SYNTHESIS, CHARACTERISATION AND APPLICATIONS OF SILICA AEROGELS

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Aerogels are sol-gel derived nanostructured materials with highly fascinating physico-chemical properties such as very high specific surface area, very low bulk density, very low thermal conductivity, very low sound velocity and very low refractive index. Much skill, however, is still required to synthesize monolithic aerogel specimens with a good reproducibility. This is because the state of the final aerogel product strongly depends on the sol-gel and supercritical drying conditions in which it is prepared. It is, therefore, of importance to determine how sol-gel parameters (such as molar ratio of precursor, solvent and water) and drying parameters (such as CO_2 pressure, CO_2 temperature and drying time) affect the monolithicity and physical properties (such as surface area and porosity) of silica aerogels, since it is still not clear how these conditions affect the final product. In this paper, some experimental results on the synthesis and characterisation of silica-based aerogels will be presented.

INTRODUCTION

Although aerogels, which are sol-gel derived nanostructured materials with an extremely high porosity, were already synthesized in the early 1930s, it lasted until the 1980s (when they were used in Cerenkov detectors) before the full potential of these fascinating materials was recognised [1]. From then on, aerogels became widely known and attracted many scientists from different fields, which resulted in the development of a wide range of aerogel applications. Due to their highly interesting physico-chemical properties such as very high specific surface area, very low bulk density, very low thermal conductivity, very low sound velocity and very low refractive index [2], aerogels are now being used as thermal and sonic sound superinsulators, catalysts and catalytic supports, containers for liquid rocket propellants, cosmic dust collectors, membranes, precursors for optical fibres, as well as in many other industrial applications [1,2,3].

The preparation of silica aerogels first involves the synthesis of a wet gel (the so-called alcogel) by using sol-gel chemistry, in which a liquid silicate precursor is hydrolysed and condensed into a polysilicate gel [4]. The remaining liquid phase, enclosed in the formed gel network, is then evacuated by supercritical drying, resulting in the formation of a dry aerogel of pure silica [4]. Much skill, however, is still required to obtain monolithic, crack-free aerogel specimens with a good reproducibility. This is because the state of the final aerogel product strongly depends on the sol-gel and drying conditions in which it is prepared [2,3].

For many applications, silica aerogels with specific physical properties (such as surface area, density and porosity) are needed. It is, however, not fully understood which combination of sol-gel parameters (such as molar ratio of precursor, solvent, and water) should be used to obtain silica aerogels with specific properties. Therefore, a systematic study on the effect of sol-gel conditions on aerogel physical properties was undertaken.

I - MATERIALS AND METHODS

Hydrolysis versus gelation time curves Brinker *et al.* [5] suggested to split up the sol-gel process in an acidic (hydrolysis) step and a basic (condensation) step to speed up the gel formation. In this synthesis procedure, a dependence of the gelation time in basic environment on the hydrolysis time in acidic environment was observed. This dependence can be used as a tool to describe the hydrolysis and condensation processes in the sol phase in order to get rapid and profound insight in both the nature and kinetics of the silica sol-gel reactions [6]. In the first part of this experimental investigation, therefore, hydrolysis versus gelation time curves were recorded to characterise the hydrolysis and condensation behaviour of a silica sol-gel system as a function of the hydrolysis temperature and the relative amounts of H_2O, C_2H_5OH, HCl and NH_4OH (respectively designated as a, b, c and d). To this end, silica alcogels were prepared from tetraethylorthosilicate (TEOS), H_2O, C_2H_5OH, HCl, and NH_4OH using a two-step acid-base-catalysed procedure, quite similar to that described by Venkateswara *et al.* [7]. In the first step, TEOS was partially hydrolysed and condensed at a certain hydrolysis temperature by mixing with H_2O, C_2H_5OH, and HCl catalyst. After a certain hydrolysis time, NH_4OH catalyst and an additional amount of H_2O were added to the hydrolysis mixture in a second step. The resulting sols, which had a final TEOS:H_2O:C_2H_5OH:HCl:NH_4OH molar ratio of $1{:}a{:}b{:}c{:}d$ with a varying from 1.5 to 3.5, b from 1.9 to 5.9, c from 3.9×10^{-4} to 1.6×10^{-3}, and d from 1.4×10^{-3} to 5.7×10^{-3}, were then transferred to 10-ml glass tubes and allowed to gel at room temperature. The hydrolyses temperature was varied from room temperature to 60°C. The amount of H_2O was divided into the HCl fraction and the NH_4OH fraction in a weight ratio of 4:1.

The hydrolysis versus gelation time curves were recorded as described by Boonstra and Bernards [6]. First, the acidic water fraction was added dropwise to a well stirred TEOS:C_2H_5OH mixture to initiate the hydrolysis. Only one bulk portion (± 100 ml) of the TEOS: C_2H_5OH mixture was hydrolysed. After hydrolysing for a few minutes, 5-ml samples were drawn every 5 minutes from the hydrolysing mixture. To each sample, a specified amount of basic water was added to initiate gelation. The resulting samples were subsequently poured into the glass test tubes and the gelation times were recorded visually. Gelation was attained when, on turning the test tube upside down, no fluidity of the sol phase was observed. The time interval between the addition of the acidic water fraction and that of the basic water fraction was taken as the hydrolysis time (t_H), while the gelation time (t_G) was defined as the time between the moment of adding the basic water fraction and the time gelation was observed [6].

Aerogel synthesis In order to assess the effect of the different sol-gel parameters on aerogel physical properties, silica alcosols with the same final TEOS:H_2O:C_2H_5OH:HCl:NH_4OH molar ratios as indicated in the preceding section were prepared using the two-step acid-base-catalysed procedure. For each different combination of sol-gel parameters, the hydrolysis time was equal to 90 min, while the hydrolysis temperature equalled 60°C. After addition of the basic water fraction, three millilitres of the resulting alcosol were transferred to teflon moulds and kept for 2 h at 50°C for gelation. After gelation, the resulting alcogels were removed from their moulds, washed in a 20 vol.% H_2O/C_2H_5OH solution for 24 h at 60°C to strengthen the gel network, after which they were covered with an excess C_2H_5OH and left at 50°C for another 24 h. Silica aerogels were then obtained by supercritical CO_2 drying of the alcogels in a 100-ml PREMEX high-pressure reactor, according to the procedure of Novak and Knez [8] which was slightly modified. Modifications comprised the use of 90 bar and 25 °C instead of 70 bar and 20 °C in the removal and diffusion steps. After supercritical drying, the aerogels were removed from the reactor and kept in a dry atmosphere.

Aerogel characterisation Linear shrinkage was calculated as $(Ø_0 – Ø)/Ø_0$, with $Ø_0$ being the diameter of the alcogel and Ø being the aerogel diameter. The apparent (bulk) density was calculated from the geometrical size and weight of the aerogel sample. The BET specific surface area and total pore volume were determined using a multiple point N_2 gas adsorption analyser of Quantachrome (Model autosorb-1) after evacuating the sample for 20 h at 393 K. The degree of porosity (% porosity) was obtained from the values of the total pore volume and the density of amorphous, nonporous silica (2.2 g/cm^3).

II - RESULTS AND DISCUSSION

Effect of H_2O:TEOS molar ratio on hydrolysis versus gelation time curves In Fig. 1, an example is shown how hydrolysis versus gelation time curves can be used to assess the influence of sol-gel conditions on sol-gel kinetics. In this figure, the effect of the amount of water used on the dependence of the gelation time, t_G, on the hydrolysis time, t_H, of a TEOS:H_2O:C_2H_5OH:HCl:NH_4OH mixture with a final molar ratio $1:a:3.9:7.8\times10^{-4}:5.7\times10^{-3}$ with a varying from 1.5 to 3.5 is shown. If 1.5 moles of H_2O are used for the hydrolysis of one mole of TEOS (a = 1.5), gelation kinetics initially become faster with an increase in the hydrolysis time, t_H. This is due to an increase in silanol concentration with progressing hydrolysis [6], which results in a decrease of the gelation time, t_G. After ±17 min of hydrolysis, almost all the added water has been consumed and a maximum silanol concentration is obtained, which corresponds with a minimum in the gelation time (t_G = 95 min). For hydrolysis times just past the minimum of the t_H-t_G curve, the gelation time increases considerably. This is caused by a decrease of the silanol concentration as a result of dimerisation of monomers in the hydrolysis step [6]. Due to the low water content (a = 1.5), a large concentration of mono-hydroxy monomers is present, which will condense to dimers without any hydroxy groups. These dimers first have to be hydrolysed again before they can participate in the polymerisation process, and hence, the increase in the gelation time after the minimum of the curve is rather pronounced. For longer hydrolysis times (t_H > 30 min), a renewed decrease in gelation time is observed. This is due to the fact that water, formed during the condensation reactions, is in turn used for the hydrolysis of the already formed silanols and the newly formed dimers [6]. Because these hydrolysed species can again take part in the condensation reactions, gelation time decreases.

If the H_2O content is increased, a more rapid gelation is found at all hydrolysis times. When 2.5 moles of H_2O are used for the hydrolysis of one mole of TEOS (a = 2.5), the increase in the gelation time after the minimum of the t_H-t_G curve is significantly less strong than in the case of 1.5 moles of H_2O per mole TEOS, which is due to a decrease of the dimerisation effect [9]. If the H_2O content in the hydrolysis stage is further increased (a = 3.5), there is always enough water available to form silanols. Hence, a hydrolysis time for which the silanol concentration is maximal is difficult to establish. In addition, dimerisation of the formed silanols results in the formation of dimeric silanols where most of the ethoxy groups are already replaced by hydroxy groups. As such, these dimers can contribute to the polymerisation process without additional hydrolysis, which explains why no increase of the gelation time is found [9].

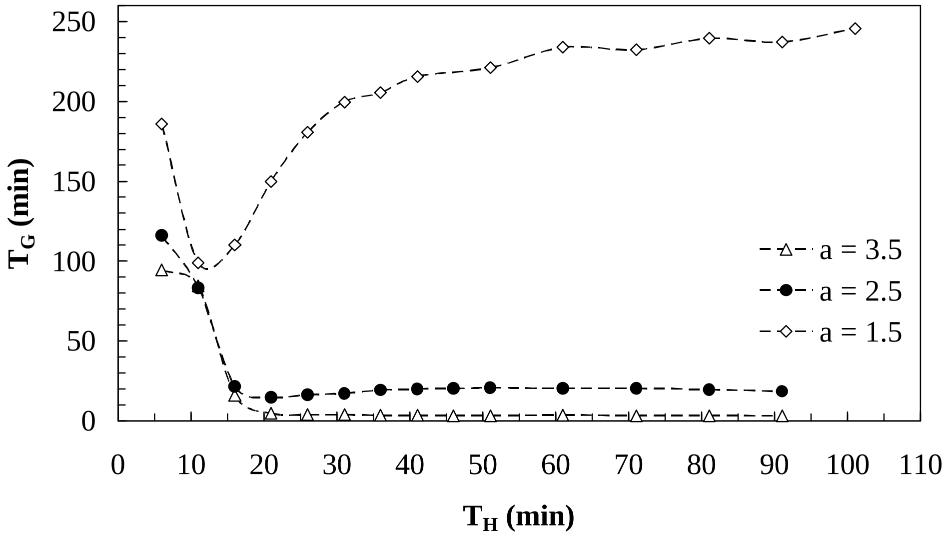

Figure 1. Effect of the amount of water on the dependence of the gelation time, t_G, on the hydrolysis time, t_H, of a TEOS:H_2O:C_2H_5OH:HCl:NH_4OH mixture with a final molar ratio 1:a:3.9:7.8×10^{-4}:5.7×10^{-3} with a varying from 1.5 to 3.5.

Aerogel physical properties Since this is an ongoing study, not all experimental results are presently at hand. As an illustrative example, however, some results are presented for silica aerogels which were prepared from TEOS, H_2O, C_2H_5OH, HCl, and NH_4OH in a total molar ratio of 1:3.5:3.9:7.8×10^{-4}:5.7×10^{-3}. As shown in Fig. 2, transparent, monolithic, and crack-free aerogels were obtained for this combination. Some important physical properties of the resulting aerogels are given in Table 1. From this table it follows that aerogels could be obtained with reproducible physical properties and a relatively high specific surface area (905 m^2/g). This high specific surface area is probably due to the fact that the rates of hydrolysis and condensation reactions also increase as a result of the presence of an excess amount of H_2O. As a consequence, this will result in isolated small spherical shaped SiO_2 particles, leading to a high surface area [3]. Total pore volume, however, was relatively low (0.82 cm^3/g). Hence, the porosity of the resulting aerogels was relatively low (64%). This is probably due to the fact that still a large number of unhydrolysed monomers is present in between the siloxane chains which leads to a decrease in the number of larger pores and hence, results in a lower degree of porosity [3]. The largest contribution to the total pore volume comes from pores of radii < 2 nm, which amounts to 55% of the total pore volume. Pores of radii 2 - 5 nm contribute for ca. 24% to the total pore volume, while only a small part of pore volume, ca. 21%, is created by pores with radii > 5 nm. On the other hand, the high surface area is almost completely related to the presence of large micropores of radii < 2 nm (85% of the overall surface area). Only a small part of the overall surface area is related to mesopores of radii 2 - 5 nm (ca. 12%). It thus seems that the contribution of the smallest pores with radii < 2 nm to the overall surface area and pore volume is high, and hence the resulting silica aerogels are microporous materials.

Figure 2. Photograph of a transparent, crack-free aerogel prepared in this study.

Table 1. Physical properties of silica aerogels, which were prepared from TEOS, H_2O, C_2H_5OH, HCl, and NH_4OH in a total molar ratio $1:3.5:3.9:7.8\times10^{-4}:5.7\times10^{-3}$ and obtained after supercritical drying of the alcogels with CO_2.

Physical properties	**Mean ± SD**[a]
Linear shrinkage (%)	4.3 ± 0.3
Apparent density (g/cm^3)	0.135 ± 0.002
Surface area (m^2/g)	905 ± 23
Total pore volume (cm^3/g)	0.82 ± 0.01
Degree of porosity (%)	64.2 ± 0.2

[a] Calculated from four replicate values

CONCLUSIONS

Although there is a wealth of information available on aerogel research, it is still not fully clear which combination of sol-gel parameters (such as molar ratio of precursor, solvent, and water) should be used to obtain silica aerogels with specific physical properties. This is due to the complex nature of the hydrolysis and condensation processes in the sol phase. Systematic and detailed experimental studies which assess the effect of sol-gel parameters on aerogel physical properties, are imperative in order to be able to tailor the physical properties of silica aerogels.

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