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Hydrophobicity and physical properties of TEOS based silica aerogels using phenyltriethoxysilane as a synthesis component

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The experimental results on the hydrophobic and physical properties of tetraethoxysilane (TEOS) based silica aerogels by incorporating phenyltriethoxysilane (PTES) as a synthesis component, are reported. The molar ratio of tetraethoxysilane (TEOS), ethanol (EtOH), water (0.001 M oxalic acid catalyst) was kept constant at 1:5:7 respectively while the molar ratio of PTES/TEOS (*M*) was varied from 0 to 0.7. After gelation, the alcogels were dried supercritically by the high temperature solvent extraction. For lower *M* values (<0.1), transparent and monolithic aerogels but for higher *M* values (>0.5) opaque and cracked aerogels were obtained. For *M* values in between 0.1 and 0.5, monolithic aerogels with decreasing optical transmission have been obtained. The hydrophobicity of the aerogels was tested by measuring the percentage of water uptake by the aerogels when exposed to 95% humidity at 40°C for 24 h and also by measuring the contact angle. The contact angle varied from 120 to 130° for *M* values from 0.1 to 0.5, respectively. It was found that as the *M* value increased, the hydrophobicity of the aerogels increased but the optical transmission decreased from 60% to 5% in the visible range. The thermal conductivity and the specific heat of the aerogels found to decrease with the increase in *M* values. In order to determine the thermal stability in terms of retention of hydrophobicity of the aerogels, they were heat treated in air in the temperature range of 25–600°C. The hydrophobic aerogels are thermally stable upto a temperature of 520°C, which is the highest value ever reported, and above this temperature the aerogels become hydrophilic. The chemical bonds, responsible for the hydrophobic nature of the aerogels, have been identified by Fourier transform infrared spectroscopy (FTIR). The aerogels have been characterized by density, optical transmission, scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). © *2003 Kluwer Academic Publishers*

1. Introduction

Silica aerogels are extremely porous ($>95\%$) [1] materials that are normally prepared by supercritical drying of silica alcogels. Because of high porosity and nanostructured nature, they have interesting physical properties such as a small refractive index (1.01 to 1.1) [2], low density (<5 kg/m^3), low thermal conductivity (<0.05 W/mk) [3, 4] and high visible transparency ($>90\%$ optical transmission at 750 nm for 1 cm sample thickness) [5]. Therefore, the aerogels have several technological applications including Cerenkov radiation detectors, thermal superinsulators in windows and heat storage systems, gas filters, catalyst supports etc. [6–8]. However, the aerogels are hydrophilic and become wet with atmospheric moisture and water, and hence they get deteriorated with time. Hydrophobicity [9] is one of the most important requirements for the long-term use of the aerogels for various applications. The hydrophilicity of the as produced silica aerogels is due to the presence of a large number of Si—OH groups on the surface of silica clusters. The attachment of hydrolytically stable ≡Si—R (R = CH_3,C_2H_5

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etc.) groups to the silica clusters results in hydrophobic aerogels that will be unaffected by moisture. In the present work, we report and discuss the results on the effect of phenyltriethoxysilane (PTES) as a coprecursor on the hydrophobicity and physical properties of silica aerogels. The aerogels have been characterized by Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA) and thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and contact angle measurements.

2. Experimental

2.1. Sample preparation

Silica alcogels were prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS) diluted in ethanol (EtOH) in the presence of an oxalic acid catalyst and phenyltriethoxysilane (PTES) as a coprecursor. The chemicals used were of "purum" grade from Fluka Company, Switzerland. The TEOS was diluted with its respective parent alcohol EtOH to avoid transesterification [10]. Double distilled water was used for the preparation of dilute oxalic acid. The molar ratio of TEOS:EtOH:H_2O (oxalic acid) was kept constant at 1:5:7 (0.001 M oxalic acid) respectively and the molar ratio of PTES/TEOS (M) was varied from 0 to 0.7. The homogeneous alcosols thus obtained, after stirring for about 15 min, were transferred to airtight Borosil glass test tubes of 18 mm outer diameter and 150 mm height and subjected to gelation. The gelation took place at an ambient temperature of 23–29°C. The gelation time varied from 2.5 to 27 days depending on the PTES/TEOS molar ratio, as shown in Table I. After gelation, the alcogels were aged in ethanol for 24 h and then dried supercritically ($T_c \approx 243°\text{C}$ and $P_c \approx 63$ bars for ethanol) in an autoclave to obtain the hydrophobic aerogels. The maximum temperature (265°C) and the resulting pressure ($\approx$100 bars) were obtained in 5 h using a PID temperature controller.

2.2. Methods of characterization

In order to study the influence of PTES/TEOS molar ratio (M) on hydrophobicity and physical properties of the aerogels, the samples were characterized by density, volume shrinkage, Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques. The bulk density of the aerogel samples was calculated from their weights (measured by a microbalance 10^{-5} gm accuracy) and known volumes. The refractive index (RI) of the aerogels was calculated using the formula [11].

$$n = 1 + 0.19\,\rho \qquad (1)$$

where n is refractive index and ρ is the bulk density of the aerogel. The percentage of the volume shrinkage (V_s) was determined from the change in the volume of the alcogel to the aerogel. An apparent co-ordination number can give the packing of the particles. Meisener *et al.* [12] derived the co-ordination number by the formula

$$N = 2\exp(2.4\,\phi) \qquad (2)$$

where ϕ is volume fraction of the solid part, N is the average co-ordination number and $(1-\phi)$ corresponds to the porosity. The hydrophobicity of the aerogels was studied by keeping the aerogel sample in 95% humidity at 40°C for 24 h and then by measuring the contact angle (θ) of a water droplet with the aerogel surface using the formula [13]

$$\theta = 2\tan^{-1}(2h/d) \qquad (3)$$

where h is the height of the water droplet and d is the width (i.e., base) of the droplet touching the aerogel surface. In addition, the water droplet on the aerogel was photographed and θ was measured from the enlargement directly. The thermal conductivity and specific heat of the hydrophobic aerogels, with various molar ratios of PTES/TEOS (M), were measured with the help of a thermal conductivity (C-T) meter (Teleph, France.) using the ring probe. The probe, a flexible printed circuit (thickness 0.2 mm- heating device diameter = 15 mm), is put in between two plane pieces of the aerogel under measurement. By giving certain heating power (0.09 W) to the sample, the probe transmits the heating power and gives the following measurements: (1) thermal conductivity (W/mk), and (2) specific heat (KJ/m^3). The DTA and TGA analyses, using SDT 2960 TA universal instruments made in USA, were used to interpret the thermal stability of the hydrophobic aerogels. In support of this data the aerogels were heated in "Therelek" furnace, India. The surface chemical modification and the amount of water adsorption by the aerogels was studied using FTIR spectroscopy (Perkin-Elmer instruments, Model: spectrum one, made in USA) which gave the information about the various chemical bonds such as O—H, Si—C, C—H and Si—O—Si.

TABLE I Some physical properties of silica aerogels

PTES/TEOS molar ratio (M)	Gelation time (T_g)	Volume shrinkage V_s(%)	Porosity (%)	Coordination number (N)	Specific heat (kJ/m^3K)	Thermal conductivity (W/mK)
0	2.5 days	30	91.16	2.3896	347	0.085
0.1	4 days	31.22	88.96	2.609	329	0.104
0.2	4.5 days	33.66	88.23	2.652	280	0.103
0.3	10.5 days	35.49	87.26	2.715	227	0.102
0.4	16 days	36.72	86.24	2.782	201	0.101
0.5	27 days	37.01	84.21	2.921	190	0.1

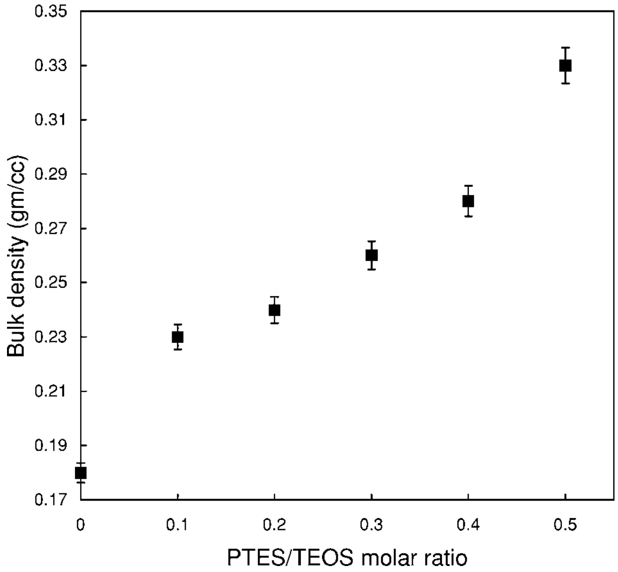


Figure 1 Bulk density as a function of PTES/TEOS molar ratio.

3. Results and discussion

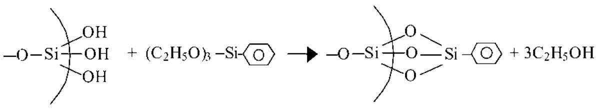
3.1. Effect of PTES/TEOS molar ratio (*M*) on gelation time and volume shrinkage

Table I shows the effect of PTES/TEOS molar ratio (M) on the gelation time for silica alcogel. As the M value increases, the gelation time increases. This is due to the fact that with increase in PTES content in the sol, the hydrolysis and condensation reactions are retarded because of the presence of less ≡Si—OH groups and more Si-phenyl groups on the silica cluster and hence an increase in gelation time.

Further, the Table I illustrates the effect of M value on the percentage of relative volume shrinkage of the aerogels. As the M value increases the volume shrinkage of the aerogels also increases. With increase in M value the steric crowding of non- hydrolyzable phenyl groups attached to the silica cluster increases and hence the cross linkage between the clusters becomes less and the network becomes weak. Therefore, the network shrinks during the supercritical drying process causing an increase in the volume shrinkage. Fig. 1 shows that the bulk density increases with an increase in M value because of increase in the volume shrinkage.

3.2. Effect of PTES/TEOS molar ratio on hydrophobicity

The hydrophobic aerogels are generally obtained by two methods: (1) co-precursor method pioneered by Schwertfeger *et al.* [14] and (2) surface derivatization of alcogel followed by Yokogawa and Yokoyama [15]. In the present work, the first method is followed because it is simple and less time consuming compared to the second method. It has been found that the hydrolysis and condensation rates of tetraethoxysilane (TEOS) are faster than phenyltriethoxysilane (PTES) during the sol-gel process because PTES contains non-reactive aryl groups. Thus the primary silica clusters formed would be mainly due to the hydrolysis and condensation reaction of TEOS with water having large number of OH groups on their surface. At later stages the O—Si—⌬ hydrolytically stable groups get attached at the surface of SiO_2 particles through oxygen bonds as per the following chemical reaction:



$$-O-Si(OH)_3 + (C_2H_5O)_3-Si-⌬ \longrightarrow -O-Si(-O-)_3Si-⌬ + 3C_2H_5OH \qquad (4)$$

In this way, the water-repellent organic phenyl groups get attached to the silica cluster surfaces by the replacement of H from the surface OH groups that make the cluster surface hydrophobic. The removed H and ethoxy groups react to form ethanol. Similar results have been obtained for TMOS based hydrophobic aerogels [16]. The hydrophobicity was studied by measuring the contact angle (θ) and also the percentage of water adsorption by the aerogel. The contact angle of

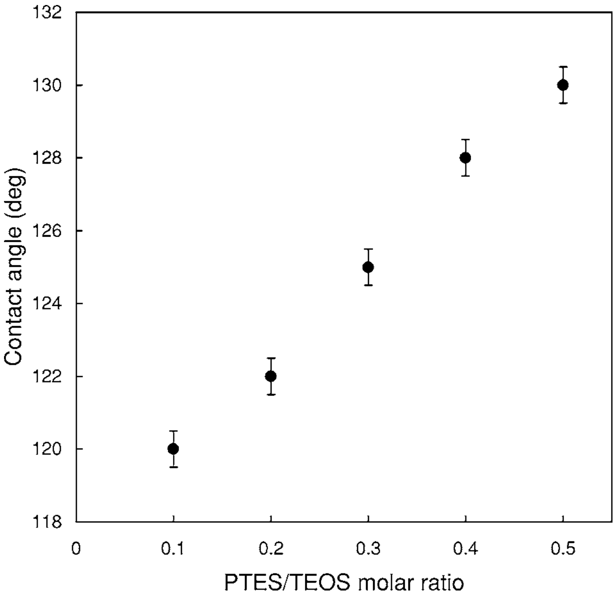


Figure 2 Contact angle (θ) versus PTES/TEOS molar ratio.

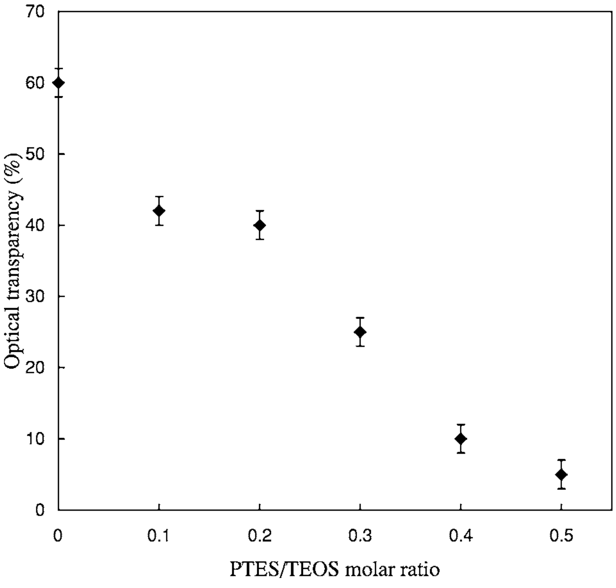
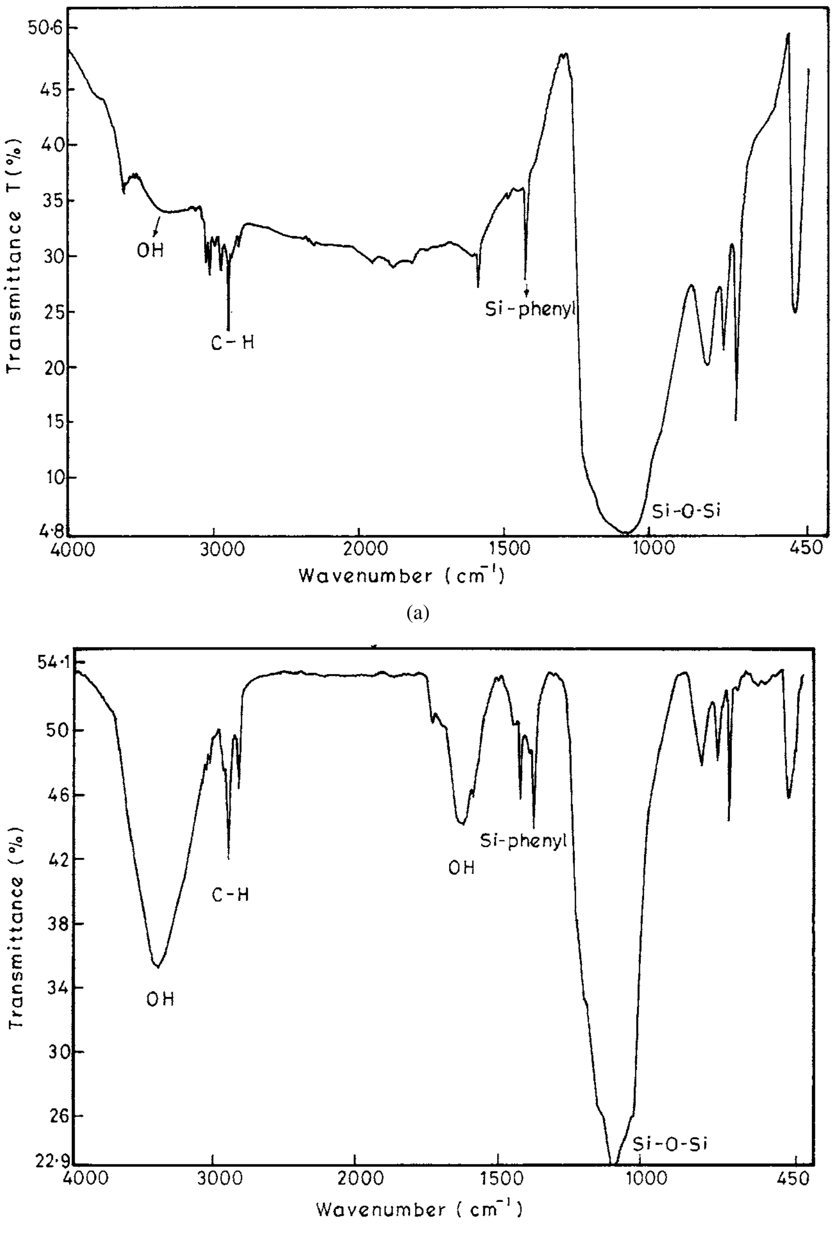


Figure 3 Optical transmission (T) as a function of PTES/TEOS molar ratio.



(a)

(b)

Figure 4 FTIR spectra of the hydrophobic aerogels not exposed to humidity and exposed to humidity for PTES/TEOS molar ratio (M): (a) $M = 0.4$ (not exposed to humidity) and (b) $M = 0.4$ (exposed to 95% humidity at 40°C for 24 h).

a water droplet with the surfaces of the aerogels was measured using Equation 3. For this, a water droplet was placed on the aerogel surface, and the dimensions of which were measured by means of a travelling microscope. It is clear from Fig. 2 that as the M value increased, the contact angle also increased, which is due to a large number of ≡Si-phenyl groups attached to the aerogel surface. The contact angle increased from 120° to 130° with increase in molar ratio M from 0.1 to 0.5 respectively (Fig. 6a and b). The hydrophobic aerogel samples were kept in humidity chamber for 24 h with 95% relative humidity at 40°C. The increase in the water absorption was confirmed by FTIR spectroscopy, which shows an increase in the OH peaks at 3500 and 1600 cm^{-1}, clearly indicating the absorption of water (Fig. 4b). On the other hand, the hydrophobic aerogel which is not exposed to humidity shows negligible OH peaks as shown in (Fig. 4a), because the addition of PTES in the gel results in (partial) dehydroxylation of the aerogel surface leading to hydrophobicity. This causes a large change in physical as well as chemical properties of surface and bulk of the aerogel. In the case of partially hydrophobic aerogels (with lower M values, <0.3) the penetrated water reacts with the structure of the silica network and cleaves the ≡Si—O bonds, as these bonds are not covered with enough Si—R groups. This leads to exposure of more ≡Si—O bonds to water and hence more the water adsorption, whereas in the aerogel with higher M values (>0.3), as the pore walls would be covered with more ≡Si-phenyl groups, the water adsorption is less.

3.3. Effect of PTES/TEOS molar ratio on optical transmittance and thermal conductivity

Fig. 3 shows the percentage of optical transmittance of the aerogels as a function of M values. An increase in

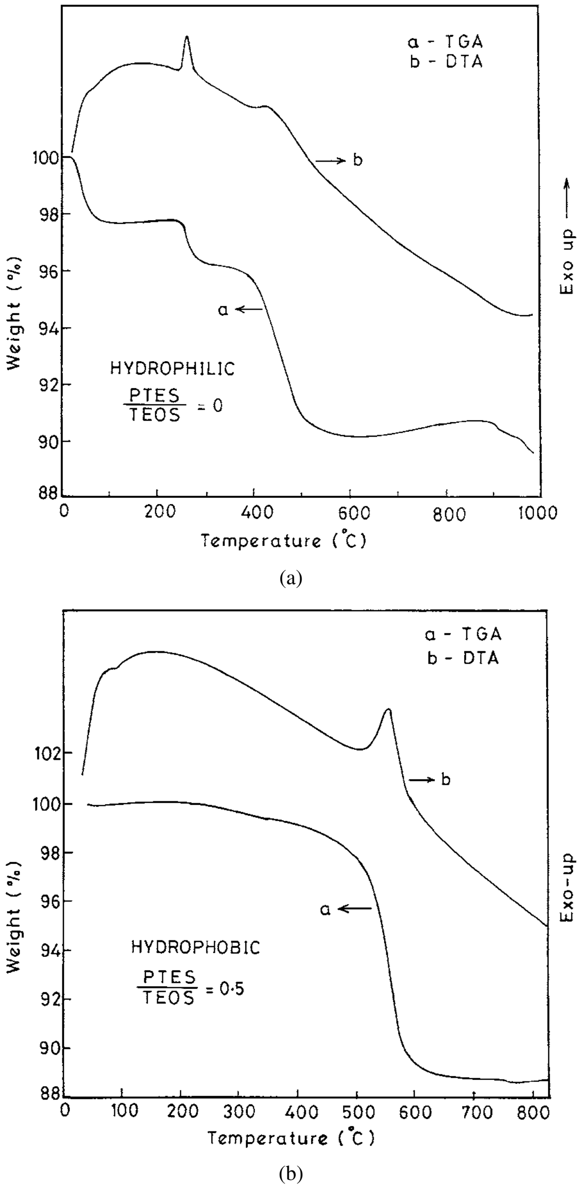
PTES content considerably decreased the optical transmittance and promoted the light scattering nature of the aerogels. The small number of ≡Si—OH groups on the cluster surface reduce the condensation reaction and prevent the progress of crosslinkage of the silaxane chains, leading to a large separation of clusters, that make particles and pores of bigger size and hence the opacity. The pores in the aerogel act as Rayleigh scattering centers and the scattered intensity of the light (I) is given by the relation [17]:

$$I \propto \frac{r^6}{\lambda^4} \tag{5}$$

where λ is the wavelength of light and r is the radius of the pore. Therefore as r increases, scattering intensity (I) also increases. It can be seen from the Table I that with an increase in the molar ratio M, the thermal conductivity and the specific heat of the aerogels decreased. With the increase in the M values, the density of the aerogels increases due to the higher volume shrinkage and hence the thermal conductivity is expected to increase. But on the contrary, it was observed that the thermal conductivity as well as the specific heat of the aerogels decreased for higher M values, which can be due to the increase in the phenyl content because in general, the organic compounds have less thermal conductivity. Hence, the specific heat (C) decreases with decrease in thermal conductivity (K) as per the equation [18].

$$C = \frac{KtA}{md} \tag{6}$$

where 't' is time for which heat is supplied through the aerogel, 'A' is area of cross-section of aerogel, 'm' mass of the aerogel and 'd' the thickness of the aerogel.



(a)

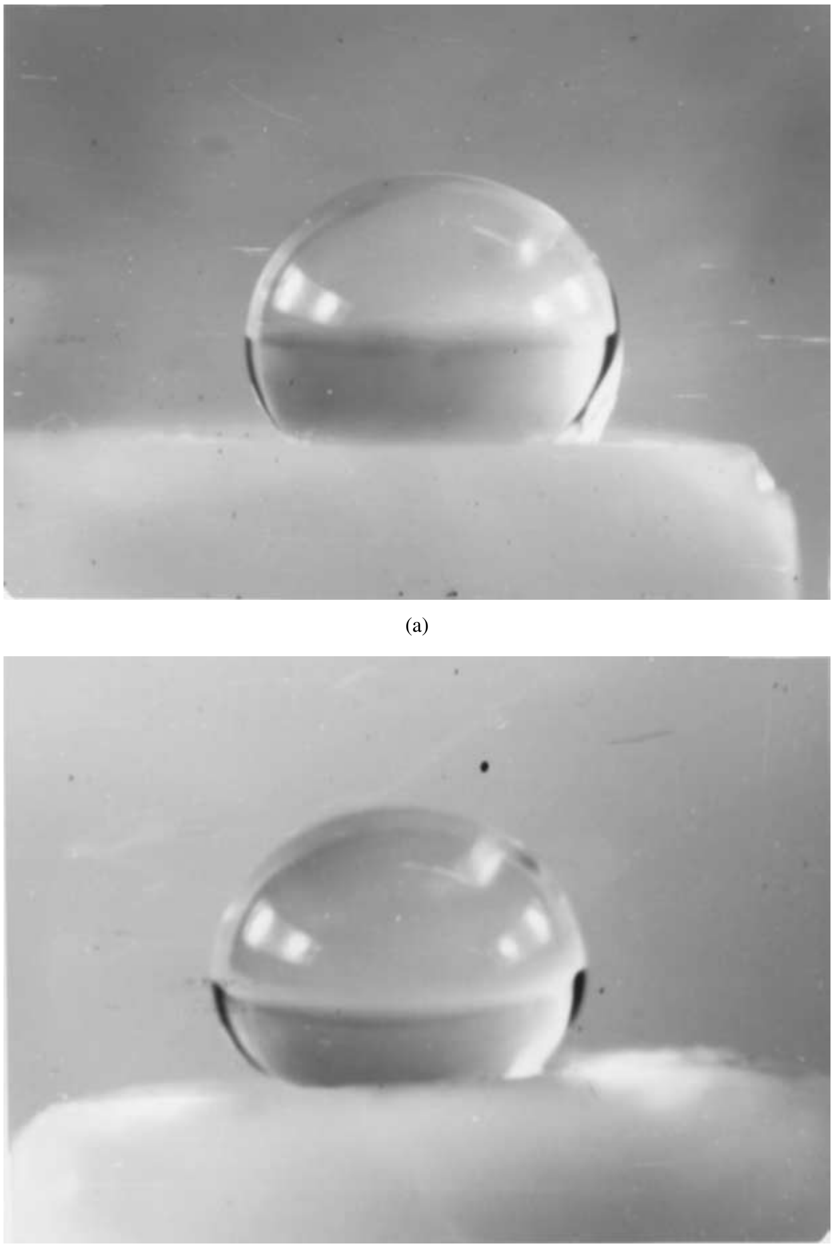
(b)

Figure 5 TGA and DTA analysis. (a) For hydrophilic silica aerogel and (b) for hydrophobic silica aerogel.

3.4. FTIR spectra of the aerogels and thermal analysis

Fig. 4a and b show the FTIR spectra of the aerogels as a function of wave number for $M = 0.4$ without and with exposure to 95% humidity and at 40°C, respectively. The absorption band observed at around 3000 cm^{-1} corresponds to C—H bond [19]. The peak at around 1600 cm^{-1} is due to the adsorbed water and the broad absorption band at 3500 cm^{-1} corresponds to Si—OH band. The sharp peak at 1430 cm^{-1} is due to the Si—phenyl bond. The peaks at around 1000, 800 and 500 cm^{-1} are due to the asymmetric, symmetric and bending modes of silicon dioxide respectively [20]. The residual Si—OH groups are the main source of hydrophilicity of the aerogels [21]. The FTIR spectrum of the hydrophobic silica aerogel, which is not exposed to humidity, shows negligible Si—OH (3500 cm^{-1}) and adsorbed H_2O (1600 cm^{-1}) peaks along with large C—H (3000 cm^{-1}) and Si-phenyl (1430 cm^{-1}) peaks (Fig. 4a). Fig. 4b shows that the intensity of the peak at 1600 cm^{-1} and the broad OH absorption peak at 3500 cm^{-1} increased, whereas the intensities of the C—H absorption peak at 3000 cm^{-1} and Si-phenyl absorption peak at 1430 cm^{-1} remain the same for the hydrophobic silica aerogel sample kept in 95% relative humidity at 40°C for 24 h.

The thermal stability of the hydrophilic and hydrophobic aerogels was tested using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The percentage of weight loss in the hydrophilic (pure TEOS based) aerogels (Fig. 5a) observed in three steps around (i) 100°C, (ii) 250°C and (iii) 400°C, is due to physically adsorbed and trapped ethanol, water and catalyst in larger (at 250°C) and smaller pores (at 400°C). For the hydrophobic aerogels (Fig. 5b), the percent of weight loss is very small up to a temperature of 550°C and at this temperature, there is a sharp exothermic peak which means most of the surface phenyl groups get oxidized at and above 550°C, whereas the exothermic peak observed in the case of hydrophilic aerogel (around 250°C) is due to the decomposition of surface ethoxy groups. The minor weight change up to ≈500°C can be due to the evaporation of the trapped solvent and water molecules inside the small pores. With the PTES co-precursor, the DTA and



(a)

(b)

Figure 6 Photograph showing a water droplet on the surface of silica aerogel using two different molar ratios of PTES/TEOS: (a) $M = 0.2$ and (b) $M = 0.4$.

TGA studies indicated that the aerogels are thermally stable up to a temperature of 550°C. However, when the hydrophobic aerogel was kept and gradually heated in a furnace, the hydrophobicity was retained up to a temperature of 520°C and above which it becomes hydrophilic and hence sinks in the water. It is clear from the TGA/DTA curves that the surface chemical modification of the aerogels is due to the PTES co-precursor.

4. Conclusions

The use of phenyltriethoxysilane (PTES) as a co-precursor with tetraethoxysilane (TEOS) resulted in hydrophobic silica aerogels. The detailed investigations using water intake, contact angle measurements and FTIR spectroscopy showed that an increase in the hydrophobicity of the aerogels with the increase in PTES/TEOS molar ratio (M). The presence of Si-phenyl groups makes the aerogels hydrophobic and they are an integral part of the network structure. For lower M values (<0.1), transparent and monolithic and for higher M values (>0.5), opaque and cracked aerogels were obtained. With an increase in M value from 0 to 0.5 the optical transmittance decreased from 60% to 5% which is due to the increased particle and pore sizes of the aerogels. Correspondingly, the gelation time increased from 3 to 27 days due to the lower number of functional groups and the possible steric effects of phenyl groups which reduces the degree of crosslinking in the gels. The contact angle increases from 120° to 130° with an increase in M value from 0.1 to 0.5 respectively. The organic Si-phenyl and the inorganic SiO_2 clusters are linked through the covalent bonds. It was found that the aerogels retained the hydrophobicity up to a temperature as high as 520°C and above this they become hydrophilic. Both the thermal conductivity and specific heat decreased with increased phenyl content of the aerogels.

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