Comparative studies of the physical and hydrophobic properties of TEOS based silica aerogels using different co-precursors

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Abstract

In the present paper, the experimental results on the physical and hydrophobic properties of tetraethoxysilane (TEOS) based silica aerogels using six different organosilane co-precursors (C.P) of the type R\textsubscript{n}SiX\textsubscript{4-n} as synthesis components, are reported and discussed. The aerogels have been produced by sol-gel processing followed by supercritical drying using methanol solvent extraction. The molar ratio of TEOS, ethanol (EtOH), water (0.001M oxalic acid (H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}) catalyst) was kept constant at 1:5:7, respectively, and the molar ratio of C.P/TEOS (A) was varied from 0.1 to 0.6 and compared the aerogel properties. The hydrophobicity of the aerogels has been tested by the contact angle measurements. The contact angle ($\theta$) has been found to be the highest ($\theta = 136^\circ$) for the trimethylethoxysilane (TMES) co-precursor, while for the other co-precursors it is in between 120$^\circ$ and 130$^\circ$. The surface chemical modification of the hydrophobic aerogels has been studied using Fourier Transform Infrared Spectroscopy (FTIR). As the C.P/TEOS molar ratio increased, the intensity of the C–H and Si–C peaks in the FTIR spectra increased, clearly indicating the organic modification of the aerogels. The aerogels based on mono-alkyl (CH\textsubscript{3}) trialkoxysilane co-precursor have shown higher optical transmission ($< 65\%$) compared to the phenyl, di or tri alkyl alkoxysilanes (5–50%). The trialkyl modified aerogels showed the lowest bulk density (118.3 kg/m\textsuperscript{3}) and volume shrinkage ($< 2\%$). The alkyl alkoxy/chloro–silane modified aerogels have been found to be thermally stable up to a maximum temperature of 573 K, whereas the phenyl trialkoxysilane modified aerogels are stable up to a temperature as high as 823 K. The aerogels have been characterized by scanning electron microscopy, thermogravimetric and differential thermal analyses.

Keywords: A. Composites; B. Sol-gel chemistry; C. Infrared spectroscopy; D. Optical properties; E. Thermal conductivity

1. Introduction

Silica aerogels are unique materials with high porosity (% of porosity up to 99%) and optical transmission (for 0.01 m thickness at 700 nm, it is $\approx 90\%$) in the visible region [1,2]. They have very low density ($< 30$ kg/m\textsuperscript{3}), low thermal conductivity ($< 0.05$ W/mK) and surface area as high as $10^6$ m\textsuperscript{2}/kg [3,4]. Due to this unusual combination of properties in the same material, aerogels find several industrial applications such as Cerenkov radiation detectors in high-energy physics, containers for liquid rocket propellants and perfumes, windows for thermal and acoustic insulating systems and automobile exhaust catalytic supports [5–7]. However, the aerogels get deteriorated with time due to the absorption of moisture from the surroundings by the hydrophilic $=$ Si–OH (or Si–OCH\textsubscript{3}) groups present on the surface. Therefore, the surface H (or CH\textsubscript{3}) groups have to be replaced by the hydrolytically stable organosilane groups (Si-alkyl or Si-aryl), thus hydrophobicizing the aerogel surface. Hence, for long-term applications, the aerogels need to have water repellent (i.e. hydrophobic) property [8]. Several co-precursors can be used for this purpose [9]. Even though there are some reports on the tetramethoxysilane (TMOS) based hydrophobic aerogels [10] but the TMOS is highly toxic and it is very expensive. Therefore, in the present studies we have used the tetraethoxysilane (TEOS) precursor to make hydrophobic silica aerogels because TEOS is non-toxic and the cost is at least four times lower compared to the TMOS precursor. We have used various organosilane co-precursors of the type R\textsubscript{n}SiX\textsubscript{4-n} having one to three functional groups. Here, we report and discuss the results on the surface chemical modification and physical properties of silica aerogels using different co-precursors (C.P). The aerogels have been...
characterized by scanning electron microscopy (SEM), contact angle measurements, Fourier transform infrared spectroscopy (FTIR), and thermogravimetric (TG) and differential thermal analyses (DTA).

2. Experimental

2.1. Sample preparation

1 Silica alcosols and gels were prepared by hydrolysis and polycondensation of ethanol (EtOH) diluted tetraethoxysilane (TEOS) in the presence of an oxalic acid [(COOH)\textsubscript{2}] catalyst by keeping the molar ratio of TEOS: EtOH: H\textsubscript{2}O(0.001M (COOH)\textsubscript{2}) constant at 1:5:7 respectively. In order to compare the physical and hydrophobic properties of the aerogels, the co-precursor C.P./TEOS molar ratio (A) was varied from 0.1 to 0.6. In the present work, six different organosilane compounds were used as the co-precursors and they are: methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES), dimethylchlorosilane (DMCS), trimethylmethoxysilane (TMES), ethyltriethoxysilane (ETES) and phenyltriethoxysilane (PTES). All the chemicals used were of ‘purum’ grade from Fluka Company, Switzerland. Double distilled water was used for the preparation of 0.001 M oxalic acid solution. After stirring for about 15 min, the resulting homogeneous sol was transferred to the test tubes of 15 mm outer diameter and 150 mm height and subjected to gelation. The gelation time is the duration after the preparation of sol, in which it seizes to move even when the test tube is tilted or inverted [11].

After gelation, the alcogels were aged in ethanol for 24 h and then dried supercritically separately for each C.P. in order to avoid the influence of pore fluid of one gel on the other. Further details of the drying procedures can be found from our earlier publication [10].

3. Methods of characterization

The bulk density of the aerogel sample was calculated by measuring its mass to volume ratio. The porosity of the aerogels was calculated using the formula:

\[
\text{Porosity} = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100
\]

where \(\rho_b\) is the bulk density and \(\rho_s\) is the skeleton density of the silica aerogels which was measured using helium pycnometer and its value was found to be 1900 kg/m\(^3\). The volume shrinkage of the samples was calculated by measuring the difference between the volumes of the alcogel and the aerogel. The contact angle (\(\theta\)) of the aerogel samples was measured by putting a water droplet on the aerogel surface and by finding the base length \(w\) and height \(h\) of the droplet using a travelling microscope. Also, the water droplet on aerogel surface was photographed and \(\theta\) was calculated from the enlargement directly. In both the cases, \(\theta\) has been determined using the following formula [12]:

\[
\tan\left(\frac{\theta}{2}\right) = \frac{2h}{w}
\]

(2)

Good agreement has been observed by both the methods in the measurement of \(\theta\). The thermal stability of the aerogels was studied by TG and DTA using SDT 2960 TA universal instruments, USA. Here, the term thermal stability refers to the temperature up to which the aerogel retains its hydrophobic property. The thermal conductivity and the specific heat of hydrophobic aerogels was measured with C-T meter (Teleph, France) using a ring probe, a flexible printed circuit (thickness 0.2 mm, dimension 60 \(\times\) 90 mm) put in between two plane pieces of the aerogel samples under measurements. By giving a certain heating power (0.09 W) to the sample, the probe transmits the heating power and thus measures the thermal conductivity of the aerogel samples. The surface chemical modification was confirmed using FTIR spectroscopy (Perkin Elmer instruments, spectrum one, made in USA). The microstructure of the aerogels was observed using scanning electron microscope (SEM) Phillips XL-30.

4. Results and discussion

The aerogels produced using alkyl and aryl alkoxy/chlorosilane co-precursors, belong to the family of organosiloxanes of the type R\textsubscript{n}SiO\textsubscript{4-n/2} (where R:alkyl or aryl group and \(n = 1 - 3\)). From the present studies, it has been found that the use of different co-precursors: MTMS, MTES, DMCS, TMES, ETES and PTES, strongly affect the physical as well as the hydrophobic properties of silica aerogels. In the case of PTES co-precursor, the substituent on the silicon atom is a phenyl group instead of an alkyl group. Table 1 shows some of the physical properties of silica aerogels prepared using

| Co-precursor (C.P) | Gelation Time (Tg) | Bulk density \(\rho_b\) (kg/m\(^3\)) | Porosity \(p\) (%) | Optical transmission \(T\) (%) | Volume Shrinkage \(u\) (%) | Thermal conductivity \(\lambda\) (W/mK) | Specific heat \(C_p\) (KJ/m\(^3\) K) |
|-------------------|-------------------|-------------------------------|-----------------|-----------------|-----------------|----------------|----------------|
| TMES              | 11 days           | 118.3                         | 94.36           | 5               | <2              | 0.060          | 271            |
| PTES              | 10.5 days         | 247.1                         | 87.26           | 25              | 35.49           | 0.102          | 227            |
| MTMS              | 5.5 days          | 198.8                         | 90.53           | 55              | 35.99           | 0.069          | 282            |
| MTE              | 9.5 days          | 202.2                         | 90.37           | 65              | 34.19           | 0.071          | 294            |
| ETES              | 14 days           | 245.2                         | 88.32           | 50              | 37.23           | 0.101          | 225            |
| DMCS              | 3 days            | 190.6                         | 90.92           | 40              | 44.31           | 0.068          | 279            |
For all the alkyl/aryl alkoxysilane co-precursors, with increase in the molar ratio of C.P./TEOS (A) the gelation time increases. This is due to the fact that the hydrolysis and condensation reactions are retarded as the A value increases because of the presence of less hydrolyzable organic groups (R/Si) on the silica clusters. In addition, for the DMCS co-precursor, the gelation time decreases with increase in the molar ratio of C.P./TEOS because chloride reacts with the surface OH groups and water yielding HCl, which makes the sol more acidic and hence decreases the gelation time.

In the case of the aerogels produced using TMES and MTEs co-precursors, it was found that the bulk density decreases with increase in the molar ratio of C.P./TEOS, which is due to the decrease in the silica and increase in the carbon contents of the aerogel. But for the aerogels prepared using PTES, MTMS, ETES and DMCS co-precursors, the bulk density increases with increase in the molar ratio (A) because of large volume shrinkage (Table 1). Further, in the case of DMCS, although the shrinkage is the highest (44%) but the density is not the highest which is due to the fact that the silica content is less compared to the other co-precursors (except the TMES). The shrinkage can also be due to the acidic nature of the DMCS based alcogels. It is known that the acid based aerogels are prone to more shrinkage [15]. It has been observed that the porosity of the aerogels decreased with increased bulk density as given in the Table 1. In general, it has been observed that lower the thermal conductivity, higher is the specific heat, as shown in Table 1. At the same time, the thermal conductivity is higher for the dense samples, which is in accordance with the observed trend.

### 4.2. Volume shrinkage and optical transmittance

The aerogels produced using TMES co-precursor were found to shrink less (volume shrinkage, vs, <2%) whereas, the volume shrinkage of the aerogels prepared using the other co-precursors, for MTEs it is ~34% and PTES, MTMS, ETES it is ~36% and for DMCS it is around 44%. The aerogels using TMES co-precursor are elastic because of the presence of more organic groups (the R/Si ratio is 3) [16]. Hence, the organic groups increase the elasticity and hence decrease the volume shrinkage of the aerogels. Similar results have been obtained for the polymethylsiloxanes/TEOS system by Kramer et al. [17]. In the case of the other co-precursors (MTS, MTEs, PTES, ETES and DMCS) the organic groups are less (R/Si ratio is in between 1 and 2) leading to less elasticity and hence more shrinkage. The negligible volume shrinkage of the TMES modified aerogels can also be due to the spring back effect [18]. Further, the large number of non-hydrolyzable organic groups (R/Si = 3) present on the silica surface retard the condensation reactions causing very less shrinkage. At this point it would be interesting to note that the structural factors affecting the properties of the aerogels are: (i) the type of organic radicals (R) and (ii) the R/Si ratio. The R/Si ratio and the SiO2 content, in the aerogels, can be given by a general chemical reaction as:

\[
R_nSiX_4 + n\text{H}_2\text{O} \rightarrow R_nSi(OH)_{4-n} + n\text{H}_2\text{O} + nSiO_2 (4) \]

where R = alkyl or aryl, X = alkoxy or chloro and n = 1 – 3. Hence, for n = 1 – 3, the R/Si ratio is 1 to 3, corresponding to the silica contents of SiO1.5, SiO1.6, and SiO2, respectively. The weight loss of the phenyl-modified aerogels (30%) is much greater than the alkyl modified aerogels (9%)(Table 2). Similar results have been obtained by Baney et al. [19] for phenyl and methyl silsesquioxanes, although theirs are not aerogels but the chemical compositions are the same.

The optical transmittance of the aerogels in the visible region at 750 nm was found to decrease with an increase in the molar ratio of C.P./TEOS (from 0.1 to 0.6) for the TMES, PTES, MTEs and ETES co-precursors, from 40 to 5% which is due to larger pore and particle sizes. While for the MTEs modified aerogels, the optical transmission decreases from 50 to 10% and for DTMS it decreases from 65 to 35% for same molar ratios as above. Out of all the co-precursors except for MTES has been found to give the highest optical

| Co-precursors | Contact angle, θ (°) | Temperature, T (K) | % weight loss at 1073 K for 2 h |
|---------------|---------------------|-------------------|-----------------|
| TMES          | 136                 | 560               | 8               |
| PTES          | 129                 | 823               | 30              |
| MTMS          | 130                 | 554               | 10              |
| MTEs          | 129                 | 548               | 9               |
| ETES          | 128                 | 558               | 18              |
| DMCS          | 130                 | 663               | 10              |

Table 2 Contact angles (θ), temperatures (T) up to which the hydrophobicity is maintained, and the percentage weight loss of the aerogels produced using different co-precursors with the molar ratio of C.P./TEOS = 0.5

The aerogels are: (i) the type of organic radicals (R) and (ii) the R/Si ratio. The R/Si ratio and the SiO2 content, in the aerogels, can be given by a general chemical reaction as:

\[
R_nSiX_4 \rightarrow R_nSi(OH)_{4-n} + n\text{H}_2\text{O} + nSiO_2 \]

where R = alkyl or aryl, X = alkoxy or chloro and n = 1 – 3. Hence, for n = 1 – 3, the R/Si ratio is 1 to 3, corresponding to the silica contents of SiO1.5, SiO1.6, and SiO2, respectively. The weight loss of the phenyl-modified aerogels (30%) is much greater than the alkyl modified aerogels (9%).
transmission of 65% for the MTES/TEOS molar ratio of 0.3 (Table 2). From these observations it is clear that the co-precursor with less number and smaller size alkyl groups with ethoxysilane (MTES) resulted in the highest optical transmission. This is due to the fact that the steric hindrance is less for the methyl groups and the SiO2 network forms with the ethoxy groups rather than the methoxy groups, (since the main precursor is TEOS), in the case of the acid catalysed sol-gel process. Hence, the co-precursors (for example TMES) with larger size and/or number of alkyl groups would lead to a lower optical transmission. Moreover, the steric hindrance would lead to a loosely packed network, which shrinks, and hence results in dense aerogels upon supercritical drying. The SEM observations shown in Fig. 1(a) and (b) indicate that the MTES modified aerogels have uniform particle and pore sizes, whereas the PTES modified aerogels show particles of non-uniform sizes. Therefore, the MTES co-precursor based aerogels are more transparent than the other co-precursor based aerogels (Table 2). In the case of the DMCS modified aerogels, the higher acidity of the alcogels resulted in faster gelation leading to cracks and scattering of light. Therefore, the optical transmission of the DMCS based aerogels is low.

4.3. Hydrophobicity of the aerogels

The hydrophobic aerogels have been obtained by the co-precursor method pioneered by Schwertfeger et al. [20], which is simple and less time consuming. It has been found that the hydrolysis and condensation rates of all the co-precursors are slower than that of TEOS because the former contains one or more non-reactive alkyl/aryl groups, which are non-hydrolyzable. However, the formation of a three dimensional solid network is achieved by the hydrolysis and polycondensation of TEOS as per the following chemical reaction:

\[ n\text{Si(OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \xrightarrow{\text{EtOH, Oxalic acid}} \text{SiO}_2 + 4n\text{C}_2\text{H}_5\text{OH} \]  

When sufficient amount of TEOS gets hydrolyzed, the silyl groups of the co-precursors get attached to the silica clusters as per the chemical reactions shown below (for different co-precursors):

(1) MTMS:

\[ \text{Si-OH} + (\text{OCH}_3)_3\text{Si-CH}_3 \rightarrow \text{Si-O-Si-CH}_3 + 3\text{CH}_3\text{OH} \]  

(2) DMCS:

\[ \text{Si-OH} + \text{Cl-Si-CH}_3 \rightarrow \text{Si-O-Si-CH}_3 + \text{HCl} \]  

(3) PTES:

\[ \text{O-Si-OH} + (\text{C}_2\text{H}_4\text{O})_3\text{Si-Ph} \rightarrow \text{O-Si-O-Si-Ph} + 3\text{C}_2\text{H}_4\text{OH} \]  

In a similar way, the chemical reactions for the other co-precursors can be presented. As the silica clusters are attached with non-hydrolyzable organic groups (silyl) on their surfaces, the aerogels become hydrophobic. More the numbers of alkyl/aryl groups get attached to the surface, more will be the hydrophobicity. The contact angle was found to be the highest for TMES modified aerogels (θ = 136°), while for all the other co-precursors the contact angle was found to be in between 120° and 130°as can be seen from Table 2 and Fig. 2 (a) and (b). It was also found that the increase in co-precursor content in the sol resulted in more hydrophobicity of the aerogels, giving higher contact angle, because of more number of \(=\text{Si-R} \) (R = CH3, C2H5, Phenyl) groups get attached to the silica clusters.

The FTIR spectra based on the DMCS and ETES aerogels shown in Fig. 3(a) and (b) indicate that apart from the Si–O–Si absorption band at 1100 and 800 cm\(^{-1}\) and O–H absorption bands observed around 1650 and
For the unmodified aerogel samples, there are additional absorption bands at 2900 and 1450, 840 and 1430 cm\(^{-1}\), corresponding to C–H, Si–C and Si-phenyl bonds respectively for the co-precursor modified aerogels [21,22]. It was observed that as the number of alkyl/phenyl groups in the organosilane co-precursor increases, the intensity of the absorption bands due to Si–C and C–H bonds increases indicating a better surface chemical modification, which was also confirmed from the contact angle measurements.

### 4.4. Thermal stability of the hydrophobic aerogels

Figs 4(a) and (b) show the TG-DT analyses of some of the aerogel samples. In the case of hydrophilic silica aerogels, the increase in weight loss is rapid from around 50–100 °C due to evaporation of trapped H\(_2\)O and alcoholic groups, produced from the condensation reactions of Si–OH and Si(OC\(_2\)H\(_5\)) groups [23], whereas for hydrophobic aerogels the percentage of weight loss is negligible up to the temperature of thermal stability. For example, an exothermic peak is produced at around 573 K, for MTES co-precursor based aerogels (Fig. 4(b)) which corresponds to oxidation of the surface alkyl groups [24]. It was found that the PTES modified aerogels are thermally stable up to a temperature as high as 823 K (Fig. 4(a)), whereas all the other co-precursor based aerogels are thermally stable in the temperature range of 548–663 K and above which they become hydrophilic. The co-precursor modified aerogels were heat treated at 1073 K for 2 h and the percentage weight loss was measured (Table 2). It has been found that the phenyl modified aerogels undergone the highest weightloss of \(\approx 30\%\), whereas MTMS, MTES, TMES, DMCS based aerogels had a weightloss of around 10% and for ETES it is \(\approx 18\%\). The initial decomposition temperature of the methyl-based aerogels is 543 K in the oxygen atmosphere, which is lower than that of the phenyl based aerogels (823 K). These results are in general agreement with those reported for methyl and phenyl silsesquioxanes by Baney et al. [19]. However, these authors reported 50% weight loss for the phenyl-based silsesquioxanes.

## 5. Conclusions

Monolithic and hydrophobic silica aerogels were produced using different co-precursors by the sol-gel process.
followed by supercritical drying. Monolithic and transparent aerogels were obtained for MTES and MTMS co-precursors, whereas the PTES, TMES, ETES co-precursors resulted in monolithic but opaque aerogels. The DMCS co-precursor gave opaque and cracked aerogels. It was observed that the contact angle increases with increase in the number of alkyl or aryl groups covering the aerogel surface. For the TMES co-precursor, the contact angle was found to be the highest \( \theta = 136^\circ \) and the volume shrinkage is the lowest (Vs < 2%). For a constant C.P./TEOS molar ratio, the optical transmittance of the aerogels (at \( \lambda = 750 \text{ nm} \) for 1 cm thick sample) varied from 5 to 65% for different co-precursors. Co-precursors with smaller size and less number of alkyl groups in combination with ethoxy groups such as MTES have been found to give rise to the hydrophobic aerogels (\( \theta = 129^\circ \)) with the highest optical transmission of (65%). The thermal stability for all the modified aerogels has been found to be in the range of 548–573 K and the PTES modified aerogels are thermally stable up to a temperature of 823 K, which is the highest value ever reported. The FTIR investigations clearly indicated that the surface chemical modification of the aerogels is due to the organic groups (alkyl or aryl), that are attached to the silica clusters through the oxygen bonds. The weight loss of the phenyl modified aerogels, at a temperature of 1073 K for 2 h, was found to be the highest (\( \approx 30\% \)) and whereas for the methyl modified aerogels it is the lowest (\( \approx 9\% \)). The ETES modified aerogels have the weight loss of around 18%. The TMES based aerogels can be used for superior moisture resistant and water repellency applications. On the other hand, the phenyl based aerogels can be used for hydrophobic and higher thermal stability (823 K) applications. Wherever, hydrophobic and optical transmission properties are required up to medium temperatures (\( \approx 523 \text{ K} \)), the MTES or MTMS co-precursor based aerogels can be preferred.

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