Chapter - 8
CHAPTER 8
Synthesis of flexible and hydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor

8.1 Introduction

Despite having several fascinating properties, the aerogels have major drawbacks that they are fragile, brittle and moisture sensitive, which limits their applications in various fields [1]. Due to the fragility and the brittleness, aerogels easily break with the application of small stress. Therefore, the present chapter describes the synthesis of flexible and hydrophobic silica aerogels using methyltrimethoxysilane precursor by two step acid-base sol-gel process. These aerogels consist of cross-linked network of silica polymer chains extended in three dimensions as can be seen from the Fig. 8.1. Due to the presence of non-polar alkyl groups (i.e. methyl) in the silica polymer chains, the inter chain cohesion is minimized resulting in the elastic and flexible three-dimensional network. Also the higher dilution of the MTMS precursor with methanol solvent yielded silica network with low degree of polymerization which exhibits flexibility. Whereas, for lower dilution of the MTMS precursor, an extensive polymerization results in dense and rigid structures. Because of this new property, i.e. flexibility in the aerogel, it can be bent to any shape and acts as a good shock absorber as well.
8.2 Experimental Procedures

8.2.1 Sample preparation

A traditional two-step (acid-base) catalyzed sol-gel process was used to prepare the silica alcosols and alcogels, as described Chapter 3. The chemicals used were MTMS (purum grade from Fluka Company, Switzerland), methanol and oxalic acid (ExcemAR and SQ grades respectively, from Qualigens company, India). The alcosols were stirred for about 15 min and then transferred to the test tubes of $1.5 \times 10^{-2}$ m outer diameter and $15.0 \times 10^{-2}$ m height. Gelation occurred at room temperature (300 K). After the gelation, the alcogels were aged for two days and dried supercritically in an autoclave.

8.2.2 Elastic property measurements

The elastic constant called Young's modulus (Y) or modulus of elasticity, is a measure of the hardness, stiffness, rigidity (or softness, flexibility, or pliability) of the solid. It is also defined as the resistance to any deformation in the solids. It means that lesser the value of Y, more flexible is the solid. The Young's modulus (Y) of the aerogels was determined by an uniaxial compression test as shown in the Fig. 8.2. In this test, various loads (e.g. 0.01 kg, 0.02 kg, 0.03 kg etc.) were applied on the cylindrical aerogel sample and the corresponding change in length (l) was measured using travelling microscope. The graphs of change in length against the mass applied were plotted and the slopes ($l / m$) of these graphs were used to calculate the Young's modulus of the aerogels by using the formula:

$$\text{Young's modulus (Y)} = \frac{mgL}{\pi r^2 l} = \frac{(Lg/\pi r^2)}{\text{slope}} \quad \text{...... (8.1)}$$
3.3. Results and Discussion

8.3.1 Effect of MeOH/MTMS molar ratio (S)

The effect of MeOH/MTMS molar ratio (S) on the elastic and other physical properties of the silica aerogels was studied by keeping the molar ratio of H₂O/MTMS constant at 8. The oxalic acid (C₂H₂O₄) and ammonium hydroxide (NH₄OH) catalyst concentrations were kept constant at 0.001 M and 10 M, respectively. It has been observed that the gelation time increased from 2 to 16 hrs with increase in S value from 14 to 35. This is due to the fact that the increase in the S value increases the separation between the reacting silica species in the sol, which takes more time for the gelation [2]. All the aerogel samples were opaque.

The Young's modulii (Y) of the silica aerogels scale with the bulk density [3]. It has been observed that with increase in S value from 14 to 35, the volume shrinkage and hence the density of the aerogels decreased from 28 to 7% and from 100 to 40 kg/m³, respectively. Fig. 8.3 shows the graphs of change in length against the mass applied for the calculation of Y. The Y was found to decrease from 14.11 x 10⁴ to 3.0 x 10⁴ N/m² resulting in increase in the flexibility the aerogels. The Figs. 8.4 (a) and (b) show the maximum possible bending of the silica aerogels (further bending resulted in breaking of the aerogel samples) prepared at two different S values of 28 and 35, respectively. It is clearly seen from the Fig. 8.4 that the aerogel with S = 35 can be bent to greater extent than that of S = 28. Figs. 8.5 (a) and (b) show the transmission electron micrographs of the aerogel samples prepared at two different S values of 14 and 35,
respectively. Since the silica chains of the aerogel with $S = 35$ are quite separated from each other and large empty spaces are available in the network, it can undergo deformation when the stress is applied. However, if the $S$ value is decreased, i.e. for $S = 14$, the degree of polymerization increased and extensive cross-linking in three dimension resulted in the rigid structure.

Keeping in view, the low Young's modulus, low density, less volume shrinkage, the MeOH/MTMS molar ratio was optimized at 35.

8.3.2 Influence of acid and base catalyst concentrations

Generally, the gelation time increases with increase in the solvent and hydrophobic reagent content (MTMS, in the present studies) in the sol [4,5]. This problem of longer gelation time was overcome by using two step acid-base sol-gel process. The effect of oxalic acid concentration ($A$) on the physical and elastic properties of the silica aerogels was studied by varying it from 0.0005 to 0.1M. The $\text{NH}_4\text{OH}$ catalyst concentration was kept constant at 10M. It was observed that the gelation time decreased from 16 to 8 hrs with increase in $A$ value from 0.0005 to 0.1M. This is due to the fact that the increase in $A$ value increases the rate of hydrolysis reaction resulting in the faster gelation [6].

The elastic property measurements revealed that the Young's modulus ($Y$) of the silica aerogels decreased from $6.2 \times 10^4$ to $3.4 \times 10^4$ N/m$^2$ with an increase in $A$ value from 0.0005 to 0.01M. As described in the earlier section, the graphs of change in length against the mass applied were plotted (Fig. 8.6) to determine the Young's modulii of the aerogels using equation (4). The decrease in the $Y$ can be explained by taking in to consideration the microstructure of the aerogels.
Figs. 8.7 (a) and (b) show the transmission electron micrographs of the aerogel samples prepared at two different A values of 0.0005 and 0.01M, respectively. It is clearly seen from the fig. 8.7 that the silica network consists big particles (~100nm) for A = 0.0005M whereas for A = 0.01M, the network consists of silica chains with large pores (~100nm). Moreover, the bulk density was also found to decrease from 61 to 42 kg/m³ with increase in the A value from 0.0005 to 0.01M. Therefore, the Young's modulus (Y) decreased with the increase in oxalic acid concentration (A). Fig. 8.8 shows three states of the flexible aerogel sample (prepared with A = 0.01M): a) without stress b) with stress and c) after releasing the applied stress, the aerogel sample regains its original dimensions.

Keeping in view, the low Young's modulus, low density, less volume shrinkage, the A value was optimized at 0.01M.

The effect of base catalyst concentration (B) on the physical properties of the silica aerogels has also been studied by varying it from 6 to 13.3 M. It was observed that for B < 10 M, the gel could not be obtained because of sedimentation due to insufficient base catalyst for the complete condensation. For the B > 10 M, the volume shrinkage and hence the bulk density of the aerogels increased from 20 to 30% and from 45 to 63 kg/m³, respectively. The volume shrinkage and the bulk density were found to be optimum at B = 10M.

8.3.3 Hydrophobicity and thermal stability of the aerogels

The precursor i.e. MTMS, used in the present studies, contains one hydrolytically stable methyl group, which is responsible for the hydrophobicity in the silica aerogels [7]. The hydrophobicity was characterized by measuring the
contact angles (θ) of the water droplet placed on the aerogel surface under investigation. The contact angle (θ) measurements revealed that all the aerogels are hydrophobic with θ values ranging from 138 to 146°.

The alkyl groups (e.g. methyl in the present studies) responsible for the hydrophobicity are thermally stable up to a threshold temperature. Above this temperature they get detached from the surface making it hydrophilic. This threshold temperature for the methyl groups was investigated by heating the aerogels up to temperature of 773K and testing them with water. It has been observed that the MTMS based aerogels are thermally stable up to a temperature of 753 K, above which the aerogels absorb water.

8.4. Conclusions

Highly flexible and hydrophobic silica aerogels could be obtained using methyltrimethoxysilane (MTMS) precursor by two step acid-base sol-gel process for the molar ratio of MTMS:MeOH:H₂O at 1:35:8, respectively. The Young's modulus of the aerogel strongly depends on the bulk density. Very high dilution of the MTMS precursor in the methanol solvent (ten times) and the presence of non-polar methyl groups in the silica polymer chains resulted in the flexible silica aerogels. The MTMS based aerogels are hydrophobic with water contact angle as high as 146°. The hydrophobic aerogels were found to be thermally stable up to a temperature of 753 K.
References:


Fig. 8.1: Transmission electron micrograph of silica aerogel showing three-dimensional cross-linked network of silica chains.
Fig. 8.2: Schematic diagram of the experimental set-up for the Young's modulus measurements of the silica aerogels.
Fig. 8.3: Plots of change in length against mass applied for the silica aerogels prepared with various MeOH/MTMS molar ratios.
Fig. 8.4: Flexible silica aerogels prepared at two different MeOH/MTMS molar ratios: (a) $S = 28$ and (b) $S = 35$. 
Fig. 8.5: Transmission electron micrographs of MTMS based aerogels prepared with: (a) $S = 14$ and (b) $S = 35$. 
Fig. 8.6: Plots of change in length against mass applied for the silica aerogels as a function of oxalic acid concentration (A).
Fig. 8.7: Transmission electron micrographs of MTMS based aerogels prepared with: (a) $A = 0.0005\text{M}$ and (b) $A = 0.01\text{M}$. 
Fig. 8.8: A photograph showing the three states of the flexible aerogel sample: a) Without stress b) With stress c) After releasing the applied stress.