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A new route for preparation of sodium-silicate-based hydrophobic silica aerogels via ambient-pressure drying

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Abstract
An in-depth investigation into the synthesis of hydrophobic silica aerogels prepared by the surface derivatization of wet gels followed by subsequent drying at ambient pressure is reported. The following sol–gel parameters were examined for their effect on the physical properties of the derived aerogels: number of gel washings with water, percentage of hexane or methanol in silylating mixture, molar ratio of tartaric acid: Na_2SiO_3, gel aging period, weight% of silica, trimethylchlorosilane (TMCS) percentage, and silylation period. These parameters were varied from 1 to 4, 0 to 100%, 0.27 to 1.2, 0 to 4 h, 1.5 to 8 wt.%, 20 to 40% and 6 to 24 h, respectively. The properties of hydrophobic silica aerogels synthesized by this new route were investigated in terms of bulk density, percentage volume shrinkage, percentage porosity, thermal conductivity and contact angle with water, and by Fourier transform infrared spectroscopy (FTIR). The as-prepared hydrophobic silica aerogels exhibited high temperature stability (up to approximately 435 °C) as measured by thermogravimetric/differential thermal analysis (TGA-DTA). The optimal sol-gel parameters were found to be a molar ratio of $Na_2SiO_3 : H_2O :$ tartaric acid $:$ TMCS of $1 : 146.67 : 0.86 : 9.46$, an aging period of 3 h, four washings with water in 24 h and the use of a 50% hexane- or methanol-based silylating mixture. Aerogels prepared with these optimal parameters were found to exhibit 50% optical transparency in the visible range, $84 \, kg \, m^{-3}$ density, $0.090 \, W \, mK^{-1}$ thermal conductivity, 95% porosity and a contact angle of 146° with water.

Keywords: gel washing, silylation, hydrophobic, silica aerogel

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silica aerogels are nanostructured porous materials obtained by removing the liquid from a wet gel without shrinkage. They are composed of highly cross-linked network of silica particles. These unique materials exhibit many fascinating properties, which include a very low density ($\sim 3 \, kg \, m^{-3}$), low thermal conductivity ($\sim 0.02 \, W \, mK^{-1}$), a low refractive index (~ 1.01 to 1.1), high optical transparency ($\sim 90\%$) and a high surface area ($\sim 1600 \, m^2 \, g^{-1}$) [1, 2]. Because of these properties, silica aerogels are employed in nuclear reactors as Cerenkov radiation detectors, containers for liquid rocket propellants, thermal superinsulators for solar energy systems, refrigerators, windows and air conditioning systems [3–7].

In 1864, Graham [8] showed that water in silica gel could readily be replaced by organic liquids. This fact led Kistler [9] to explore replacing the liquid in a wet gel with gas by extracting the liquid from the gel at a high temperature and high pressure. He produced aerogels in an autoclave, which was an expensive process. Since the drying takes place at a high temperature and pressure, it is a very difficult and unreliable method. Furthermore, the Kistler method was very
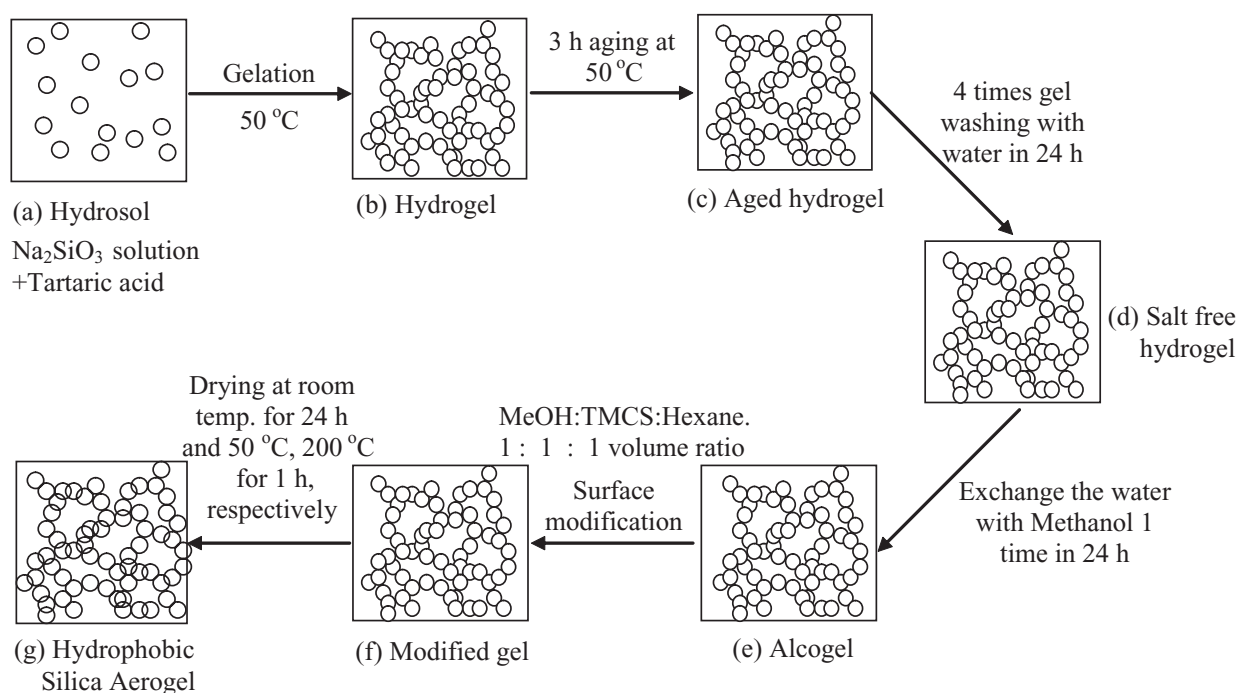
Figure 1. Preparation of the hydrophobic silica aerogels.

tedious and time-consuming. In 1968 a team of researchers headed by Teichner developed a method for producing silica aerogels within one day using (albeit costly) silicon alkoxide precursors [10]. For commercial production, however, it is desirable to produce the silica aerogels using a low-cost precursor such as sodium silicate and to dry the wet gels at ambient pressure. Pure silica aerogels are hydrophilic and adsorb atmospheric moisture. Thus, the aerogels deteriorate with time in humid environments due to the adsorption of water molecules because of the polar –OH groups on their surface that can take part in hydrogen bonding with H_2O [11, 12]. The replacement of H from Si-OH groups with hydrolytically stable Si-R groups through the oxygen bond prevents the adsorption of water and hence results in hydrophobic aerogels [13, 14].

In continuation of research work on the hydrophobic aerogels, Schwertfeger and co-workers [15, 16] have produced the silica aerogels using a water glass precursor using ion-exchange resin by surface modification and drying at ambient pressure. They passed sodium silicate solution through an ion-exchange resin to replace Na^+ ions from the solution with H^+ ions. However, ion-exchange resin is costly and requires repeated washing with water. To regenerate the resin, repeated washing with HCl is needed to replace Na^+ ions with H^+ ions, which is a lengthy and time-consuming process. Kang and Choi [17], Jeong *et al* [18] and Wei *et al* [19] have prepared silica aerogels by employing surface modification and drying at ambient pressure. Kim and Hyun [20] as well as our group [21–23] have synthesized the silica aerogels employing the similar method.

We reported the synthesis of hydrophobic silica aerogels from a water glass precursor employing an inexpensive and simple method involving the aging of a gel, washing with

water, the subsequent surface modification of the gel, and finally drying at ambient pressure. This method is expected to produce aerogels at a cost of approximately $50 per litre.

2. Experimental procedure

2.1. Sample preparation

The preparation of hydrophobic silica aerogels by drying at ambient pressure using the sodium silicate solution is depicted schematically in figure 1. The chemicals used were a sodium silicate solution (Na_2SiO_3, LOBA, India, Na_2SiO_3 content 36 wt.%, $Na_2O : SiO_2 = 1 : 3.33$) as a precursor with a specific gravity of 1.05 (diluted from 1.36), tartaric acid ($C_4H_6O_6$) (Merck Company, Mumbai) as a catalyst and reactant, trimethylchlorosilane (TMCS) (Fluka, pursis grade, Switzerland) as a surface modifier, and methanol (MeOH, CH_3OH) and hexane (C_6H_{14}) (Merck, India) as solvents. Double-distilled water was used to prepare the sodium silicate and tartaric acid solutions.

Silica hydrosols were prepared by adding 3.6N tartaric acid solution dropwise to sodium silicate solution followed by stirring for 5 min. For gelation, temperature was kept at 50 °C in a temperature-controlled oven. After gelation, the gel was aged for 3 h at 50 °C to strengthen the gel network. The gel was then washed four times with water over 24 h. Next, methanol was exchanged with the gel, then surface modification was carried out by soaking the gel in a mixture of methanol : TMCS : hexane with a volume ratio of 1 : 1 : 1 for 24 h. The positions of the gel in water, methanol and silylating mixture are shown in figure 2. Notably, the gel sank in water and methanol but floated in the silylating mixture. After decanting the solvents, the silylated gel was dried at ambient pressure for 24 h followed by heating at 50 °C for
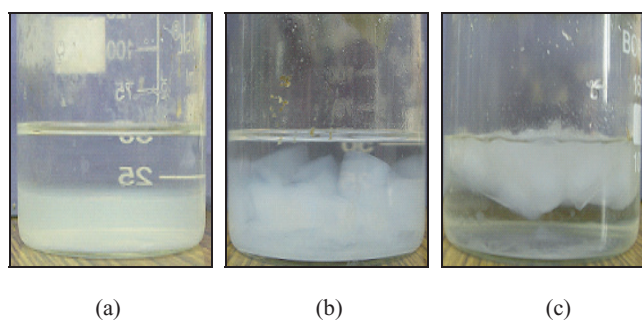
Figure 2. Gel positions in (a) water (b) methanol and (c) mixture of methanol + TMCS + hexane.

1 h then at 200 °C for 1 h. After cooling the oven to room temperature, the aerogel was removed from the oven and used for characterization.

2.2. Methods of characterization

The bulk density of the aerogels was calculated using a known volume of aerogel and dividing by its mass (measured by a microbalance, 10^{-5} g precision). The volume shrinkage and porosity of the aerogels were calculated as explained in our previous paper [24]. The degree of hydrophobicity was quantified by measuring the contact angle (θ) of a water droplet placed on an aerogel surface, which was measured by a traveling microscope (least count 0.001 cm) using the formula [25]

$$\theta = 2 \tan^{-1}(2h/b), \tag{1}$$

where h is the height and b is the base width of the water droplet on the aerogel surface. The contact angle was also measured using a contact angle meter (Ramé-hart instrument, USA). The surface modification of the aerogels was confirmed by Fourier transform infrared spectroscopy (FTIR) studies. The thermal stability of the aerogel hydrophobicity was tested by thermogravimetric analysis-differential thermal analysis (TGA-DTA) using a 2960 TA model by Universal Instruments, USA.

3. Results and discussion

3.1. Effect of number of gel washings with water on optical transmission

Gel washing with water removes trapped salt in the pores of the gel network. The effect of the number of gel washings with water on the optical transmission (%) of the aerogels was studied by keeping the tartaric acid: Na_2SiO_3 molar ratio constant at 1.08 and varying the number of washing in 24 h from 1 to 4 times. It was observed that upon increasing the number of washings from 1 to 4 times, the aerogel optical transmission increased from 20 to 50% while the aerogel density decreased from 91 to 84 kg m^{-3} (see figure 3). This is due to the fact that sodium tartarate, which is formed during hydrolysis, becomes trapped in the pores of the gel network causing a decrease in the optical transmission and an increase in the density of the aerogel since the solubility of
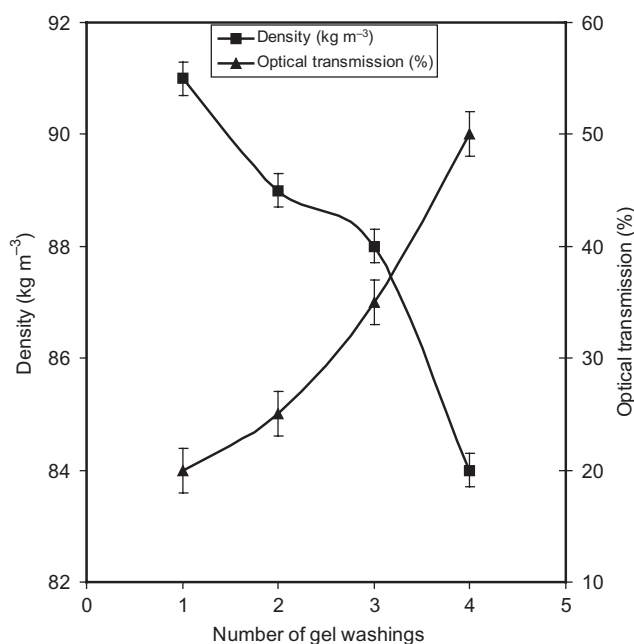
Figure 3. Changes in the optical transmission (%) and density of the silica aerogel with the variation of number of gel washings with water.
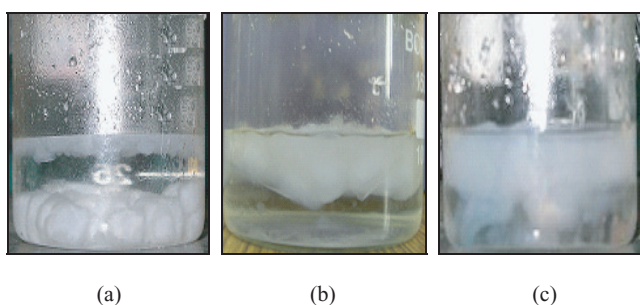
sodium tartarate in water is low (29 kg/100 litres). Therefore, multiple washings are required to remove the salt from the pores of the gel to enhance the transparency of the aerogel. The best method of quantitatively extracting the solute from one solvent to another is to employ several washings instead of one [26]. The quantity of Na$^+$ ions present in the pores of the aerogels was estimated by atomic absorption spectroscopy (AAS) and was found to be 1.23%, while, on the basis of stoichiometry, the hydrosol is known to contain 36.5% Na$^+$ ions. Hence, washing the gel with water after aging decreases the percentage of Na$^+$ ions from 36.5 to 1.23 to produce a transparent aerogel.

3.2. Effect of hexane (or methanol) percentage in silylating mixture

In the silylation process, hexane is used as an inert dilution medium and MeOH is used to eliminate remaining water from the pores of the alcogel. Figure 4 shows the gel positions for mixtures containing 0, 50 and 100% hexane in methanol. The gel did not float in 0% hexane, whereas it floated in the solution with 50% hexane and partially floated in 100% hexane. This is because, for the complete silylation of the gel, an inert medium (hexane) is required. The effect of the hexane percentage on the physical properties of the silica aerogels was studied by varying it from 0 to 100% while keeping the Na_2SiO_3 : H_2O : tartaricacid : TMCS molar ratio constant at 1 : 146.67 : 0.86 : 9.46 (table 1). As shown in figure 5, it was observed that volume shrinkage (%) and density of the silica aerogels decreased upon increasing the hexane concentration to 50% in the silylation mixture, and then increased with a further increase in hexane concentration up to 100%. The reason for this is that at 0% hexane (100% MeOH) due to the absence of an inert medium, which reduces the reaction

Table 1. Physical properties of silica aerogels with the variation of the tartaric acid/Na_2SiO_3 molar ratio and TMCS percentage.

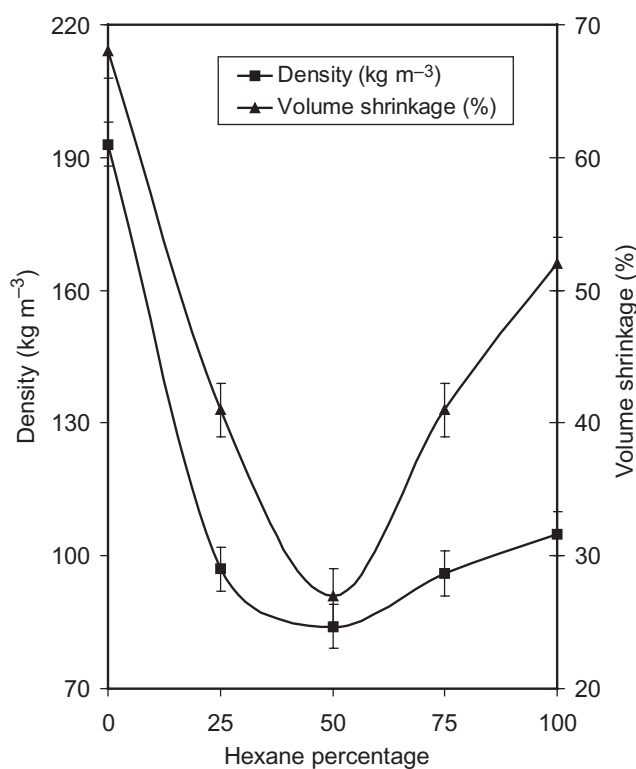| Sr. No.	Variation	Volume shrinkage (%)	Porosity (%)	Pore volume $10^{-3}(m^3\,kg^{-1})$	Contact angle (degree)	Thermal conductivity (W mK^{-1})
A Effect of tartaric acid/Na_2SiO_3 molar ratio						
1	0.27	70	94	8.6	140	0.105
2	0.51	79	89	4.6	132	0.124
3	0.72	59	93	7.5	137	0.110
4	0.90	50	94.5	9.2	142	0.102
5	1.08	45	94.7	9.5	143	0.099
6	1.20	72	89.5	4.5	130	0.125
B Effect of TMCS percentage (%)						
1	20	59	92	6.1	133	0.118
2	26.67	41	94.5	9.2	140	0.100
3	33.33	24	95.6	11.4	146	0.090
4	40	9	95.9	12.3	146	0.089

Figure 4. Gel positions in the silylation process for (a) 0% hexane (b) 50% hexane and (c) 100% hexane.

rate of TMCS with pore water, the silylation of the surface does not occur systematically. Also, the low surface tension of hexane helps to reduce the capillary pressure, which is associated with shrinkage due to drying. Hence, because of the incomplete surface modification, more shrinkage occurs in the gels producing the dense aerogels. At 100% hexane (0% MeOH) due to absence of MeOH, which facilitates the formation of polar intermediates in silylation, silylation does not occur as effectively and the density of the aerogels increases. The effects of the presence of hexane and MeOH in the mixture are dependent on each other. On the other hand, at 50% hexane and 50% MeOH, sufficient surface modification occurs resulting in low shrinkage and low-density (84 kg m^{-3}) aerogels.
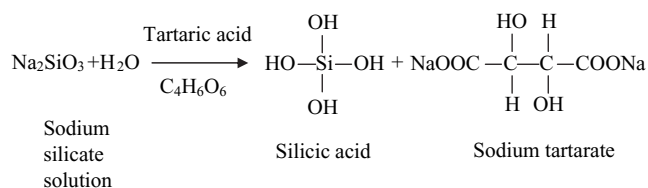

Figure 5. Changes in the volume shrinkage (%) and density of the silica aerogels with the variation of the hexane percentage.

3.3. Effect of tartaric acid: Na_2SiO_3 molar ratio

The effect of the tartaric acid: Na_2SiO_3 molar ratio (A) on the physical properties of the silica aerogels was studied by varying A from 0.27 to 1.2 (table 1). The gel aging period and the Na_2SiO_3 : H_2O : TMCS molar ratio were kept constant at 3 h and 1 : 146.67 : 9.46, respectively. During the gel formation the following hydrolysis and condensation reactions take place.
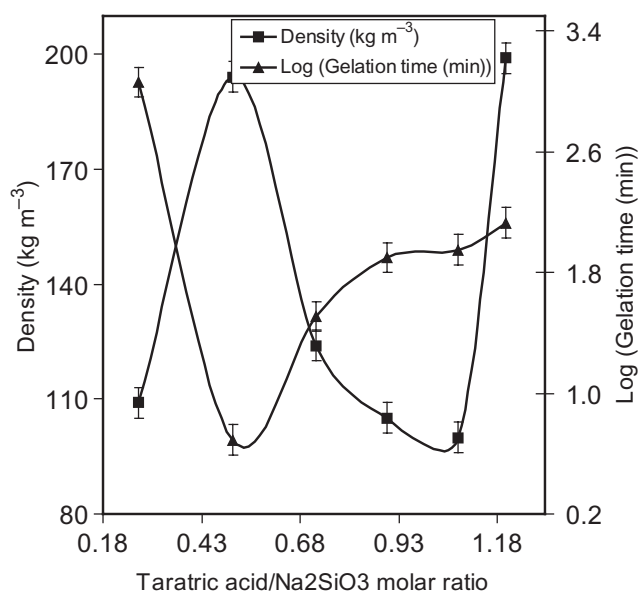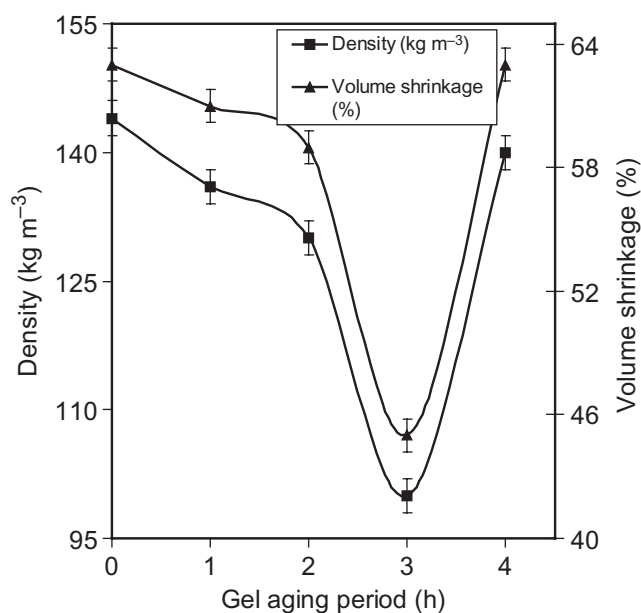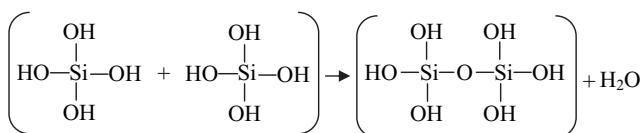
Hydrolysis:

(2)

Figure 6. Changes in the gelation time and density of the silica aerogels with the variation of the tartaric acid/Na$_2$SiO$_3$ molar ratio.

Figure 7. Changes in the volume shrinkage (%) and density of the silica aerogels with the variation of the gel aging period.

Condensation:

$$
\begin{pmatrix}
& OH & & OH \\
HO-&Si-OH & + & HO-Si-OH \\
& OH & & OH
\end{pmatrix}
\rightarrow
\begin{pmatrix}
OH & & OH \\
HO-Si-O-&Si-OH \\
OH & & OH
\end{pmatrix}
+ H_2O
$$

Silicic acid

(3)

The amount of catalyst added strongly affects the gelation time and density of the silica aerogels. As shown in figure 6, it was observed that with an increase in A to 0.51, the gelation time decreased and density increased. This is because, with increasing catalyst concentration, the rates of hydrolysis and condensation reactions increase, and as a result, silica clusters aggregate at a faster rate to form a three-dimensional, dense silica network in a short time [27]. The gelation time increased with further increases in A (>0.51); this may be because the silica particles are negatively charged and, therefore, particle cross-linking is slowed down by charge repulsion. At lower A (<0.51) the gelation time may be high because silica particles are positively charged, and hence repel each other [27]. The density of the aerogels decreased as A increases up to 1.08 due to the presence of excess tartaric acid, which enhances the rates of hydrolysis and condensation reactions, which lead to cluster formation, thus resulting in denser aerogels [28]. At A $\approx$ 1.08, because of the complete hydrolysis and condensation of particles, the formation of a uniform network is believed to take place, which leads to low-density (100 kg m^{-3}) silica aerogels.

3.4. Effect of gel aging period

Aging a gel before drying helps to strengthen the network and thereby reduces the risk of fracture [29]. The effects
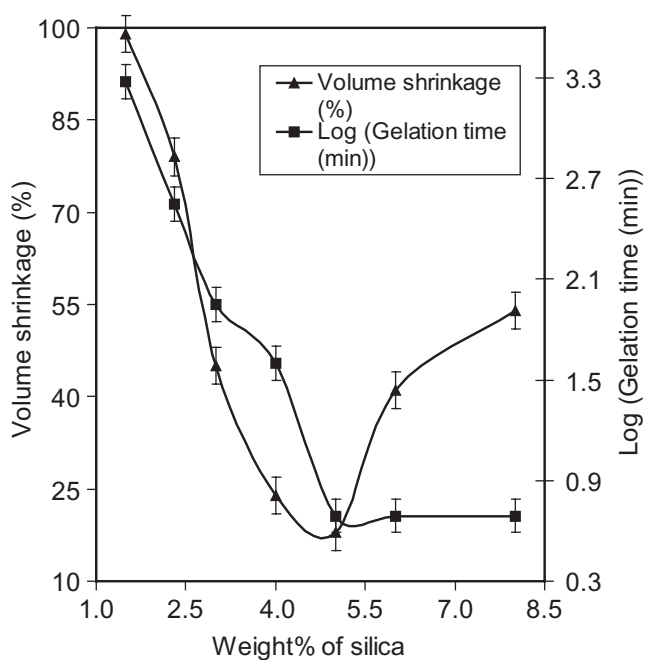
of the gel aging period on the volume shrinkage (%) and density of aerogels were studied varying the aging period from 0 to 4 h (table 2) by keeping the tartaric acid/Na$_2$SiO$_3$ molar ratio constant at 1.08. At lower and higher gel aging periods (<3 h$<$) the volume shrinkage (%) and density were high, while the volume shrinkage and density were low for an aging period of about 3 h, as shown in figure 7. This is because during the gel aging, a number of chemical and physical changes take place, such as the condensation of surface –OH groups, syneresis, coarsening and segregation, all of which strongly affect the properties of aerogels [22]. The lower volume shrinkage (%) and bulk density of the gels aged for about 3 h indicates that they were coarse, meaning that dissolution and reprecipitation driven by differences in solubility between surfaces with different radii of curvature occurs. This causes the growth of necks between particles; thus, the capillary pressure was lower and the aerogels were probably stiffer and stronger.

3.5. Effect of weight% of silica (B)

The effect of the weight% of silica (B) in the hydrosol on the physical properties of the silica aerogels was studied by varying it from 1.5 to 8 wt.% (table 2). The aerogels were aged for 3 h, keeping the tartaric acid/Na$_2$SiO$_3$ molar ratio constant at 1.08. From figure 8, it can be seen that as the value of B was increased to 5, the gelation time decreased. As B was further increased, the gelation time remained constant. The volume shrinkage of the aerogels decreased and then increased as B increased from 5 to 8 wt.%. This is likely to be because, at lower value of B, the lower silica content in the hydrosol slows the rates of hydrolysis and condensation reactions, resulting in longer gelation time and a weaker silica network. Shrinkage during the drying process thus increases due to the weak silica network. At higher values of B, the rates

5

Table 2. Porosity, pore volume, contact angle and thermal conductivity of silica aerogels with variation of the sol–gel parameters.

Sr. No.	Variation	Porosity (%)	Pore volume 10^{-3} (m³ kg⁻¹)	Contact angle (θ, degree)	Thermal conductivity (W mK⁻¹)
		C Effect of percentage of hexane (or methanol) (%)			
1	0	89.8	4.7	132	0.124
2	25	94.8	9.8	144	0.098
3	50	95.5	11.4	146	0.090
4	75	94.8	9.9	145	0.098
5	100	94.5	9	142	0.102
		D Effect of aging period (hours)			
1	0	92.4	6.4	134	0.118
2	1	92.8	6.8	136	0.113
3	2	93.1	7.2	137	0.112
4	3	94.7	9.5	143	0.099
5	4	92.3	6.3	135	0.117
		E Effect of weight % of silica			
1	1.5	89.5	4.5	130	0.125
2	2.3	89.8	4.7	132	0.124
3	3	94.7	9.5	143	0.099
4	4	95.5	11.4	146	0.090
5	5	95.7	11.8	146	0.090
6	6	91.7	5.8	134	0.120
7	8	89.4	4.5	130	0.126

Figure 8. Changes in the gelation time and volume shrinkage (%) of the silica aerogels with the variation of weight% of silica.

of hydrolysis and condensation increase and cluster formation takes place, leading to a shorter gelation time and a higher silica content per unit volume (i.e. a denser aerogel).

During the drying process, evaporation of a liquid from the gel creates a capillary tension (P) in the liquid. This tension is balanced by the compressive stresses on the solid network, causing the shrinkage of the dried gel. The stresses during the drying depend on the interfacial energy (surface tension of pore liquid), the bulk modulus of the network and

the pressure gradient in the liquid. According to Darcy's law, the liquid flow (J) through the gel is given by

$$J = (D/\eta_L)\nabla P, \qquad (4)$$

where D is the permeability of the gel, ∇P is the pressure gradient and η_L is the viscosity of the liquid. During liquid evaporation, the pressure (P) in the liquid phase of the gel is related to the volumetric strain rate of the gel (ε) by

$$(D/\eta_L)\nabla^2 P = -\dot{\varepsilon}. \qquad (5)$$

The resulting stress in the solid phase of a gel plate of thickness L is given by [30]

$$\sigma_x \approx C_N(L\eta_L \dot{V}_E/3D), \qquad (6)$$

where $C_N \equiv (1-2N)(1-N)$, N is Poisson's ratio, and $\dot{V}_E$ is the liquid evaporation rate. Equation (6) indicates that the stress is proportional to the thickness of the gel plate and the liquid evaporation rate. Also, if the permeability is high, then the stress is small. Therefore, monolithic aerogels thicker than 0.8 cm were not obtained. Hence, at B ≈ 4, due to the high permeability and low stress, the shrinkage of the aerogel decreased resulting in a low density silica aerogel.

As shown in figure 9, at both lower and higher values of B ($<4<$) the thermal conductivity of the aerogel is higher because of the greater shrinkage and, thus, the higher density of the aerogel. At B ≈ 4, faster pertinent hydrolysis and condensation reactions result in less shrinkage and thus result in aerogels with low density (84 kg m⁻³) and lower thermal conductivity (0.09 W mK⁻¹).

3.6. Effect of TMCS percentage on silylation

The drying of a wet gel without surface modification causes its shrinkage due to the continuous condensation of end –OH
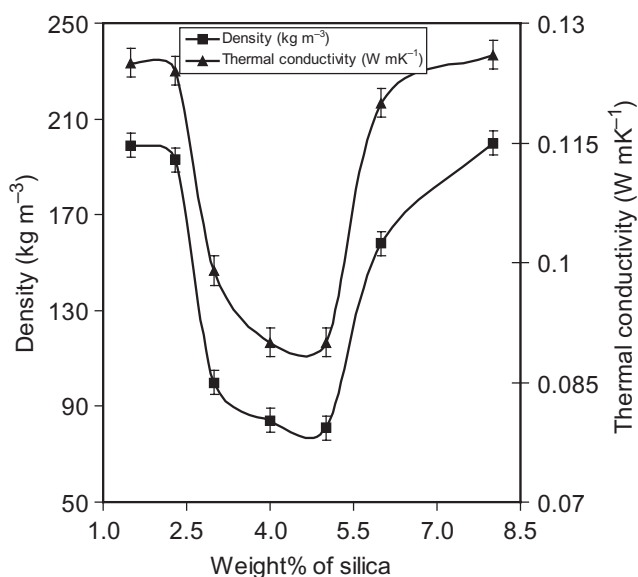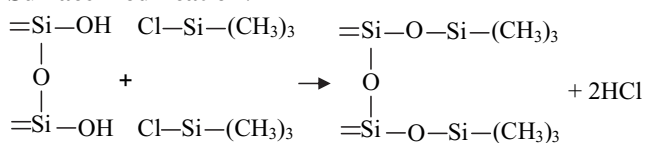
Figure 9. Changes in the density and thermal conductivity of the silica aerogel with the variation of weight% of silica.

Figure 10. Changes in the optical transmission (%) and density of the silica aerogels with the variation of the TMCS percentage.

groups leading to a dense aerogel. This is because capillary pressure exerted by pore fluid evaporation causes irreversible shrinkage in the aerogels. Capillary collapse in a wet gel can be prevented by replacing the hydrophilic –OH groups on the surface of the gel backbone with unreactive Si–CH$_3$ species by surface modification using silane coupling agents such as TMCS. The capillary pressure generated during drying is given by the Laplace equation [31].

$$P = -2\frac{\gamma_{LV}\cos\theta}{r_p\text{-}\delta_t},\qquad(7)$$

where γ_{LV} is the liquid–vapor surface tension, θ is the contact angle of the liquid with a pore wall, r_p is the pore radius and δ_t is the thickness of the liquid layer absorbed on the surface. The negative sign is due to the negative radius of curvature of the meniscus at the liquid–vapor interface. TMCS minimizes the shrinkage of the gel through reductions in the surface tension of the solvent and the contact angle between the solvent and the surface of the silica network [32]. Hence, hydrophobic aerogels are obtained by replacing the end-capped silanol groups with nonpolar hydrolytically stable –Si − (CH$_3$)$_3$ groups [33] using TMCS as follows.
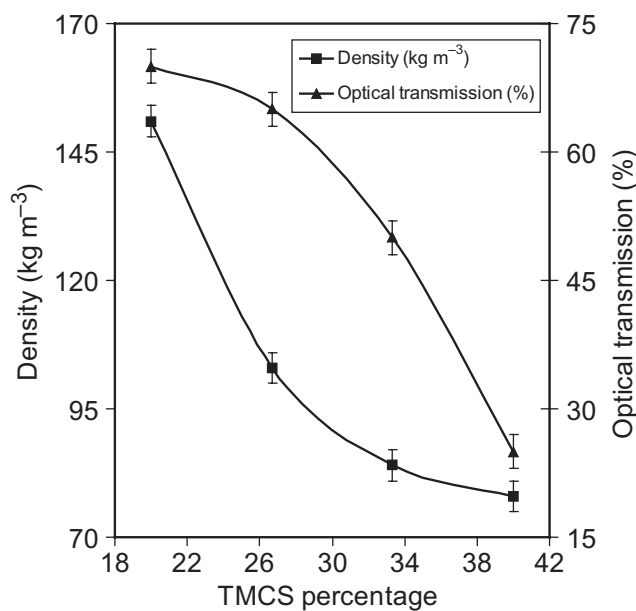
Surface modification:

$$
\begin{array}{ccccc}
\equiv\text{Si--OH} & \text{Cl--Si--(CH}_3)_3 & & \equiv\text{Si--O--Si--(CH}_3)_3 & \\
| & & & | & \\
\text{O} & + & \rightarrow & \text{O} & + \ 2\text{HCl} \\
| & & & | & \\
\equiv\text{Si--OH} & \text{Cl--Si--(CH}_3)_3 & & \equiv\text{Si--O--Si--(CH}_3)_3 & \\
\end{array}
$$

Silica surface   TMCS   Modified silica surface

$$(8)$$

The percentage of TMCS in the silylating mixture was found to be a parameter that predominantly affects the silylation, and hence the physical properties of silica aerogels (table 1). The

effect of the TMCS percentage on silylation was studied by varying the concentration of TMCS from 20 to 40% while keeping the Na$_2$SiO$_3$: H$_2$O : tartaric acid molar ratio constant at 1 : 146.67 : 0.86. Figure 10 shows the decreases in density and percentage of optical transmission of the aerogels with increasing TMCS percentage. This is likely to be due to the fact that at lower percentages of TMCS (<33%), incomplete silylation occurs and unsilylated –OH groups can undergo condensation, thus causing more shrinkage and denser aerogels. Furthermore, because of the smaller particle and pore sizes caused by the increased shrinkage, the percentage of optical transmission of these aerogels was higher. At higher percentages of TMCS (>26.67%), a complete modification between silanol groups and nonpolar, hydrolytically stable –Si(CH$_3$)$_3$ groups occurs, which causes repulsion between the end-capped −Si(CH$_3$)$_3$ groups. Because of this, the springback of the solid gel network occurs, resulting in an increase in the aerogel volume with big pores and thus low-density and semitransparent aerogels. At higher percentages of TMCS (>33%), the excess TMCS deposited in the pores causes opacity of the aerogels. Thus, for subsequent experiments 33% TMCS was used. The hydrophobicity of the aerogels increased with the TMCS percentage, which was quantified by contact angle measurement. Figures 11(a) and (b) show the water droplets placed on the hydrophobic silica aerogel surfaces and contact angles (θ) are 133° and 146° for 20 and 33% TMCS, respectively.

3.7. Effect of silylation period

The silylation period plays a significant role in the surface modification of gels. The effect of the silylation period on the physical properties of silica aerogels was studied by varying the silylation period from 6 to 24 h by keeping the Na$_2$SiO$_3$: H$_2$O : tartaricacid : TMCS molar ratio constant at
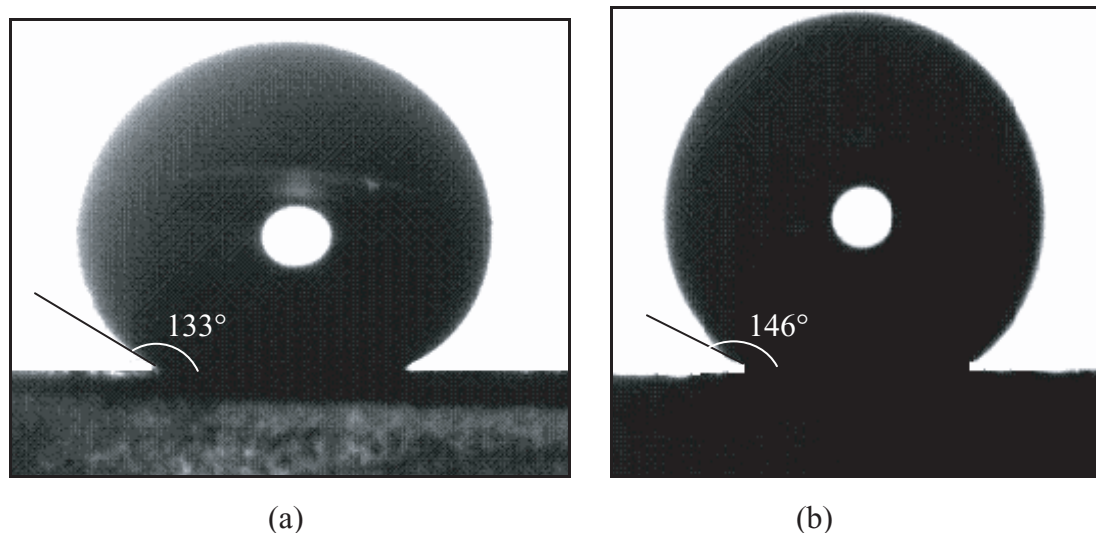
Figure 11. Water droplets on the hydrophobic silica aerogel surfaces for (a) 20% TMCS (b) 33% TMCS.

$1 : 146.67 : 0.86 : 9.46$. Figure 12 shows that with increasing the silylation period, the aerogel density decreased and hydrophobicity increased. This is believed to be because, for shorter periods of silylation, incomplete surface modification of the wet gel occurs leading to a dense and less hydrophobic aerogel. For the longer silylation periods the bulk density decreases because of the complete surface modification of the gel, thus increasing the hydrophobicity of the aerogel. The effects of the silylation period on the porosity and thermal conductivity of silica aerogels is depicted in figure 13. Increasing the silylation period to 24 h led to an increase in porosity and a decrease in the thermal conductivity. This may be because, after longer silylation periods, more complete surface modification results in better springback. The thermal conductivity, which depends on the porosity of the aerogel, is lower because there is less solid content per unit volume of the aerogel [21]. Springback implies that the gels densify and then undensify upon drying [34]. Figure 14 shows the variation of the percentage volume change with drying temperature. It was found that the percentage volume change decreased up to 100 °C, increased above 100 °C then remained constant above 150 °C, clearly indicating the effect of springback. The surface modification of the aerogel for different silylation periods from 6 to 24 h is confirmed by the FTIR spectra of the aerogels as shown in figure 15. It was observed that with increasing silylation period, the intensity of –OH bond peaks at 1600 and 3400 cm^{-1} [35] decreased, and the peaks related to C–H at 2960 and 1450 cm^{-1} and those related to Si–C at 840 and 1260 cm^{-1} increased [36]. Thus, the dependence of surface modification on the silylation period was clearly observed.

3.8. Thermal stability of hydrophobic silica aerogels

The thermal stability of the hydrophobic silica aerogels with respect to hydrophobicity was tested by TGA-DTA as shown in figure 16. Results show that the percentage weight loss is negligible and constant up to 435 °C. There is an exothermic
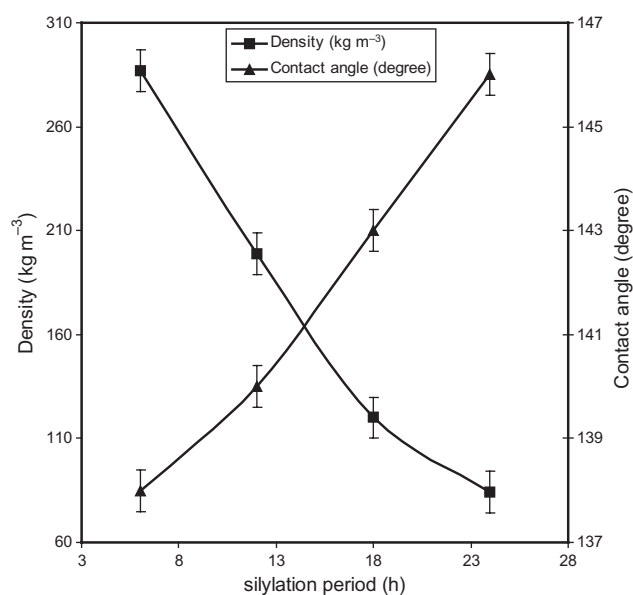

Figure 12. Changes in the contact angle and density of the silica aerogels with the variation of the silylation period.

peak at 435 °C corresponding to the oxidation of $–Si(CH_3)_3$ groups and residual groups [23]. Thus, it is clear that the silica aerogels have high heat resistance up to approximately 435 °C and lose their hydrophobicity above 435 °C to become hydrophilic due to oxidation of $–(CH_3)_3$ groups.

4. Conclusions

Superhydrophobic, low-density and semitransparent silica aerogels were obtained using a sodium silicate precursor and drying at ambient pressure. Both repeated the gel washing with water and the sol–gel parameters have marked effects on the physical properties of the silica aerogels produced by this technique. It was observed that for a large number of gel washings, the optical transmission
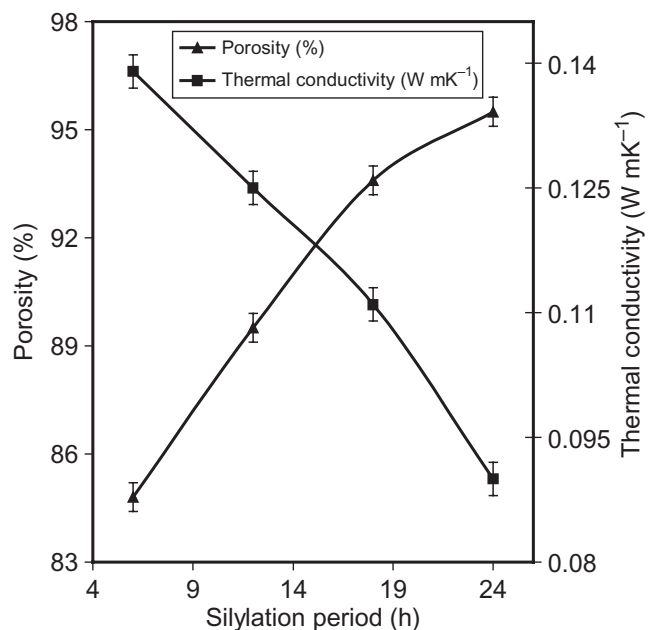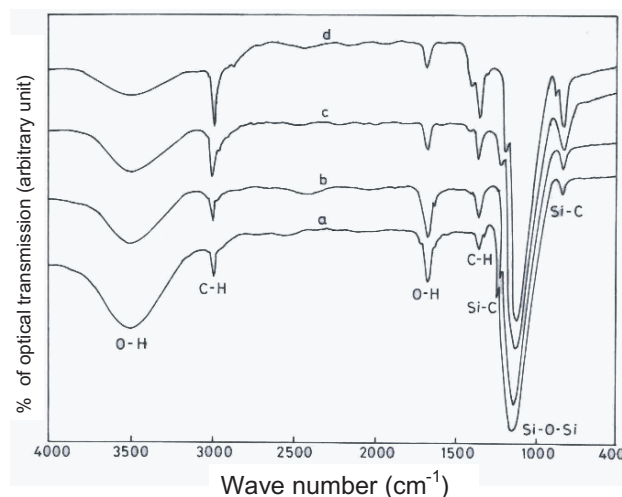
Figure 13. Changes in the porosity (%) and thermal conductivity of the silica aerogels with the variation of the silylation period.
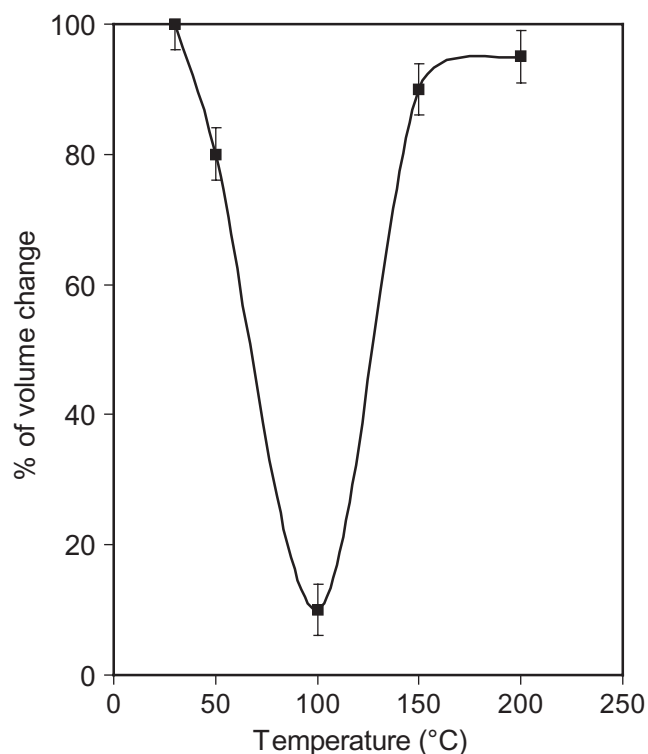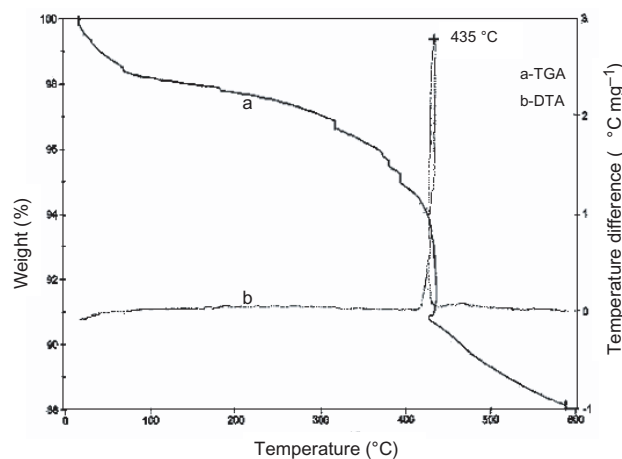

Figure 14. Variation of the percentage of volume change of the gel with the drying temperature ($^\circ$C).

Figure 15. Infrared spectra of silica aerogels for different silylation periods: (a) 6 h, (b) 12 h, (c) 18 h and (d) 24 h.

Figure 16. TGA-DTA of the hydrophobic silica aerogel.

of the aerogel improved. Increasing the silylation period and TMCS percentage reduced the density of the aerogels. Also, 50% hexane (or methanol) in the silylating mixture produced aerogels with the lowest density. From the FTIR spectra of the aerogels, it was observed that the intensity of the –OH bond peaks at 1600 and 3400 cm^{-1} decreased and those of the C–H bond peaks at 2960, 1450 cm^{-1} and the Si–C bond peaks at 840 and 1260 cm^{-1} increased with increasing silylation period. The TGA-DTA showed that the silica aerogels were thermally stable with respect to hydrophobicity up to 435 $^\circ$C. The highest-quality aerogels with low density (84 kg m^{-3}), high porosity (95%), low thermal conductivity (0.090 W mK^{-1}), hydrophobicity (146°), and high optical transmission (50%) were obtained for a molar ratio of Na$_2$SiO$_3$: H$_2$O : tartaricacid : TMCS of 1 : 146.67 : 0.86 : 9.46, with 4 washings of the water in 24 h, 3 h aging, 24 h silylation period and 50% hexane (or methanol) in the silylating mixture using the ambient-pressure drying method.

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