Chapter - 4
CHAPTER 4

Low density TEOS based aerogels using methanol solvent

4.1 Introduction

In the previous chapter, the experimental results on the synthesis of TEOS based aerogels using ethanol solvent, by the two step sol-gel process, have been reported and discussed. However, ethanol solvent contains longer chain and more branching of alkyl groups (-C$_2$H$_5$), due to more steric hindrance, the aerogels could not be obtained for EtOH/TEOS molar ratio values greater than 6.9. Therefore, in the present chapter, using methanol as the solvent attempts have been made to produce the TEOS based aerogels. 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. Moreover, the methanol solvent is cheaper (4 times) and easily available than the ethanol solvent thereby decreasing the cost of the aerogels. 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 [1].
4.2 Experimental Procedures

4.2.1 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 an oxalic acid.

ii) Condensation of these hydrolyzed species (i.e. Si-OH) was carried out in the presence of a base catalyst, ammonium hydroxide (NH₄OH).

The resulting silica sols were stirred for 30 min, and then kept for gelation at ambient temperature of 27 to 30°C. After ageing for two days, the alcogels were supercritically dried in a 600 ml autoclave (Parr Instruments Company, Moline Illinois, U.S.A.). 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. At these supercritical conditions, the methanol solvent gets transformed into a supercritical fluid state. The vapours 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 minutes and finally the autoclave was flushed three times with dry nitrogen (~3bar) in order to remove the trapped solvent molecules, from the autoclave.

The chemicals used were, TEOS and NH₄OH (from Fluka Company, Switzerland), methanol and oxalic acid (ExelaR grade and L. R. grade, respectively, from Qualigens, 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 0.0005M to 0.1 M and 0.6M to 1.8M, respectively. The molar ratios of MeOH/TEOS (S), acidic H₂O/TEOS (W₁) and basic H₂O/TEOS (W₂) 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 NH₄OH addition to the acidic sol was studied from 0 to 48 hours.
4.2.2 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 1cm) was measured at a wavelength of 750nm using the optical spectrophotometer (Systronic, Model 119, U.S.A.). 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 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 the Chapter 3.

4.3 Results

To study the effect of oxalic acid catalyst concentration, A, the alcogels were prepared by keeping the molar ratio of TEOS: MeOH: H₂O constant at 1:33:5.7, respectively, and the base catalyst NH₄OH (1M) was added to the sol after T = 24h. The A value was varied from 0.0005M to 0.1M. Table 4.1 shows that with an increase in A value from 0.001M to 0.1M, the gelation time decreased from 2 h to 15 min. However, for the A value less than 0.001M, 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 to 0.001M. The thermal conductivity of the aerogels decreased from 0.057 to 0.04 W/mK, with the decrease in A value from 0.1 to 0.001M, as shown in Fig. 4.2. Monolithic and transparent (~88\%) aerogels, with minimal volume shrinkage (~15\%) and bulk density (0.05 g/cm\(^3\)), were obtained for the A = 0.001M 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 to 0.055 g/cm\(^3\) and 37 to 15\%, respectively, as the S value increased from 11 to 33, (Fig. 4.3 and Table 4.2). The optical transmission was found to be nearly the same (~92\%) for all the aerogels. 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 4.2. 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 (1M, NH$_4$OH) addition to the acid catalyzed sol has also been studied from 0 to 48h. The gelation time decreased from 18 days to 5 min with an increase in T value from 10 to 48h. For T values below 10 h, the alcosols do not form the gels. All the aerogels prepared with T values in between 10 h and 48h, 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 24h. Therefore, this value of T = 24h was kept constant for all the further experiments.

The NH$_4$OH catalyst concentration, B, was varied from 0.6 to 1.8M. It has been observed that all the aerogels prepared using the B values in between 0.6 to 1.8M were highly transparent (~93%). The gelation time decreased from 3 h to 20 min with an increase in the B value from 0.6 to 1.8M. However, in the absence of NH$_4$OH 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 1M, beyond which it increased with a further increase in the B value (> 1M), as shown in Fig. 4.5. Keeping in view the low density and minimum volume shrinkage, the B value was fixed at 1M.

The molar ratios of acidic H$_2$O ($W_1$) and basic H$_2$O ($W_2$) were varied from 2.2 to 8.7 and 0 to 4.4, respectively. The gelation time decreased from 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 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.

### 4.4 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 [2]. However, for the A value less than 0.001M, 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. 4.1). This would lead to differential drying stresses resulting in higher volume shrinkage and hence higher density [3], (Table 4.1). The higher A value (0.1M) resulted in more compact (shrunk) aerogel network (Fig. 4.1 (a)) compared to that of A = 0.001M (Fig. 4.1 (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 [4]. Micro-heterogeneity, (e.g. pore size distribution), has been observed in the TEM micrographs e.g. Fig 4.1 (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.

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 [5]. In the present studies, the TEOS precursor was hydrolyzed in
the methanol solvent, which contains smaller chain alkyl groups (i.e. -CH₃) resulting in transesterification, as per the following chemical reaction:

\[ \text{Si(OC}_2\text{H}_5\text{)_4 + CH}_3\text{OH} \leftrightarrow \text{Si(OC}_2\text{H}_5\text{)_3 OCH}_3 + \text{C}_2\text{H}_5\text{OH} \] 

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 alkoxy silane [6]. 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 alkoxy silane. 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. [7]. 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 [8]. Figs. 4.4 (a) and 4.1 (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 4.2).

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$_4$OH 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 1M, but it increased with a further increase in $B$ values (> 1M) as shown in Fig. 4.5. As the $B$ value increases up to 1M, 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. 4.6, which in turn decreases the bulk density of the aerogels for the B values up to 1M. Figures 5(b) and 2(a) show the transmission electron micrographs for two different B values, 0.6 and 1M, respectively. The aerogel network for B = 0.6 is denser than for B = 1M. However, for the B values > 1M, the rate of condensation becomes so fast that sudden gelation occurs, leading to smaller particle sizes. 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.

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 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 [9]. Also the excess amount of the water in the sol resulted in the sub-critical drying of the alcogels and hence increase in the volume shrinkage and bulk density.

Fig. 4.7 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 4.3). 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.

4.5 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/cm³), higher optical transmission (~ 93%) and monolithicity, than those obtained using the ethanol solvent. The bulk density and volume shrinkage decreased from 0.087 to 0.05 g/cm³ and 40 to 15%, respectively with decrease in oxalic acid concentration from 0.1M to 0.001 M. The bulk density and volume shrinkage of the aerogels decreased from 0.146 to 0.05g/cm³ 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 hrs.
The best quality silica aerogels in terms of high optical transmission (~93%), low density (0.055 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.
References


Table 4.1: Effect of the oxalic acid concentration on the physical properties of the TEOS based aerogels

<table>
<thead>
<tr>
<th>Oxalic acid concentration (M)</th>
<th>Gelation time (min)</th>
<th>Bulk Density (g/cm³)</th>
<th>% Volume shrinkage</th>
<th>Porosity (%)</th>
<th>% Optical Transmittance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>No Gelation</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.001</td>
<td>120</td>
<td>0.055</td>
<td>15</td>
<td>97.08</td>
<td>89</td>
</tr>
<tr>
<td>0.01</td>
<td>30</td>
<td>0.079</td>
<td>33</td>
<td>95.83</td>
<td>88</td>
</tr>
<tr>
<td>0.1</td>
<td>15</td>
<td>0.087</td>
<td>40</td>
<td>95.41</td>
<td>69</td>
</tr>
</tbody>
</table>

Table 4.2: Variation of the physical properties of TEOS based aerogels as a function of MeOH/TEOS molar ratio.

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

Table 4.3: Comparison of the physical properties of the TEOS based aerogels prepared by single step and two step sol-gel process

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Single step sol-gel process</th>
<th>Two step sol-gel process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical transmission</td>
<td>60%</td>
<td>93%</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.21 g/cm³</td>
<td>0.05 g/cm³</td>
</tr>
<tr>
<td>Volume shrinkage</td>
<td>30%</td>
<td>10%</td>
</tr>
</tbody>
</table>
Fig. 4.1 Transmission electron micrographs of TEOS based aerogels prepared with: (a) $A = 0.001 \text{M}, B = 1\text{M and } S = 33$; (b) $A = 0.1\text{M, } B = 1\text{M and } S = 33$
Fig. 4.2 Variation of thermal conductivity of the aerogels as a function of oxalic acid catalyst concentration.
Fig. 4.3 Effect of MeOH/TEOS molar ratio (S) on the bulk density of TEOS based aerogels.
Fig. 4.4 Transmission electron micrographs of TEOS based aerogels prepared with: A = 0.001M, B = 1M and S = 11; (b) A = 0.001M, B = 0.6M and S = 33
Fig. 4.5 Bulk density of the TEOS based aerogels as a function of NH$_4$OH catalyst concentration.
Fig. 4.6 Effect of base catalyst (NH₄OH) concentration on the volume shrinkage of the TEOS based aerogels.
Fig. 4.7 Photograph showing (a) single-step, i.e. acid catalyzed, and (b) two-step, i.e. acid-base catalyzed, TEOS based aerogels.