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Low density TEOS based silica aerogels using methanol solvent

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Abstract Highly transparent monolithic silica aerogels based on the TEOS precursor were prepared by the two-step (acid-base) sol–gel process. The hydrolysis and condensation reactions of tetraethoxysilane (TEOS) proceeded in methanol solvent with oxalic acid and NH_4OH as the catalysts, respectively. The wet gels were supercritically dried using methanol. The aerogels were characterized by transmission electron microscopy (TEM) and measurements of optical transmission, bulk density, volume shrinkage, porosity and thermal conductivity. Monolithic silica aerogels with high optical transmission (~93%), low density (~0.055 g/cm^3), low thermal conductivity (~0.04 W/mK), and minimum volume shrinkage (~10%), were obtained for the molar ratio of TEOS:MeOH:acidic H_2O:basic H_2O at 1:33:3.5:3.5 alongwith the oxalic acid and NH_4OH concentrations at 0.001 M and 1 M, respectively.

Introduction

Silica aerogels are the porous nanostructured form of silicon dioxide. They are open cell inorganic polymers with an intricate internal structure, resulting in an extremely high surface area (~1000 m^2/g) [1–3]. Due to their highly porous (minimum of 95% porosity) and nanostructured nature, they exhibit remarkable electrical, thermal and acoustic insulating properties. These fascinating properties of the aerogels make them prime candidates for a variety of scientific and technological applications such as Cerenkov radiation detectors in high energy physics, thermal and acoustic super insulators in window systems, low dielectric constant (~2) oxide layers for MOS devices, Inertial Confinement Fusion (ICF) targets for the thermonuclear fusion reactions, heterogeneous catalyst supports [4–7], storage media for liquid rocket propellants [8] and radio luminescent devices [9], etc.

However, the high cost of the aerogels prevents their widespread applications in various fields. It is well known that tetramethoxysilane (TMOS) gives better quality aerogels in terms of high optical transmission (~90%) [10, 11], low density (~0.05 g/cm^3) [12], faster gelation (~30 min) [13] and negligible volume shrinkage (2 to 5%), as compared to the aerogels produced using tetraethoxysilane (TEOS) precursor. However, TMOS is five times costlier than the TEOS and also it is highly toxic, the fumes of which can cause blindness. Therefore, TEOS can be used as a cost effective and environmental friendly precursor for the production of silica aerogels. In general, only acid catalysts are used to produce the aerogels using the TEOS precursor [14–16]. But the TEOS based, acid catalyzed (single step) aerogels posses the disadvantages such as higher densities (~0.2 g/cm^3), lower optical transmission (~60%), larger volume shrinkage (~ 30%) and longer gelation times (~3 days) [13]. A few reports are available on the production of low-density TEOS-based silica aerogels using a two-step sol–gel process

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[12, 17]. However, the aerogels were produced using strong acids such as HCl, which corrodes the autoclave system. Also the processing involves several solvent exchange steps and low temperatures (253 K) [18].

In our earlier publication [19] we have reported the synthesis of TEOS based silica aerogels using ethanol solvent, by the two-step sol–gel process. As ethanol solvent contains longer chain and more branching of alkyl groups (–C_2H_5), due to more steric hindrance, the aerogels could not be obtained for EtOH/TEOS molar ratio values greater than 6.9. However, in the present studies, for the first time, using methanol as the solvent we could produce the TEOS based silica aerogels with increased optical transmission (~93%) and low density (0.05 g/cm^3). Due to the less steric hindrance compared to that of the ethanol, it was possible to obtain the aerogels with MeOH/TEOS molar ratio as high as 55, resulting in larger volume of the aerogels with the same amount of the precursor. Also, a weak organic acid such as oxalic acid has been used as an acid catalyst, which does not corrode the autoclave system. The slightly different processing conditions of the two-step sol–gel process impart subtle but important changes in the physical properties of the final aerogel product, as it allows an excellent control over the rates of hydrolysis and condensation reactions [20].

Experimental procedures

Preparation of aerogels

The synthesis of an aerogel, in general, involves two major steps; the preparation of an alcogel and the supercritical drying of the alcogel to remove the solvent. The alcogels were prepared by the two-step (acid-base catalyzed) sol–gel process as per the following two steps:

(i) Tetraethoxysilane (TEOS) was first diluted in methanol, and it was hydrolyzed with partial amount of water under acidic conditions using the oxalic acid.

(ii) Condensation of hydrolyzed species (i.e. Si–OH) was carried out in the presence of a base catalyst, ammonium hydroxide (NH_4OH).

The resulting silica sols were stirred for 30 min, and then kept for gelation at ambient temperature of 27 °C to 30 °C. After ageing for two days, the alcogels were supercritically dried in a 600 ml autoclave (Parr Instruments Company, Moline Illinois, USA). The conditions above the critical temperature (243°C) and the critical pressure (79 bar) of methanol solvent were achieved in three hours of heating time, using a PID temperature controller. Figure 1 shows the ramp rates of temperature and pressure used to achieve the supercritical conditions in the autoclave. At these supercritical conditions, the methanol solvent gets transformed into a supercritical fluid state. The vapors were then vented out of the autoclave in about two hours time. After reaching the atmospheric pressure, the heating was continued at a constant temperature of 265°C for about 15 min and finally the autoclave was flushed three times with dry nitrogen (~3 bar) in order to remove the trapped solvent molecules, from the autoclave.

The chemicals used were, TEOS and NH_4OH (from Fluka Company, Switzerland), methanol and oxalic acid (ExcelaR grade and L. R. grade, respectively, from Qualigens Company, India). Double distilled water was used throughout all the experiments.

In order to obtain good quality silica aerogels in terms of high optical transmission, low density, low thermal conductivity, less volume shrinkage, etc., acid (A) and base (B) catalyst concentrations were varied from 0.0005 M to 0.1 M and 0.6 M to 1.8 M, respectively. The molar ratios of MeOH/TEOS (S), acidic H_2O/TEOS (W_1) and basic H_2O/TEOS (W_2) were systematically varied from 11 to 55, 2.2 to 7.3 and 0 to 4.4, respectively. Also the effect of time intervals (T) before NH_4OH addition to the acidic sol was studied from 0 to 48 h.

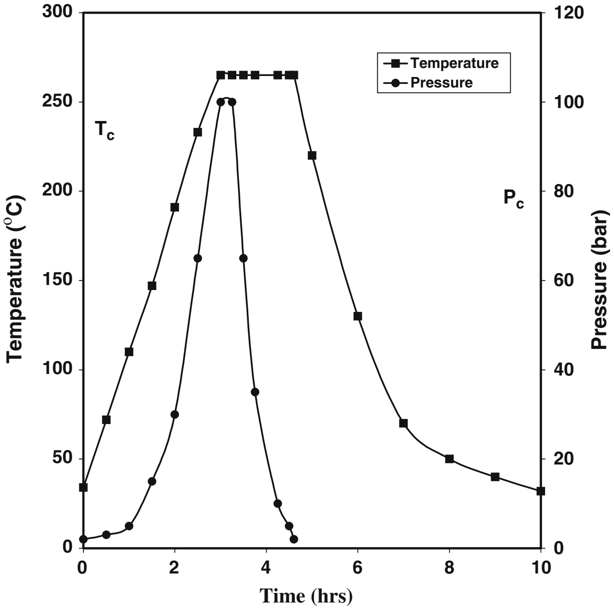

Fig. 1 Pressure and temperature variation, as a function of time, during supercritical drying process

Methods of characterization

The microstructure of the aerogels was studied by the Transmission Electron Microscopy (TEM, Philips, Tecnai F20 model, The Netherlands). The optical transmittance of the aerogels (sample thickness of 1 cm) was measured at a wavelength of 750 nm using the optical spectrophotometer (Systronic, Model 119, USA). The thermal conductivity of the aerogels was measured (using C-T meter, Teleph, France) by sandwiching the ring probe sensor in between two plane aerogel sheets. The chemical bonding in the aerogel was studied using the Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer instruments, spectrum one, made in USA).

The bulk densities of the aerogels were calculated from their weight to volume ratios. The percentage of volume shrinkage (Vs %) and porosity (P%) were determined as described in our earlier publication [20].

Results

To study the effect of oxalic acid catalyst concentration, A, the alcogels were prepared by keeping the molar ratio of TEOS:MeOH:H_2O constant at 1:33:5.7, respectively, and the base catalyst NH_4OH (1 M) was added to the sol after $T = 24$ h. The A value was varied from 0.0005 M to 0.1 M. Table 1 shows that with an increase in A value from 0.001 M to 0.1 M, the gelation time decreased from 2 h to 15 min. However, for the A value less than 0.001 M, the alcosols did not set. The bulk density and the volume shrinkage of the aerogels decreased from 0.087 to 0.055 g/cm^3 and 40 to 15%, respectively, with decrease in A value from 0.1 M to 0.001 M. The thermal conductivity of the aerogels decreased from 0.057 to 0.04 W/mK, with the decrease in A value from 0.1 M to 0.001 M, as shown in Fig. 2. Monolithic and transparent (~88%) aerogels, with minimal volume shrinkage (~15%) and bulk density (0.05 g/cm^3), were obtained for the $A = 0.001$ M and this value was fixed for the further investigations.

The influence of MeOH/TEOS molar ratio, S, was studied by varying it systematically from 11 to 55. The gelation time increased from 5 min to 2 days with an increase in S value from 11 to 38.5. The bulk density and volume shrinkage of the aerogels decreased from 0.146 g/cm^3 to 0.055 g/cm^3 and 37 to 15%, respectively, as the S value increased from 11 to 33, (Fig. 3 and Table 2). The optical transmission (at 750 nm) was found to be nearly the same (~92%) for all the aerogels. Figure 4 shows the optical transmission spectrum obtained by scanning the two step processed, TEOS based aerogel over a range of wavelength from 750 nm to 450 nm. The optical transmission decreased with decrease in the incident wavelength. This is because the Rayleigh scattering becomes more effective at shorter wavelengths and thereby reducing the optical transmission. The dependence of the scattering on the incident wavelength is given by the following relation:

$$I_s \alpha (1/\lambda^4) \tag{1}$$

Where, I_s is the scattering intensity and λ is the incident wavelength.

For the S values greater than 33, i. e. for the higher dilutions of the TEOS precursor ($S = 38.5$ to 55), the gelation time was found to be longer (>2 days). However, when the sols were stirred for 5 h, a considerable reduction in the gelation time was observed (for $S = 55$, the gelation time reduced from 14 days to 8 days with increase in the stirring time from 30 min to 5 h). The thermal conductivity of the aerogels decreased from 0.085 to 0.04 W/mK with an increase in S value from 11 to 44, as shown in Table 2. Keeping in view, the minimum volume shrinkage, high optical transmission, low bulk density and the lower gelation time, the S value was kept constant at 33 for further studies.

The effect of different time intervals, T, before the base catalyst (1 M, NH_4OH) addition to the acid catalyzed sol has also been studied from 0 h to 48 h. The gelation time decreased from 18 days to 5 min with an increase in T value from 10 h to 48 h. For T

Table 1 Effect of the oxalic acid concentration on the physical properties of the TEOS based aerogels

Oxalic acid concentration (M)	Gelation time (min)	Bulk Density (g/cm^3)	% Volume shrinkage	Porosity (%)	% Optical Transmittance
0.0005	No Gelation	–	–	–	–
0.001	120	0.055	15	97.08	89
0.01	30	0.079	33	95.83	88
0.1	15	0.087	40	95.41	69

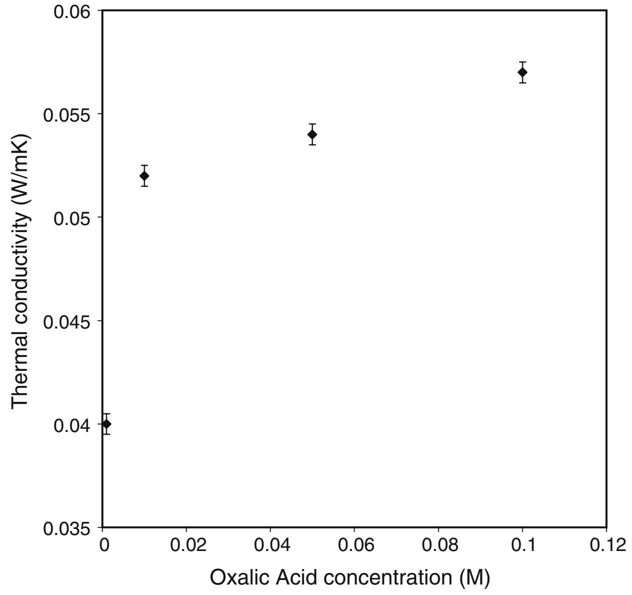

Fig. 2 Variation of thermal conductivity of the aerogels as a function of oxalic acid concentration

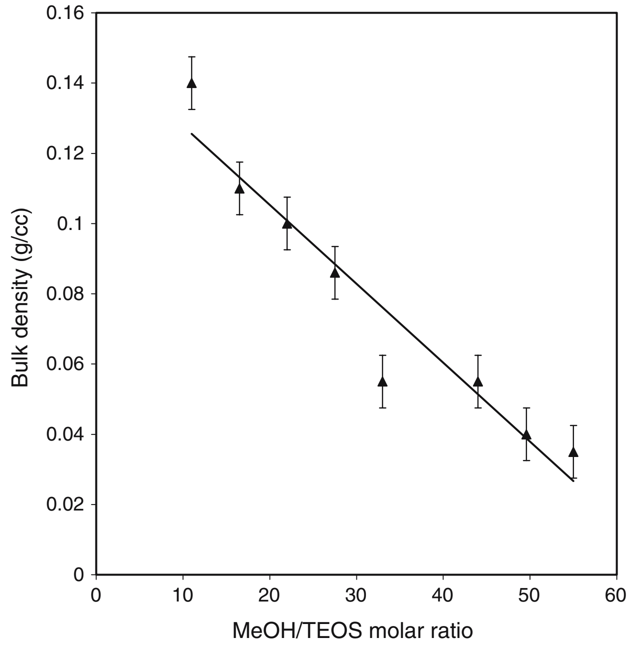

Fig. 3 Effect of MeOH/TEOS molar ratio (*S*) on the bulk density of TEOS based aerogels

values below 10 h, the alcosols do not form the gels. All the aerogels prepared with *T* values in between 10 h and 48 h, were highly transparent (92%). The bulk density (0.05 g/cm^3) and the volume shrinkage (~10%) were found to be minimum for the *T* value of 24 h. Therefore, this value of $T = 24$ h was kept constant for all the further experiments.

Table 2 Variation of the physical properties of TEOS based aerogels as a function of MeOH/TEOS molar ratio

MeOH/TEOS molar ratio	Gelation time (min)	Volume Shrinkage (%)	Porosity (%)	Thermal conductivity (W/mK)
11	5	37	92.30	0.085
16.5	5	35	94.09	0.073
22	5	30	94.69	0.058
27.5	30	20	95.42	0.049
33	90	15	97	0.042
44	2 days	22	97.98	0.04

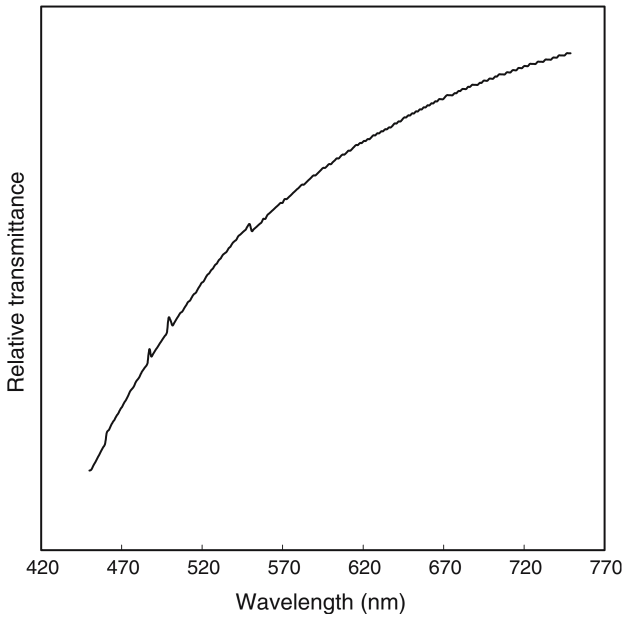

Fig. 4 Optical transmission spectrum of the TEOS based aerogel

The NH_4OH catalyst concentration, *B*, was varied from 0.6 M to 1.8 M. It has been observed that all the aerogels prepared using the *B* values in between 0.6 M to 1.8 M were highly transparent (~93%). The gelation time decreased from 3 h to 20 min with an increase in the *B* value from 0.6 M to 1.8 M. However, in the absence of NH_4OH catalyst i.e. the alcosols catalyzed only with the oxalic acid, had longer gelation times (minimum 3 days). The bulk density of the aerogels was found to decrease with an increase in the *B* values up to 1 M, beyond which it increased with a further increase in the *B* value (>1 M), as shown in Fig. 5. Keeping in view the low density and minimum volume shrinkage, the *B* value was fixed at 1 M.

The molar ratios of acidic H_2O (W_1) and basic H_2O (W_2) were varied from 2.2 to 8.7 and 0 to 4.4, respectively. The gelation time decreased form 2 h to 5 min and 3 days to 2 min with increase in the W_1 and W_2 values from 2.2 to 8.7 and 0 to 4.4, respectively. The variation in $W_1$and W_2 values did not show significant

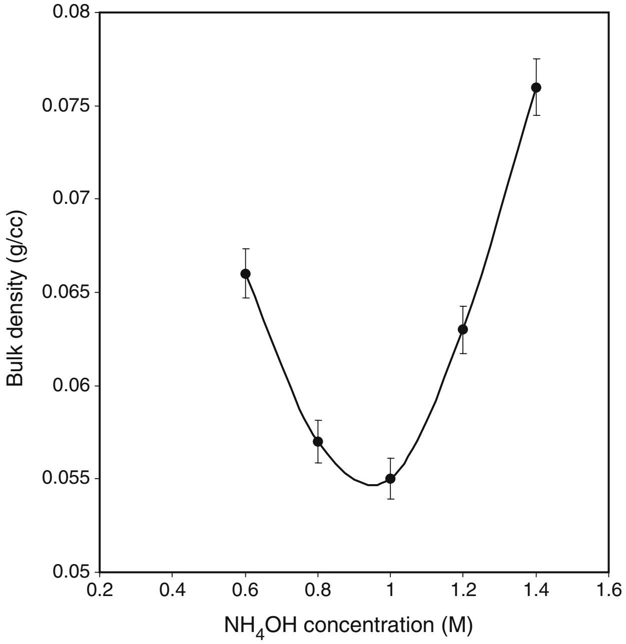

Fig. 5 Bulk density of the TEOS based aerogels as a function of NH_4OH catalyst concentration

change in the optical transmission of the aerogels. All the aerogels are highly transparent (~93%). Monolithic aerogels with optimum volume shrinkage (~10%) have been obtained for $W_1 = 3.5$ and $W_2 = 3.5$. For the values of W_1 and W_2 greater than 3.5, the bulk density and volume shrinkage increased up to 0.08 g/cm^3 and 40%, respectively.

Discussion

The decrease in the gelation time with an increase in the A value (oxalic acid concentration) is due to the increase in the rate of hydrolysis, which leads to faster condensation upon the addition of the base catalyst [21]. However, for the A value less than 0.001 M, the alcosols did not set due to the slow hydrolysis rate. It is reported earlier that an increase in the acid catalyst concentration results in aerogels with a network of mostly smaller pores and particles and with a few larger pores, as can be seen in the transmission electron micrographs (Fig. 6). This would lead to differential drying stresses resulting in higher volume shrinkage and hence higher density [22], (Table 1). The higher A value (0.1 M) resulted in more compact (shrunk) aerogel network (Fig. 6 (a)) compared to that of $A = 0.001$ M (Fig. 6 (b)). The thermal conductivity of the aerogels increased with increase in the bulk density. This result shows that the major heat transfer through the aerogels takes place via the solid thermal conduction [23]. Micro-heterogeneity, (e.g. pore size distribution), has been observed in the TEM micrographs e.g. Fig 6 (a). The effects of such heterogeneity on thermal properties of the aerogel is also important, but in this paper, the effects of sol–gel parameters on the physical properties of the aerogels have been discussed from the macroscopic point of view.

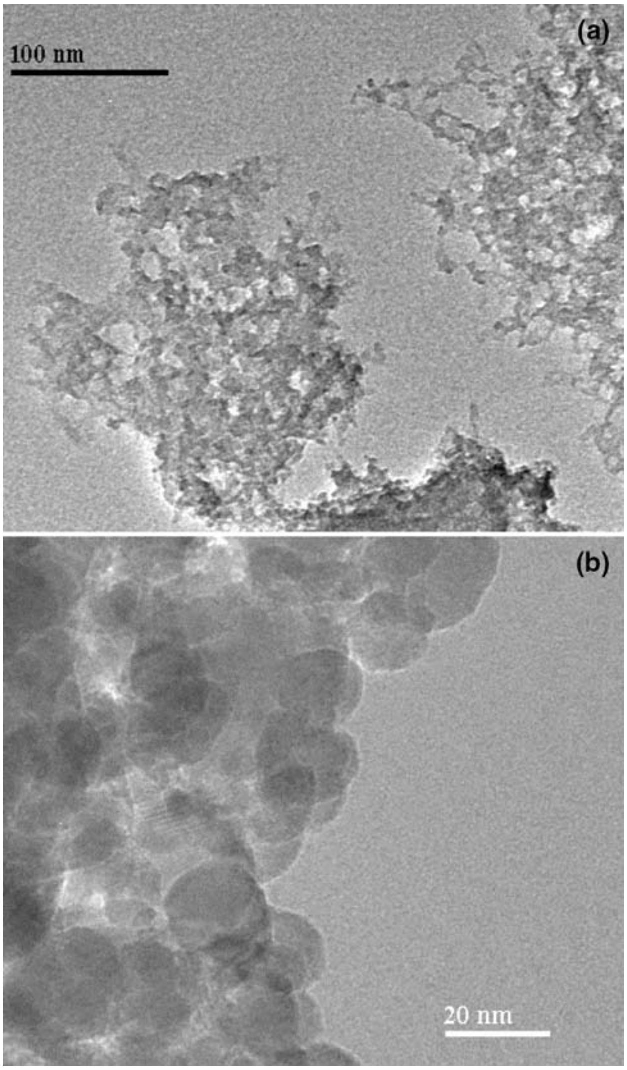

Fig. 6 Transmission electron micrographs of TEOS based aerogels prepared with: (**a**) $A = 0.001$ M, $B = 1$ M and $S = 33$; (**b**) $A = 0.1$ M, $B = 1$ M and $S = 33$

In the sol–gel process, transesterification occurs when alkoxides are hydrolyzed in alcohols containing different alkyl groups. For example, Brinker et al. observed the transesterification when the TEOS was hydrolyzed in *n*-propanol [24]. In the present studies, the TEOS precursor was hydrolyzed in the methanol solvent, which contains smaller chain alkyl groups (i.e. $-CH_3$) resulting in transesterification, as per the following chemical reaction:

$$\mathrm{Si\,(OC_2H_5)_4 + CH_3OH \leftrightarrow Si\,(OC_2H_5)_3OCH_3 + C_2H_5OH} \quad (2)$$

Voronkov et al. have also reported that any complication (i.e. increase in the size of the alkyl group) to the alkoxy group retards the rate of hydrolysis of the alkoxysilane [25]. For the alkyl groups, the chain length increases from methyl to butyl and so on, and results in the lowering of the hydrolysis rate of alkoxysilane. The use of methanol as a solvent resulted in an increase in the rate of hydrolysis reaction due to the least steric hindrance compared to that of all the other solvents such as ethanol, propanol, butanol, etc. [26]. Hence, it was possible to obtain the alcogels using the TEOS precursor, even for higher dilution (maximum up to the molar ratio of MeOH/TEOS = 55), using methanol solvent resulting in the low-density aerogels.

With an increase in S value, the silica content per unit volume in the sol decreases and also the separation between the silica clusters increases. As a result, the bulk density and the volume shrinkage decrease with the increase in the solvent content in the sol [27]. Figures 7 (a) and 6 (a) show the TEM images for the aerogels prepared with two different *S* values of 11 and 33, respectively. It is clearly seen that the *S* = 11 resulted in the compact network compared to that of *S* = 33. The thermal conductivity of the aerogels decreased with an increase in *S* value, which is due to the decrease in the bulk density of the aerogels (Table 2).

The decrease in the gelation time with an increase in the *T* (time interval before base catalyst addition) is due to the fact that the hydrolysis reaction approaches to completeness, resulting in faster gelation upon the addition of the base catalyst. The early addition of the base catalyst cancels the effect of the acid catalyst that is why gels could not be obtained for *T* values less than 10 h due to the incomplete hydrolysis of the TEOS precursor.

The increase in the *B* value increases the rate of condensation reactions resulting in the lowering of gelation time. However, in the absence of NH_4OH catalyst, the alcosols catalyzed only with oxalic acid, had a longer gelation time (minimum 3 days) because of the slow condensation rate.

The bulk density of the aerogels was found to decrease with an increase in the *B* values up to 1 M, but it increased with a further increase in *B* values (>1 M) as shown in Fig. 5. As the *B* value increases up to 1 M, the particle size increases and hence the connectivity between the particles increases. Therefore, the silica gel network can withstand the thermal stresses developed during the supercritical drying process, leading to the lowering of the volume shrinkage, as shown in Fig. 8, which in turn decreases the bulk density of the aerogels for the B values up to 1 M. Figures 7(b) and 6 (a) show the transmission electron micrographs for two different *B* values, 0.6 and 1 M, respectively. The aerogel network for *B* = 0.6 is denser than for *B* = 1 M. However, for the *B* values >1 M, the rate of condensation becomes so fast that sudden gelation occurs, leading to smaller particle size. Thus, the connectivity between the particles decreases and the aerogel shrinks during the supercritical drying process causing an increase in the volume shrinkage and consequently in the bulk density.

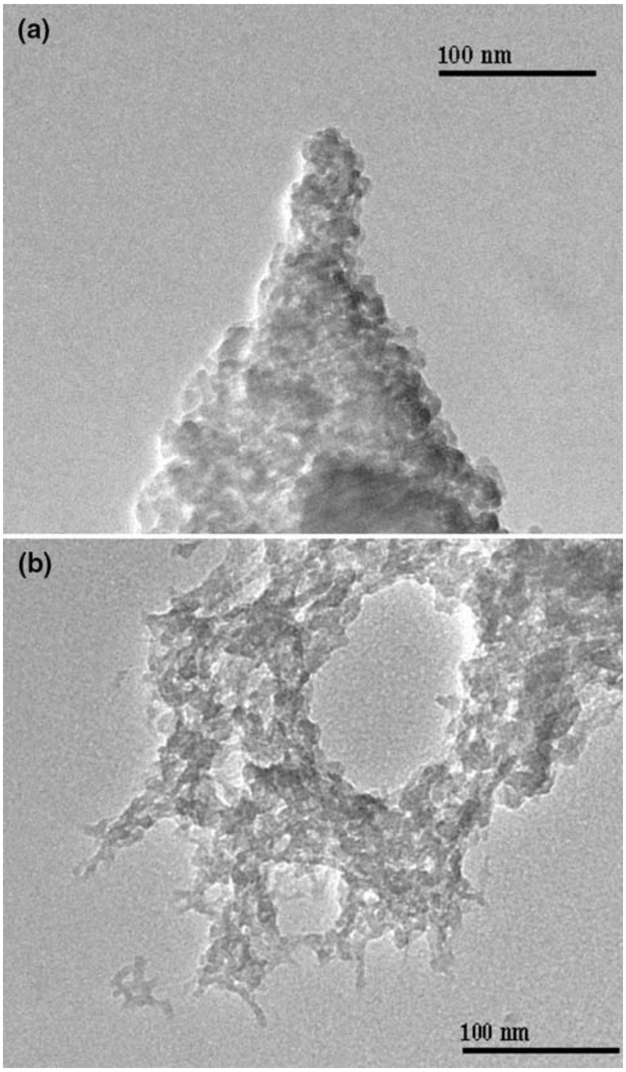

Fig. 7 Transmission electron micrographs of TEOS based aerogels prepared with: (**a**) *A* = 0.001 M, *B* = 1 M and *S* = 11; (**b**) *A* = 0.001 M, *B* = 0.6 M and *S* = 33

The decrease in gelation time with increase in W_1 and W_2 values is due to the increase in hydrolysis and condensation rates of the TEOS precursor. For the

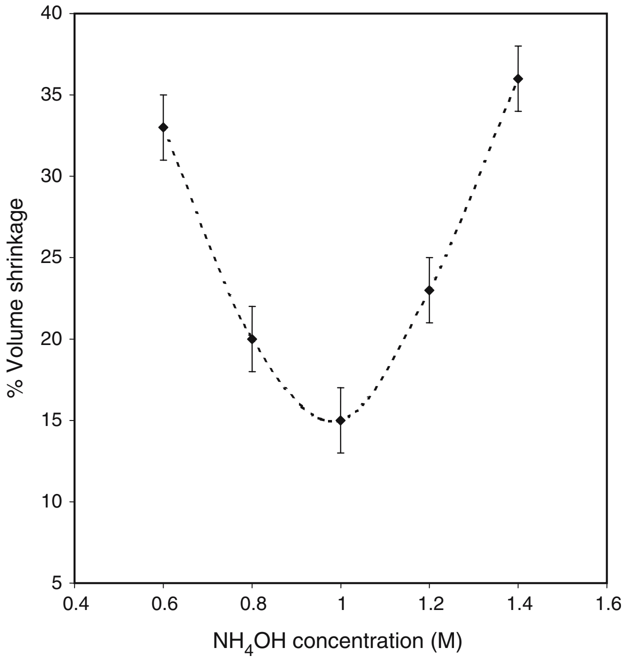

Fig. 8 Effect of base catalyst (NH_4OH) concentration on the volume shrinkage of the TEOS based aerogels

values of W_1 and W_2 greater than 3.5, due to the excess water, faster gelation occurred resulting in the smaller pore and particle sizes [28]. Also the excess amount of water in the sol resulted in sub-critical drying of the alcogels and hence an increase in the volume shrinkage and bulk density.

The chemical bonding in the aerogel was studied by means of FTIR spectroscopy. In Fig. 9, the absorption peaks at 800 cm^{-1} and 1000 cm^{-1} correspond to the $\equiv$Si–O–Si$\equiv$ bonding which confirms the polymerization of $\equiv$Si–OH species resulting in a three dimensional $\equiv$Si–O–Si$\equiv$ aerogel network.

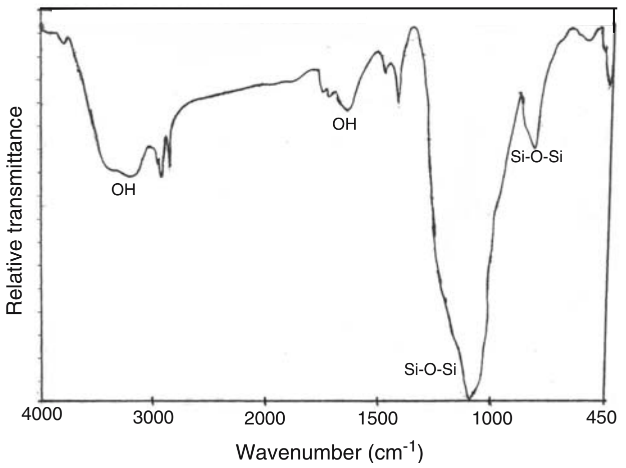

Fig. 9 FTIR spectrum of the two-step processed TEOS based aerogel

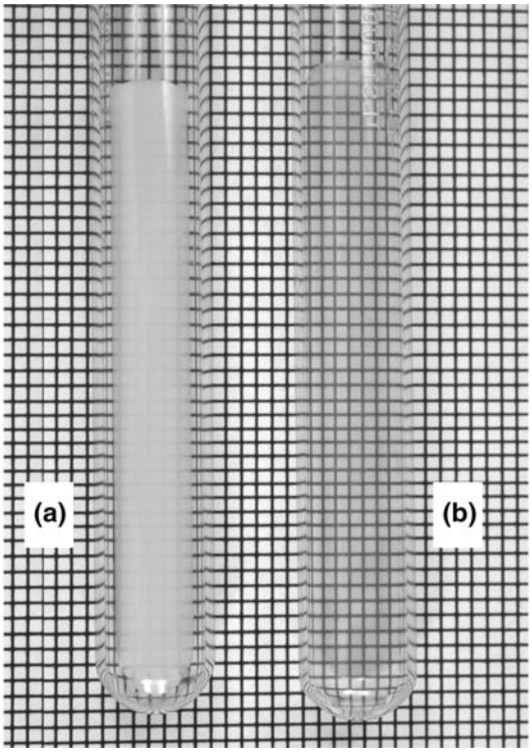

Fig. 10 Photograph showing (**a**) single-step, i.e. acid catalyzed, and (**b**) two-step, i.e. acid-base catalyzed, TEOS based aerogels

Figure 10 shows the photographs of TEOS based aerogels prepared with (a) single-step (oxalic acid catalyzed) and (b) two-step (acid-base catalyzed) sol–gel process, using oxalic acid and ammonium hydroxide. The two-step (acid-base) sol–gel process resulted in TEOS based aerogels with higher optical transmission, lower volume shrinkage and hence lower bulk density as compared to that of the single step (acid catalyzed) sol–gel process (Table 3). The enhancement in the optical transmission of aerogels derived by the two-step sol–gel process is because of the smaller and uniform silica particles formation due to faster gelation compared to those of single step derived aerogels.

Table 3 Comparison of the physical properties of the TEOS based aerogels prepared by single step and two-step sol–gel process

Physical property	Single step sol–gel process	Two step sol–gel process
Optical transmission	60%	93%
Bulk density	0.21 g/cm^3	0.05 g/cm^3
Volume shrinkage	30%	10%

Conclusions

It is shown that the use of methanol (MeOH) as a solvent in combination with the tetraethoxysilane (TEOS) precursor, in the two step sol gel process gives better quality aerogels, in terms of low bulk density (~0.05 g/cm^3), higher optical transmission (~93%) and monolithicity, than those obtained using the ethanol solvent. The bulk density and volume shrinkage decreased from 0.087 g/cm^3 to 0.05 g/cm^3 and 40 to 15%, respectively with decrease in oxalic acid concentration from 0.1 to 0.001 M. The bulk density and volume shrinkage of the aerogels decreased from 0.146 to 0.05 g/cm^3 and 37 to 15%, respectively, as the S value increased from 11 to 33 but the gelation time increased from 5 min to 2 days. The time interval before base catalyst (ammonium hydroxide) addition was found be optimum at 24 h.

The best quality silica aerogels in terms of high optical transmission (~93%), low density (0.55 g/cm^3), low thermal conductivity (0.04 W/mK), less volume shrinkage (~10%), could be produced using tetraethoxysilane and methanol (the cheapest combination of an alkoxide precursor and a solvent) by the two-step (acid-base) sol–gel process.

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