JOURNAL OF MATERIALS SCIENCE 28 (1993) 3021–3026

Effect of gel parameters on monolithicity and density of silica aerogels

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As part of continuing investigation of the preparation and characterization of silica aerogels, detailed experimental results on monolithicity and density of the aerogels as a function of catalysts and their concentrations, molar ratios of tetraethylorthosilicate (TEOS), ethanol (EtOH) and H_2O, gel pH and gel ageing, are reported. With large concentrations of catalysts, lower and higher aged alcogels have been found to produce opaque, cracked and high-density silica aerogels; however, good-quality monolithic, transparent and low-density aerogels have been obtained at lower catalyst concentration (0. 01 N HCl) with alcogel ageing periods between 9 and 30 days. The best quality silica aerogels, in terms of transparency and monolithicity, have been obtained using TEOS:EtOH:H_2O in the molar ratio of 1:5:8.

1. Introduction

Aerogels are low-density porous materials prepared by supercritical drying of alcogels. Silica aerogels were first produced by Kistler [1] in 1931 and were characterized as an open, cross-linked silica structure with a high fraction of voids with extremely fine pore sizes [2]. They typically exhibit very large surface area ($1000\ m^2\,g^{-1}$), lowest refractive index (1.01–1.05), lowest thermal conductivity ($0.01\ W\,m^{-1}\,K^{-1}$), lowest sound velocity ($100\ m\ s^{-1}$) and visible transparency [3]. This unusual combination of properties makes the silica aerogel a unique material suited for a diverse array of applications: Cerenkov radiation detectors in nuclear reactors [4–6], catalyst supports [7–10], thermal superinsulators for solar ponds and hot-water systems [11–13], low-temperature glass formation [14, 15], very high quality glasses for optical fibres [16], filters, membranes, acoustic delay lines, collectors for micrometeorites in space and gellifying rocket propellants [17]. Use of silica aerogels in refrigerators, refrigerated vehicles and containers reduces the environmental pollution which is presently being caused by CFC gases [18].

Most of the published literature deals with the preparation of silica aerogels by base-catalysed hydrolysis of tetramethylorthosilicate (TMOS) [19–21]. Because TMOS is highly toxic, a lesser toxic and cheaper material, tetraethylorthosilicate (TEOS) is more suitable for large-scale commercial production of silica aerogel. Even though a few reports are available on the TEOS aerogels [22, 23], no detailed studies have been made on the preparation and characterization of silica aerogels by varying gel parameters such as molar ratios of TEOS:EtOH:H_2O, catalysts and their concentrations, gel pH, gel setting time and gel ageing. These gel parameters affect to a great extent the monolithicity, density and other physical properties of silica aerogels. Therefore, the present paper deals with the systematic experimental results on the preparation and characterization of silica aerogels.

2. Experimental procedure

2.1. Preparation of silica alcogels

Silica alcogels have been prepared by hydrolysis and condensation of tetraethylorthosilicate (TEOS) according to the following chemical reactions in the presence of a catalyst (basic or acidic)

Hydrolysis

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow{K} Si(OH)_4 + 4C_2H_5OH \quad (1)$$

Condensation

$$Si(OH)_4 + Si(OH)_4 \rightarrow Si{-}O{-}Si + 4H_2O \quad (2)$$

or

$$Si(OH)_4 + Si(OC_2H_5)_4 \rightarrow -Si{-}O{-}Si- + 4C_2H_5OH \quad (3)$$

where K is a catalyst (acid or base).

The gel solutions were prepared in two steps. Because TEOS and water are not miscible without an additional solvent, TEOS was first dissolved in a solvent such as ethyl alcohol (EtOH). Then, with constant stirring of the mixture of TEOS and EtOH, acid or base in water was added. The whole solution was stirred using a magnetic stirrer for about 30 min. All the gel solutions were prepared in 50 ml beakers. However, in order to vary several gel parameters, such

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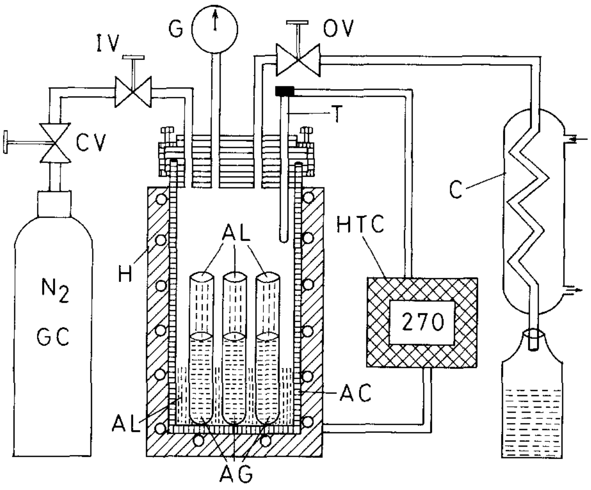

Figure 1 Schematic diagram of the autoclave system: AC, autoclave; HTC, heater temperature controller; C, condenser; AG, alcogel; AL, alcohol; H, heater; G, gauge; CV, cylinder valve; GC, gas cylinder; IV, inlet valve; T, thermocouple; OV, outlet valve.

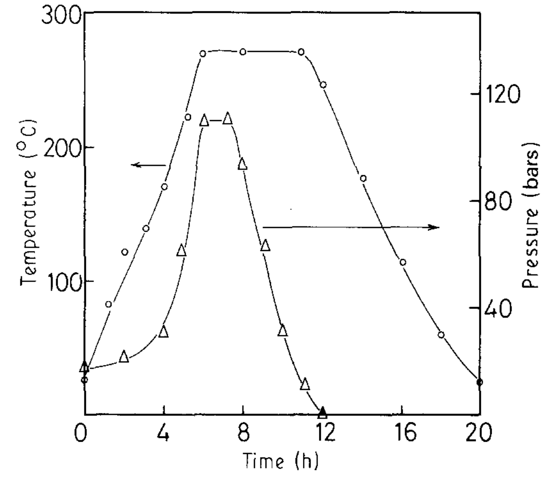

Figure 2 Temperature and pressure inside the autoclave as a function of time.

as molar ratios of TEOS : EtOH : H_2O, gel ageing, type and concentration of catalyst etc., we found that test tubes were more convenient in terms of volume and for keeping in the autoclaves, than were the beakers. Therefore, after stirring, the gel solutions were transferred to test tubes (Borosil) of 1.8 cm diameter and 15 cm height. The test tubes were then closed air-tight, to avoid the evaporation of EtOH, using rubber corks, and kept for gelation at ambient temperature (22–27 °C). After setting, EtOH was added over the set gels in order to avoid shrinkage and cracking of the gels. The gels prepared in this way occupy practically the same volume as the initial gel solution. All the gel solutions were prepared in molar ratios. Guaranteed reagent grade chemicals and triply distilled water were used throughout this study.

2.2. The solvent evacuation by hypercritical drying

The alcogels were placed in a Pyrex liner of the autoclave and sufficient EtOH was added over the gels and in the liner to give the required pressure above the critical pressure (100 bar). In each run, six test tubes were placed in the autoclave.

The dimensions of the autoclave (Fig. 1) are 2.5 in (~ 6.35 cm) diameter, 8 in (~ 20.32 cm) length and 600 ml total volume, and can attain maximum pressure and temperature up to 200 bar and 350 °C, respectively.

After the liner was placed in the autoclave, it was closed, flushed and pressurized with dry nitrogen gas to 20 bar to rarefy the oxygen concentration. This is necessary for safety reasons. It also serves to keep the EtOH from boiling which would destroy the aerogel structure. The temperature was then slowly increased above the critical temperature (243 °C) and pressure (63 bar) of EtOH. Then at a constant temperature of 270 °C, the EtOH vapour was slowly released (from 100 bar) until the atmospheric pressure was reached (Fig. 2). Heating was continued for approximately 2 h more at 270 °C while flushing with nitrogen in order to remove the remaining EtOH vapour. Afterwards, the heater was switched off and the autoclave was cooled to room temperature within 15 h. The physically as well as the chemically bound EtOH was removed by heating the aerogels at 400 °C in air. Then the EtOH was burnt to acetaldehyde and acetic acid which escaped easily. The transparency of the aerogels increased by 10%.

In order to obtain the best quality silica aerogels in terms of density, monolithicity and transparency, a series of experiments was undertaken in which the gel parameters (type and concentration of catalysts, molar ratios of TEOS : EtOH : H_2O, gel pH, gel setting time and gel ageing) were systematically varied. The aerogels were characterized by infrared spectroscopy (Perkin–Elmer) and density measurements.

3. Results and discussion

3.1. Effect of catalysts

To study the effect of different catalysts on the monolithicity and density of silica aerogels, alcogels were prepared by keeping the molar ratio of TEOS:EtOH:H_2O constant at 1:5:5. Ammonium hydroxide (NH_4OH), hydrochloric acid (HCl) and nitric acid (HNO_3) were tried as the catalysts. The concentration of the catalysts was varied from 0.001–6 N. The catalysts were added in the form of water. In the case of NH_4OH, it was found that clear silica alcogels were obtained, with only 0.01 N concentration of catalyst by keeping the maximum molar ratio of TEOS:EtOH:H_2O at 1:5:4. With either a molar ratio of NH_4OH in water above 4 or with normality greater than 0.01 N, only turbid and milky sols were obtained. Even after 2 months, these sols did not form gels. This may be due to the reaction between TEOS and NH_4OH, and leading to the formation of silica precipitation with larger amounts or greater concentrations of NH_4OH in the sol. In the case of HCl and HNO_3, below 0.005 N concentrations, only turbid sols were obtained, due to insufficient amount of catalyst and, therefore, incomplete hydrolysis of TEOS. Clear and transparent alcogels were obtained with the acid catalyst concentrations above 0.008 N. It was found that the gelation time of the sols strongly depended on the concentration of the acid catalysts. It was observed that at lower (< 0.06 N) and higher (> 0.06 N) concentration of the acids, the gel setting time decreases, as shown in Fig. 3. This is due to the fact that at lower catalyst concentrations the reaction speed compensates for the increased surface charge of all ions in the sol and provides for fast gelation [20]. On the other hand, at higher concentrations of the acid catalysts, the reaction rates are faster and hence faster gelation occurs. It was found that the silica aerogel density increases as the concentration of the catalyst increases, in agreement with our previous results [24].

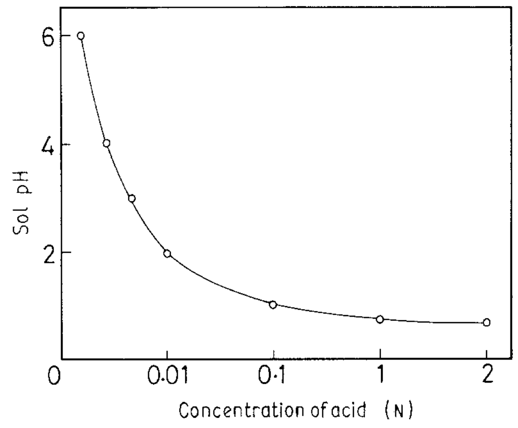

Figure 4 pH of the sol versus normality of acid (HCl).

3.2. Effect of pH of sols

The rheological properties of the sols depend on the pH of the sol. Fig. 4 shows the evolution of pH versus the concentration of acid (HCl) added to the TEOS, EtOH mixture. In the first part of the curve, pH decreases linearly with increasing concentration of the acid. Above 1 N acid concentration, the pH remains constant. At very low concentrations (≤ 0.005 N), only turbid sols and gels were formed. Clear and transparent sols were obtained for pH values below 4. It was observed that the pH of the gels is stable during sol–gel transition.

3.3. Effect of EtOH/TEOS molar ratio

The molar ratios of EtOH/TEOS were varied from 1–20 by keeping the H_2O/TEOS ratio constant at 5, 6, 8, 10 and 12. The catalyst used was 0.01 N HCl. Up to a molar ratio of 2 EtOH/TEOS, only turbid sols and gels were obtained. The resulting silica aerogels were opaque, as shown in Fig. 5a. This is due to the fact that the EtOH volume is insufficient to dissolve the TEOS completely to make it ready to react with H_2O. Above the EtOH/TEOS molar ratio of 2, clear sols and gels were formed. The aerogels obtained from these gels were monolithic and transparent, as shown in Fig. 5b. However, on further increasing the molar ratio of EtOH/TEOS, the gel setting time increased as shown in Fig. 6. This is due to the dilution of TEOS solution, and the reacting species being widely separated from each other for the hydrolysis and condensation reactions to proceed. It was observed that with increasing molar ratio of EtOH/TEOS, the density of the aerogels decreased (Fig. 7) and the transparency increased, due to the greater dilution of the alcogels.

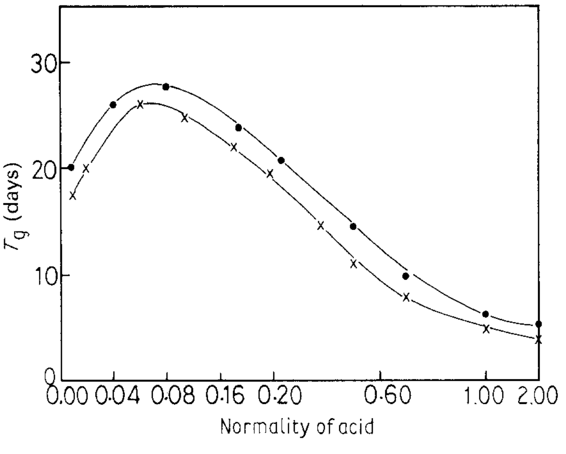

Figure 3 Gelation time versus normality of acids: (×) HCl, (●) HNO_3.

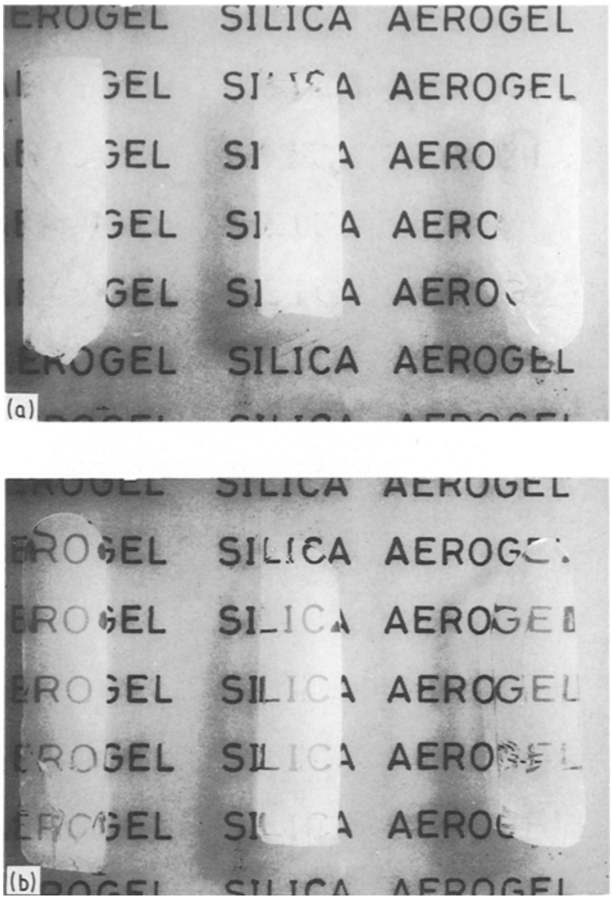

Figure 5 A few silica aerogel samples obtained at (a) lower EtOH/TEOS (< 2), and (b) higher EtOH/TEOS (> 2) molar ratios.

The EtOH/TEOS ratio affects the diffusion rates of the reacting species – H_2O and the partially hydrolysed species. For this reason, gels have a higher density with lower amounts of alcohol, indicating greater polymerization. With increasing EtOH/TEOS

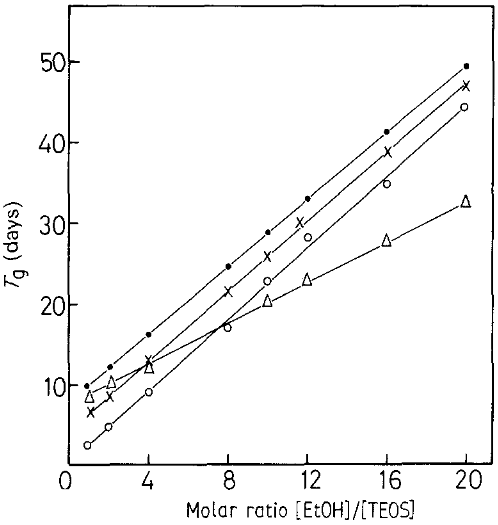

Figure 6 Gel setting time versus molar ratio of EtOH/TEOS for four H_2O/TEOS molar ratios: (△) 5, (○) 8, (×) 10, (●) 12.

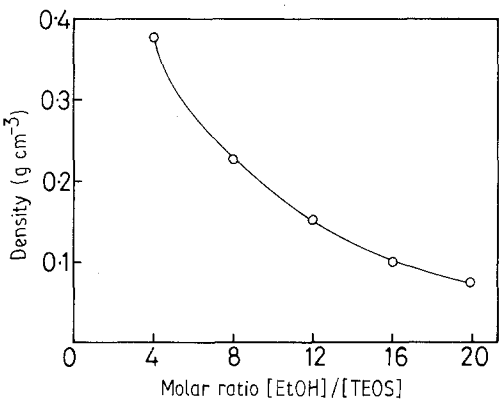

Figure 7 Density of silica aerogel versus molar ratio of EtOH/TEOS for a constant H_2O/TEOS molar ratio of 8.

ratio, lower density gels were obtained, because an increase of ethanol separates the reacting species and favours the reactions which depend less on the diffusion of larger species. This means that hydrolysis reactions are favoured more than the polymerization, and consequently, the polymer size decreases as the alcohol concentration increases.

The infrared spectra indicate that not only the extent of polymerization but also the structure of the oxide network is affected, as shown in Fig. 8. The spectra show peaks at 1085, 800 and 465 cm^{-1} corresponding to different modes (asymmetric and symmetric and bending, respectively) of silicon oxides [25]. In addition, the absorption band at 960 cm^{-1} has been assigned to the stretching vibration of the external Si–O group. With increasing EtOH/TEOS molar ratio, the intensity of the peaks at 1085, 800 and 465 cm^{-1} decreased, which is due to the dilution of the medium. This will lead to the decrease in polymerization and condensation, and hence the strength of the Si–O–Si network decreases. There was no change in the peak at 3400 cm^{-1} which corresponds to O–H stretching vibration of water.

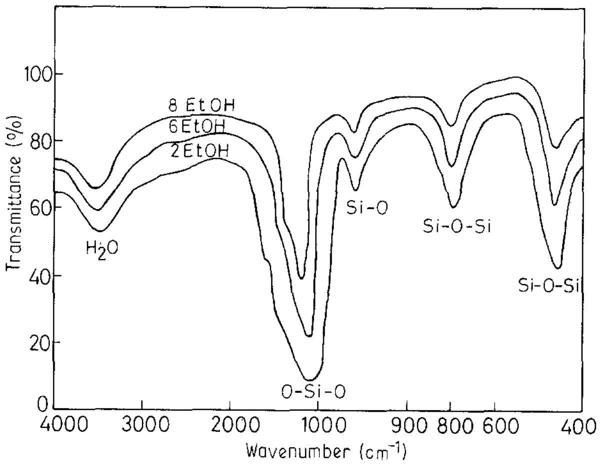

Figure 8 Infrared spectra of silica aerogels for three different EtOH/TEOS molar ratios at $[H_2O]/[TEOS] = 4$.

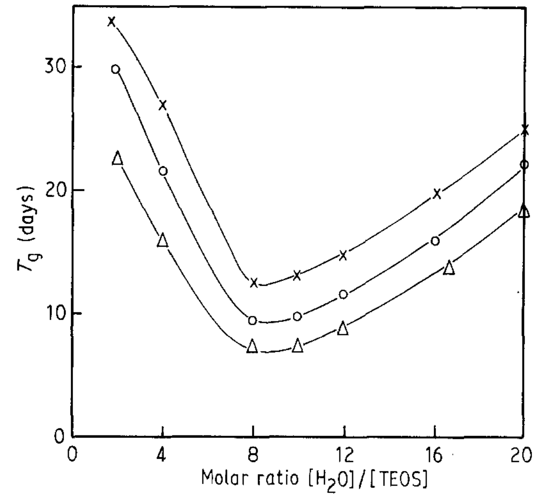

Figure 9 Gelation time versus molar ratios of H_2O/TEOS for three different EtOH/TEOS molar ratios: (△) 3, (○) 5, (×) 8.

3.4 Effect of H_2O/TEOS molar ratio

Gels were prepared by varying the H_2O/TEOS molar ratio, R, from 1–20 by keeping the EtOH/TEOS molar ratio constant at 5, 6, 8, 10 and 12 and the HCl catalyst at 0.01 N. At lower and higher molar ratios, the gelation time was higher as shown in Fig. 9. This is due to the fact that at lower molar ratio, H_2O is not sufficient to complete the hydrolysis reaction with TEOS and, the gelation occurs via linear chain formation with residual organic groups which lead to dense gels. On the other hand, at higher molar ratio, even though the hydrolysis proceeds faster, condensation takes place slowly, so the gelation time is longer. A minimum gelation time was obtained at $R \simeq 8$.

At molar ratios lower than 4 and higher than 12, dense and cracked aerogels were obtained as shown in Fig. 10a. The molar ratio of H_2O/TEOS versus density of the aerogels is shown in Fig. 11. For molar ratios between 4 and 12, monolithic, low-density and transparent aerogels were obtained as shown in Fig. 10b. The lowest density (0.08 g cm^{-3}) and most transparent (90%) aerogels were obtained with molar ratios between 6 and 10.

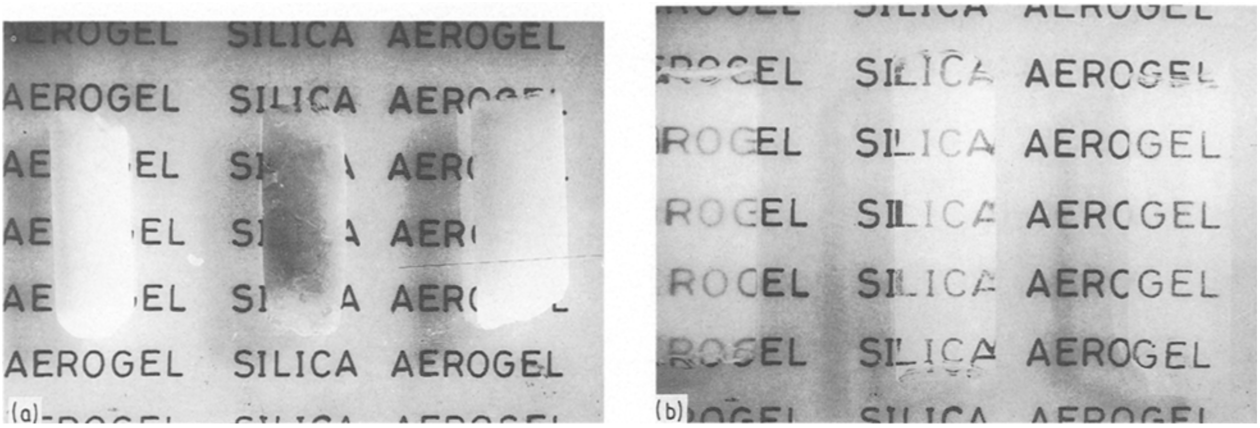

Figure 10 A few silica aerogel samples obtained at (a) lower (< 4) and (b) higher (> 4) molar ratios of H_2O/TEOS.

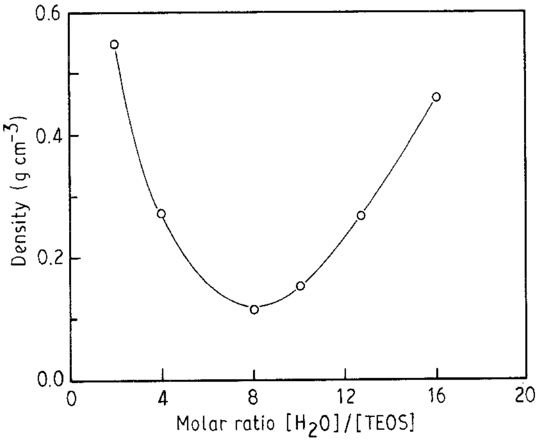

Figure 11 Density of silica aerogel versus molar ratio of H_2O/TEOS with constant EtOH/TEOS molar ratio of 5.

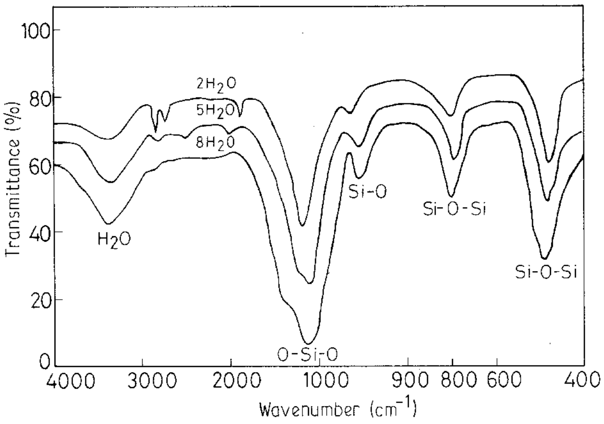

Figure 12 Transmission infrared spectra of silica aerogel for various H_2O/TEOS molar ratios for a constant EtOH/TEOS molar ratio of 5.

At R values lower than 4, due to insufficient amount of water, the incompletely hydrolysed species were polymerized among them with residual organic groups via linear chain formation which leads to longer setting times and dense aerogels (Fig. 11). At higher R values (> 4), due to the presence of excess water, polymerization is lower than condensation, producing cyclization and enhancing the siloxane bond formation within the particles. Gelation occurs as a result of the packing of these densified particles, resulting in a three-dimensional network with higher density (Fig. 11). For R values between 6 and 10, due to the presence of an optimum amount of water, hydrolysis and polymerization occur systematically which gives rise to a cross-linking three-dimensional siloxane network and leads to lower density and more transparent aerogels (Fig. 10b).

Infrared spectra of silica aerogels with R values 2, 5 and 8 were taken. Fig. 12 shows that with increasing R values, the intensity of the 1080, 960, 800 and 465 cm^{-1} peaks increases, which is due to the increase of the Si–O–Si network. The peaks around 2800 and 1500 cm^{-1} can be associated with C–H bonds which are due to incomplete hydrolysis at low R values. These peaks disappear with increasing R values, due to the completion of hydrolysis. The peak around 3500 cm^{-1} is associated with OH bonds of water, and it increases with increasing R.

3.5. Effect of alcogel ageing

To investigate the effect of alcogel ageing, gels of the same pH (2) and molar ratio of TEOS:EtOH:H_2O (1:5:8) were prepared. The gels were allowed to age for various periods ranging from 2–80 days, before the supercritical drying. Immediately after gelation, the area of contact between the colloidal particles was rather small. The autoclave drying of the alcogel was strongly influenced by the structure developed during gel ageing. During the gel-ageing process, neck growth occurs between the kernels which makes the alcogel more resistant to drying stresses. If the ageing was less than 10 days or longer than 40 days (for 0.01 N HCl catalysed gels), several cracks were observed in the supercritically dried aerogels, as shown in Fig. 13a. In the case of lower aged alcogels, the cracks in the aerogels may be due to the fact that the neck growth between the kernels might not have been completed, which results in soft gels and the autoclave drying leads to cracked aerogels. On the other hand, if the alcogel ageing is more than 40 days, because of slow drying, a small differential evaporation of alcohol

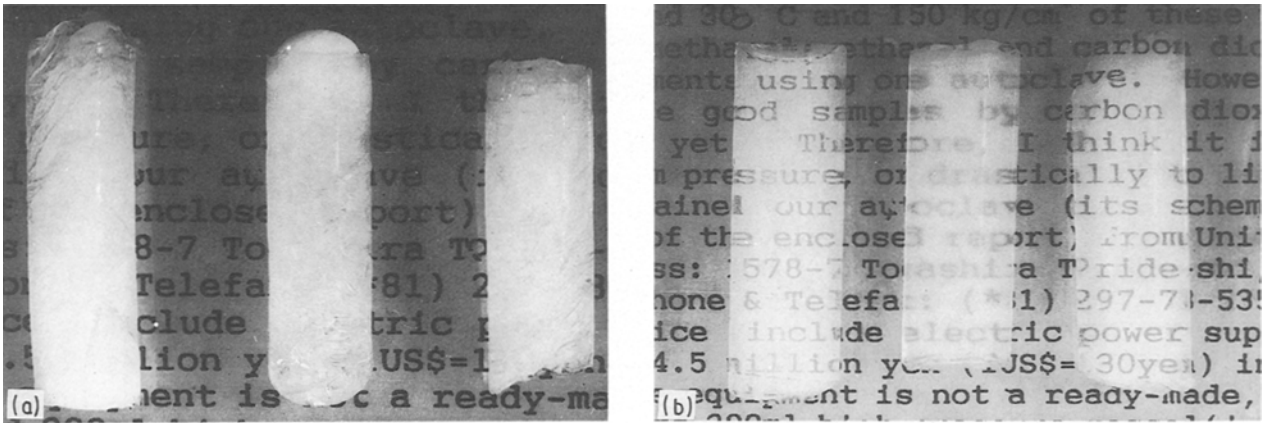

Figure 13 A few silica aerogel samples obtained at (a) lower (< 10 days) and higher (> 30 days), and (b) medium, (10–30 days) gel-ageing periods.

occurs in the alcogels with different pore sizes which give rise to drying stresses due to capillary forces [26, 27]. Monolithic and transparent aerogels were obtained in the case of gels aged between 10 and 30 days (for 0.01 N HCl), as shown in Fig. 13b. The period of cracking decreases as the concentration of the HCl catalyst increases, as shown in Fig. 14, which is due to a faster gel-setting period and incomplete neck formation between the kernels.

4. Conclusions

The best quality silica aerogels in terms of monolithicity and transparency were obtained using (i) 0.01 N HCl as the catalyst, (ii) alcogel pH of 2, (iii) a molar ratio of TEOS:EtOH:H_2O = 1:5:8, and (iv) a gel-ageing period of 15 days. Further work on the physical and chemical properties of the silica aerogels is in progress.

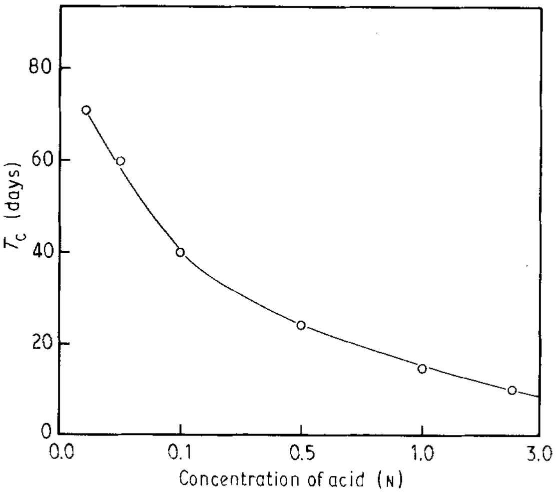

Figure 14 Crack formation time during ageing of silica aerogel versus concentration of HCl catalyst.

Acknowledgements

The authors are grateful to Professor G. M. Pajonk, University of Claude Bernard, Lyon, France and Dr F. Chaput, Ecole Polytechnique, Palaiseau, France for helpful discussions regarding critical drying aspects. This work was supported by the Department of Atomic Energy, Government of India, under BRNS project no. 34/12/90-G. The authors thank the Materials Science Committee, BRNS, DAE for recommending the present project for the grant.

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Received 24 April
and accepted 11 August 1992