. Owing to this low temperature at which the process is operated, equipment costs can be low and the drying time will be shorter because it is not necessary to heat and cool the autoclave. Because of these advantages a process using supercritical carbon dioxide will be much cheaper and thus more attractive for the production of large quantities of the monolithic silica aerogel.

The effects of pressure and temperature on the aerogels produced are investigated and compared with aerogels which are dried with a high-temperature autoclave process. Finally, the structure and economics of a large-scale commercial production process for the preparation of monolithic silica aerogel plates with a thickness of 3 cm are discussed.

2. Experimental procedure
2.1. Gel preparation
The complete hydrolysis–condensation of TEOS requires a minimal amount of 2 mol water per mol TEOS [12]. For our investigations, gels were prepared from a mixture with a final molar ratio TEOS/ethanol/water of 1:2.2. The amount of water was divided in an acidified fraction (0.5 mol/water/mol TEOS) added in the first step of the two-step sol–gel process, in
order to catalyse the hydrolysis reactions and a basic fraction (1.5 mol water/mol TEOS). A base was used to enhance the polymerization reactions. In the acid step, an HCl concentration of $10^{-2}$ M in water and in the basic step an $NH_4OH$ concentration of $6 \times 10^{-2}$ M in water was used. Both water fractions were diluted with equal weight amounts of ethanol to avoid immiscibility during the addition [12]. The rest of the ethanol was used for the initial TEOS/ethanol mixture.

The reactions started the moment the acidic water–ethanol mixture was added drop by drop to the initial TEOS–ethanol mixture that was vigorously stirred and maintained at a constant temperature of 50 °C. Including the time spent for addition of the acid fraction, the total hydrolysis time was chosen at 30 min. This time is beyond the point at which a maximum hydrolysis degree is obtained [12].

The basic fraction was then added in less than 5 min to the well-stirred mixture which was maintained at 50 °C. Before gelation occurred, the solution was poured into test tubes, with an internal diameter of 1.5 cm and a length of 18 cm. The inner wall of the test tubes was coated with a two-component silicon rubber in order to prevent adhesion of silica gel to the glass. After gelation at 50 °C the samples were aged at 60 °C for 48 h [13]. Finally, the gels were dried with supercritical carbon dioxide or with the high-temperature autoclave process [14, 15].

2.2. Supercritical carbon dioxide drying

The supercritically carbon-dioxide-dried silica aerogel rods were produced with the equipment shown in Fig. 1. At the beginning of the drying experiments it is essential to minimize the evaporation of the ethanol from the gel rods. The wet gel rods were carefully taken out of the coated glass tubes and immersed in pure ethanol. The extractor (1), with a volume of 600 ml, was then completely filled with cold ethanol to avoid the occurrence of cracks during pressure build-up. Subsequently a wet gel was taken from the ethanol and inserted quickly into the extractor. A specially designed steel wire construction was used to keep the gel rod vertical in the centre of the extractor and to ensure that the complete rod surface was in contact with the supercritical carbon dioxide.

During most of the experiments the carbon dioxide was taken directly from a gas-bottle (4) and not recycled through the equipment to ensure that no residual amounts of ethanol were present. The extractor (1), with a volume of 600 ml, was then completely filled with cold ethanol to avoid the occurrence of cracks during pressure build-up. Subsequently a wet gel was taken from the ethanol and inserted quickly into the extractor. A specially designed steel wire construction was used to keep the gel rod vertical in the centre of the extractor and to ensure that the complete rod surface was in contact with the supercritical carbon dioxide.

During most of the experiments the carbon dioxide was taken directly from a gas-bottle (4) and not recycled through the equipment to ensure that no residual amounts of ethanol were present. The carbon dioxide was first liquefied at $-15 °C$ (3) and then pumped (6) to a pressure above the critical pressure of carbon dioxide (73.8 bar).

Before entering the extractor, the carbon dioxide is heated to a chosen temperature above its critical temperature (31 °C) by a hot-oil circuit. After closing, the extractor is pressurized with carbon dioxide until the desired operating pressure is reached. Fig. 2 shows a $PT$-projection of the binary system ethanol–carbon dioxide [16, 17]. The carbon dioxide are completely miscible, is depicted. During our experiments, the carbon dioxide flow to the extractor (depending on the experiment, typically 1.0–1.3 kg h$^{-1}$) is controlled independently of the pressure by adjusting the pump stroke length and measured with a micromotion flowmeter. A pressure-control valve is used to maintain the extractor pressure at the desired operating pressure by releasing small amounts of the ethanol carbon dioxide mixture from the extractor into the separator (2). During most of the experiments the separator was operated at 1 bar and 0 °C to separate almost all the ethanol from the carbon dioxide. The carbon dioxide was vented. After several hours the ethanol in the extractor had been replaced completely by supercritical carbon dioxide (Fig. 2) and the pump was stopped. The pressure in the extractor, which was heated with an oil jacket was slowly released (Fig. 2) at a rate of 2–3 bar min$^{-1}$ and the dried aerogels could be taken out of the extractor.