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Improvement in optical and physical properties of TEOS based aerogels using acetonitrile via ambient pressure drying

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Abstract

The experimental results on the improvement in optical and physical properties of TEOS based aerogels using acetonitrile via ambient pressure drying are reported herein. Silica gels were prepared by a two step sol–gel process using hydrochloric acid (HCl) as an acid catalyst and tertrabutyl ammonium fluoride (TBAF) as a base catalyst. Acetonitrile acts as a strong diluting solvent in the preparation of silica sol which considerably lowers the density and improves the optical transmission of silica aerogels. To study the effect of acetonitrile on the properties of TEOS based aerogels, acetonitrile::TEOS molar ratio was varied from 1.09 to 5.45. Optical transmission study of these aerogels was carried out by comparing the photos of aerogel granules. Optically transparent silica aerogels with low density (0.065 g/cc) as well as low thermal conductivity (0.068 W/mK) were successfully prepared using 1×10^{-3} M HCl, 0.1M TBAF and TEOS::MeOH::H_2O(A)::H_2O(B)::Acetonitrile::TMCS molar ratio at 1::16.75::3.5:2.5::1.69::0.88 respectively by ambient pressure drying method.

Keywords: Silica aerogels; Acetonitrile; Optical transmission; Ambient pressure drying

1. Introduction

Silica aerogels are highly porous materials with low density, low thermal conductivity as well as large surface area. They have significant attention in heat insulation [1], waste treatment [2], drug delivery and targeting systems [3,4] and many others. Generally, the synthesis of silica aerogels using silicon alkoxide takes place in two steps: (1) sol–gel process to prepare gel, and (2) supercritical drying of gel to obtain aerogel [5–11]. Sol–gel process is the primary step for the synthesis of aerogels in which the hydrolysis of silicon alkoxides generates intermediate species and these species then undergo a stepwise polycondensation reaction to form a three-dimensional gel network. The secondary step is the supercritical drying of gel which involves the drying at critical temperature and pressure of the solvent present in the pores of gel. However, this conventional method of supercritical drying for the synthesis of silica aerogels requires special type of autoclave assembly which prohibits their large scale production. So, to produce aerogels for commercial purpose, a simple and cost effective method of ambient pressure drying was developed. Later on many groups have synthesized silica aerogels using tetraethoxy silane precursor (TEOS) by ambient pressure drying method wherein the surface chemical modification of silica surface was carried out prior to drying [12–15]. However, silica aerogels prepared using TEOS precursor have the disadvantages of high density and low optical transmission that hinder wider application of these materials. It was observed that in a system with a highly polar solvent, the solvent is expected to affect the rate determining step and therefore the nature and size of the resulting polymeric particles. [16]. It has been reported that, acetonitrile is a highly polar aprotic solvent which does not form hydrogen bonds with the silicate nucleophile but reduce the rate of condensation reaction. This is due to high polarity of acetonirile which stabilise the anionic reactants with respect to the activated complex [17]. Further, acetonitrile is an easily displaceable ligand and miscible with water and methanol. Therefore, to obtain optically transparent and low

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density silica aerogels acetonitrile has been employed in the sol–gel process [18,19]. But, in these reports the methods used for the preparation of aerogels are non-commercial and time consuming. Hence in the present work, attempts were made to obtain the low density silica aerogels along with high optical transmission by introduction of acetonitrile as a strong diluting solvent via ambient pressure drying method within short processing period.

2. Experimental

2.1. Materials and synthesis

The chemicals used for the synthesis of silica aerogels were tetraethoxysilane (TEOS, Sigma-Aldrich Chemie, Germany), hydrochloric acid (HCl, Merck India), tetrabutyl ammonium fluoride (TBAF, $N(C_4H_9)_4F$, Alfa Aeser), acetonitrile (CH_3CN, 99.8%, Merck), methanol (MeOH) and hexane (s.d Fine-Chem. Ltd., India) and trimethylchlorosilane (TMCS, Fluka, Puriss grade, Switzerland). The required concentrations of HCl and TBAF were prepared using double distilled water and all other chemicals were used as received.

The schematic for the preparation of TEOS based aerogels using acetonitrile as a strong diluting solvent via ambient pressure drying is presented in Fig. 1 and it involves the following three steps.

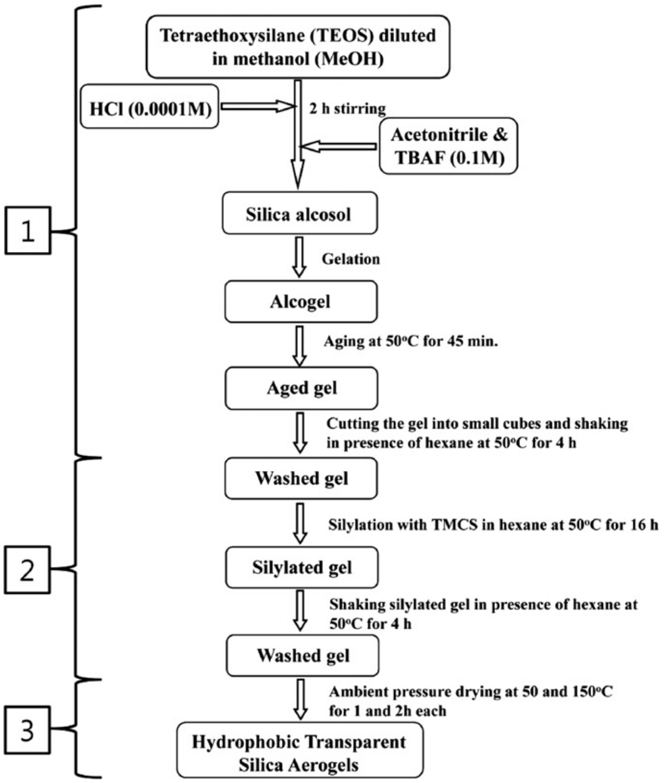


Fig. 1. Schematic flow of preparation of TEOS based aerogels by ambient pressure drying.

2.1.1. Preparation of alcogel

A two step sol–gel process was employed for the preparation of silica sol. In the first step, hydrolysis of diluted TEOS (using MeOH) was carried out by adding HCl (1×10^{-3} M). This solution was stirred for 2 h with the help of magnetic stirrer. In the second step, acetonitrile was introduced in this solution and stirred for 5 min. Subsequently, TBAF (0.1 M) was added to the hydrolyzed sol to initiate the condensation reaction. As the condensation reaction proceeds, the viscosity of sol increased and gel formation occurs when the sol loses its fluidity. The hydrolysis and condensation reaction of TEOS using two step sol–gel process are as follows.

2.1.1.1. Hydrolysis.

$$Si(OC_2H_5)_4 + H_2O \overset{HCl}{\rightarrow} Si(OH)_4 + 4C_2H_5OH. \tag{1}$$

2.1.1.2. Condensation.

Water condensation

$$Si(OH)_4 + (OH)_4Si \overset{TBAF}{\rightarrow} (OH)_3{-}Si{-}O{-}Si{-}(OH)_3 + H_2O \tag{2}$$

Alcohol condensation

$$Si(OH)_4 + Si(OC_2H_5)_4 \overset{TBAF}{\rightarrow} (OH)_3{-}Si{-}O{-}Si{-}(OC_2H_5)_3 + C_2H_5OH \tag{3}$$

During the experiment the molar ratios of H_2O(A)::TEOS and H_2O(B)::TEOS were kept constant at 3.5 and 2.5 respectively. After gelation, aging was performed by immersing the gel in methanol for 2 h at 50 °C in a PID controlled oven (Termaks, U.S.A.) to strengthen the network. The aged gel was cut into small cubes and then immersed in excess methanol for 15 min to ensure complete removal of unreacted chemicals remained within the gel.

2.1.2. Solvent exchange/silylation/washing of alcogel

In this step, methanol present in the pores of gel was exchanged with hexane. For this purpose the small gel cubes were immersed in hexane and subjected to shaking in a shaker (Remi instrument company, India) at the speed of 120 RPM and temperature of 50 °C for 4 h. After solvent exchange, the silylation was carried out by soaking the small gel cubes in the mixture of hexane and TMCS (7%) and shaking it for the period of 16 h. During silylation, the surface of gel was modified as given in the following reaction.

2.1.2.1. Silylation.

$$\equiv Si{-}OH + Cl{-}Si{-}(CH_3)_3 \rightarrow \equiv Si{-}O{-}Si{-}(CH_3)_3 + HCl \tag{4}$$

Later on, the mixture was decanted and the silylated gels were washed by immersing in hexane and shaking for 4 h to remove the unreacted TMCS and HCl produced during the silylation of the gel.

2.1.3. Ambient pressure drying

In the final step, hexane present in the pores of gel was taken out by ambient pressure drying at 50 and 150 °C for

1 and 2 h each in oven. The resulting hydrophobic silica aerogels were used for the characterization after cooling of oven to ambient temperature.

2.2. Characterization

The bulk density of silica aerogel was calculated by using the ratio of its mass (measured by microbalance, Teleph company, 10^{-5} accuracy) and volume (measured by filling the granules of aerogels in a cylinder of known volume). The porosity was calculated from the bulk density (ρ_b) and skeletal density ($\rho_s = 1.9$ g/cc, measured by helium pycnometer) of silica aerogels using following:

$$\text{Porosity}\,(\%) = \left[1 - (\rho_b/\rho_s)\right] \text{x}100 \tag{5}$$

The volume shrinkage was calculated from alcogel volume (V) and aerogel volume (V_o) using following:

$$\text{Volume shrinkage}\,(\%) = \left[1 - (V/V_o)\right] \text{x}100 \tag{6}$$

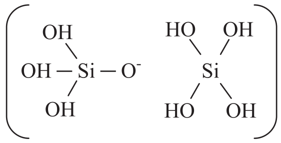
The thermal conductivity of the silica aerogels was measured using C-T meter (Teleph Company, France, accuracy 10^{-3} W/mK) of ring probe type. The microstructural study of silica aerogels was carried out by transmission electron microscopy (TEM, Model FEI TECNI SPRIT, Japan, accelerating voltage: 120 kV). The TEM samples were prepared by dispersing aerogels into a copper grid coated with an amorphous carbon film. The optical transmission study of silica aerogels was performed by comparing the photos of the aerogel granules. The chemical bondings present in the aerogels were confirmed by fourier transform infrared spectroscopy (FTIR, Perkin Elmer, USA). The granules of aerogels were ground into powders, mixed with KBr, and pressed to form a sample disk for FTIR measurements. The degree of hydrophobicity was quantified by measuring the static contact angle (θ) of a water droplet placed on the surface of aerogel with contact angle meter (Rame-Hart instrument, USA). The thermal stability of the hydrophobic silica aerogels, in terms of the retention of hydrophobicity, was measured using thermal analysis (TGA-DTA, Perkin Elmer, USA).

3. Results and discussion

As reported earlier [20] at neutral pH the condensation reaction proceeds by a nucleophilic substitution mechanism whereby a negatively charged deprotonated silanol ion attacks a silanol group, according to:

$$\equiv \text{SiO}^- + \text{OH}-\text{Si} \rightleftarrows \equiv \text{Si}-\text{O}-\text{Si} \equiv + \text{OH}^- \tag{7}$$

wherein the OH^- ions are abstracted by H^+ ions in order to maintain the required pH of the solution. The activated complex of this reaction consists of a transition state species of the form:



In presence of acetonitrile the reactants get stabilized with respect to the activated complex and as a result slow down the reaction to some extent. Therefore, the effect of acetonitrile::TEOS molar ratio (M) on the optical and physical properties of silica aerogels was studied by varying it from 1.09 to 5.45. During the experiments, the molar ratio of TEOS::MeOH::H_2O(A)::H_2O(B)::TMCS was kept constant at 1::16.75::3.5::2.5::0.88 respectively.

Fig. 2 manifests the influence of M value on the gelation time. From Fig. 2 it seems that initially with increase in M value upto 2.73 the gelation time is same which increased for M > 2.73. This may be due to more dilution of sol at higher M value leading to longer gelation time. More dilution causes the smaller primary particles with larger separation which require more time to condensate during gelation. Moreover, the influence of M value on bulk density and contact angle of aerogels is shown in Fig. 3. From Fig. 3 it has been observed that with increase in M value from 1.09 to 2.18, the bulk density of aerogels decreased to 0.065 g/cc and contact angle increased to 150°. Further increase in M > 2.18 produced dense aerogels with low contact angle. The variations in the density and contact angle of silica aerogels with increase in *M* value (Fig. 3) are attributed to the rate of hydrolysis and condensation reactions taking place during gel formation. Such a trend can be understood in view of the gelation mechanism as explained earlier. Since acetonitrile acts as an easily displaceable ligand in the chemical reactions, therefore, in presence of acetonitrile TBAF dissociates easily and hence the dissociation of TBAF in acetonitrile produces "free" fluoride ions during sol–gel synthesis. The extent of dissociation of TBAF, i.e. the concentration of "free" fluoride ions increases with increase in acetonitrile

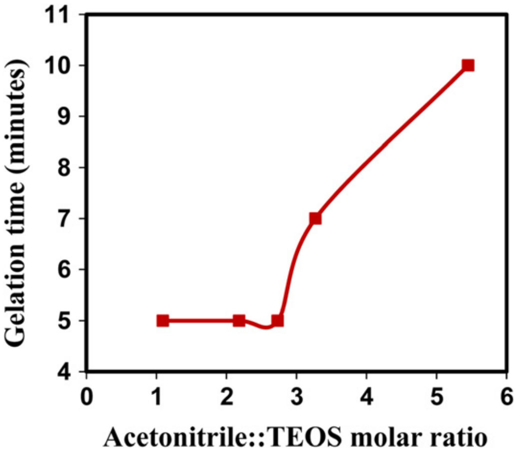


Fig. 2. Effect of Acetonitrile::TEOS molar ratio on gelation time of silica aerogels.

concentration [16] affecting strongly on the network formation. At M > 2.18, the presence of more acetonitrile may produce more free fluoride ions which increases the acidic nature of sol. It is observed that more acidity of sol may weaken the gel network producing highly shrunk and dense aerogels with small pore and particle sizes. The contact angle decreased because of insufficient silylation of surface of weak silica gel. Therefore, the silica aerogels have high density and low contact angle at higher M values. Hence at M value of 2.18, the acetonitrile facilitates the well tailored network formation which sustained the effects of surface tension during ambient pressure drying producing low density aerogels with high contact angle. Similarly, the variation in M value affects on the porosity and thermal conductivity of silica aerogels. As seen from Fig. 4, with increase in M value upto 2.18 the porosity of aerogel increased to 96.5% and thermal conductivity decreased to 0.068 W/mK. Moreover, the porosity and thermal conductivity of silica aerogels decreased and increased respectively with increase in the M > 2.18. Since thermal conductivity of silica aerogel depends on its porosity i.e. higher is the porosity lower will be thermal conductivity and vise a versa. The variations in the porosity and thermal conductivity of aerogels can be explained on the basis of surface modification of gel during silylation. The complete silylation of gel leads to spring back effect in the gel increasing the porosity and decreasing the thermal conductivity of final aerogels. Therefore, the thermal conductivity of aerogels is low because of high porosity. Thus, at M value of 2.18, the sufficient dilution of precursor forms a strong gel network leading to low density, low thermal conductivity and highly porous silica aerogels.

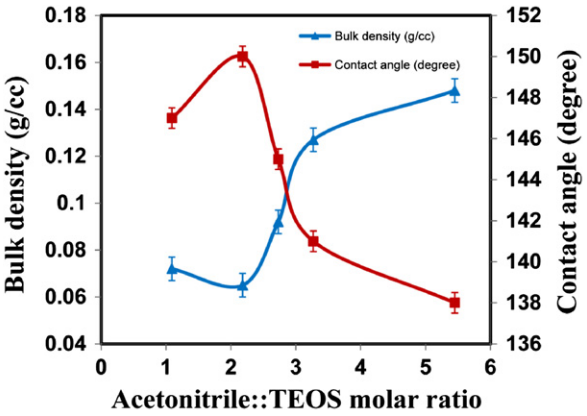


Fig. 3. Effect of Acetonitrile::TEOS molar ratio on the bulk density and thermal conductivity of silica aerogels.

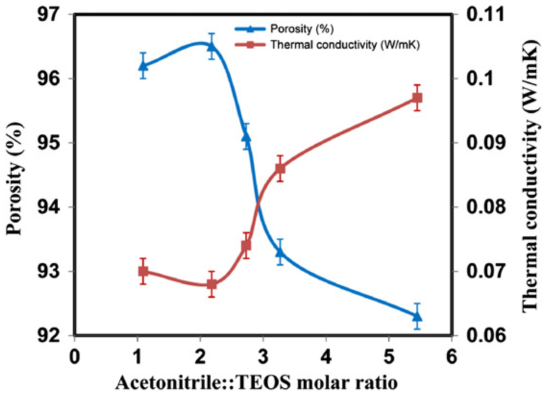


Fig. 4. Effect of Acetonitrile::TEOS molar ratio on the porosity (%) and contact angle of silica aerogels.

TEM images of the silica aerogels prepared using M ~ 2.18 and 5.45 via ambient pressure drying are shown in Fig. 5(a) and (b). From Fig. 5(b) it observes that the aerogel consists of small particles forming compact structure due to more shrinkage (~67%) while in case of Fig. 5(a) the particles are comparatively larger in size forming well connected silica network with low shrinkage (~8%). The photographs of these aerogels are shown in Fig. 6(a) and (b) respectively which clearly differentiate the optical transmission of these aerogels. The compact nature of aerogels prepared using M ~ 5.45 as seen in TEM image (Fig. 5b) may be because of more dilution of sol leading to weak network formation which results in more shrinkage of aerogels. And TEM image (Fig. 5a) of silica aerogels prepared using M ~ 2.18 have particles larger in size as compare to earlier one. Therefore, the

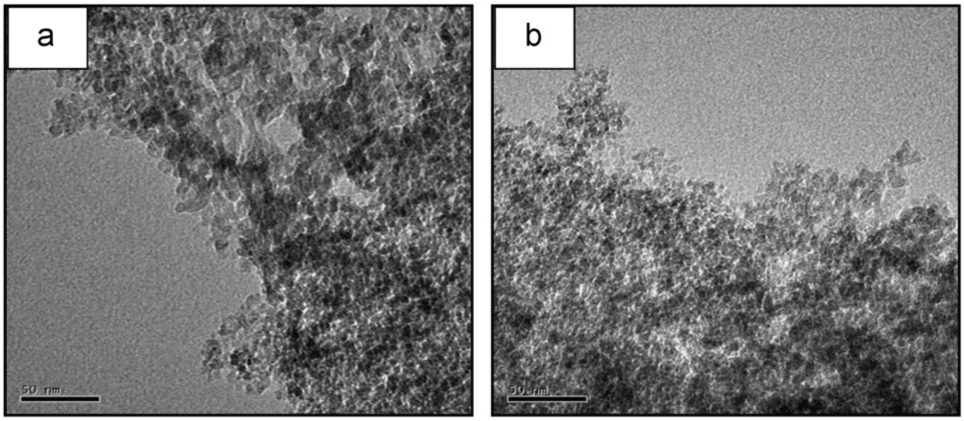


Fig. 5. TEM images of silica aerogels prepared using Acetonitrile::TEOS molar ratio (M) of (a) 2.18 and (b) 5.45.

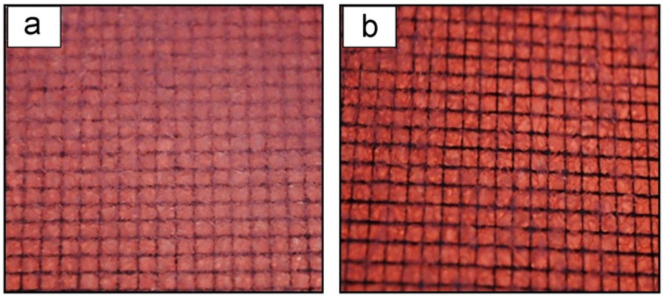


Fig. 6. Photographs of silica aerogels prepared using Acetonitrile::TEOS molar ratio (M) of (a) 2.18 and (b) 5.45.

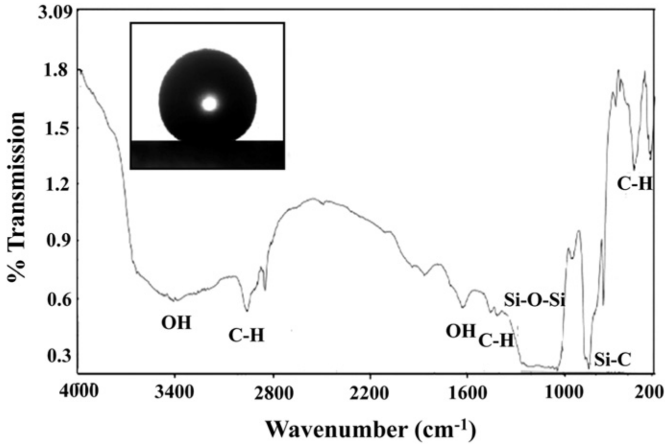


Fig. 7. FTIR spectrum of the silica aerogel prepared using Acetonitrile::TEOS molar ratio (M) of 2.18.

optical transmittance of the aerogels prepared using M ~ 5.45 is more due to small particles (Fig. 6b) as compared to the aerogels with M ~ 2.18 (Fig. 6a). The optical transmission is generally related to the scattering intensity, i.e. to the abundance of scattering centers. In silica aerogels the scattering of light is mainly affected by the particle and pore sizes. Smaller pores and particles lead to lower scattering, as predicted by the Rayleigh scattering equation [21]:

$$I \propto a^6/\lambda^4 \tag{8}$$

where a is the pore or particle size and λ is the wavelength of the incident light.

FTIR spectrum of silica aerogel prepared using M ~ 2.18 is shown in Fig. 7. From Fig. 7 it seems that the peaks at around 3400 and 1630 cm^{-1} correspond to –OH absorption band [22]. The absorption peaks at 2923, 1450 and 550 cm^{-1} correspond to terminal $–CH_3$ and peak at 845 cm^{-1} corresponds to Si–C group [23] which is a reason for the hydrophobic nature of the synthesized silica aerogels. The presence of absorption peak at 1096 cm^{-1} corresponds to Si–O–Si indicating the silica network formation [23]. Moreover, the hydrophobicity of the aerogel is tested by measuring the static contact angle i.e. wetting angle of drop on silica aerogel surface. The water droplet on surface of silica aerogels is shown in the inset of Fig. 7 and the contact angle is measured to be 150°. In FTIR spectrum (Fig. 7), though the intensity of –OH peak at 3400 cm^{-1} is high, at the same time the intensities of Si–C and C–H peaks at around 845 and 550 cm^{-1} are also high which manifest the higher hydrophobicity of these aerogels with contact angle of 150°. The as prepared silica aerogel sample showed the thermal stability in terms of retention of hydrophobicity up to around 300 °C as seen from TGA-DTA plot in Fig. 8. In TGA-DTA plot three major weight losses were observed with an exothermic peak at around 300 °C. The first weight loss was attributed to the removal of moisture and adsorbed water from the system at around 100 °C. The second weight loss was observed as an exothermic peak at 299 °C. This was attributed to the oxidation of organic groups and the dissociation of the $Si–CH_3$ bonds. The third weight loss was observed above the temperature of 300 °C which is a gradual and continuous weight loss. This can be attributed to the condensation of silanols and formation of the glassy structure further. This manifests that as synthesized aerogels show the hydrophobic nature upto 300 °C and become hydrophilic above this temperature.

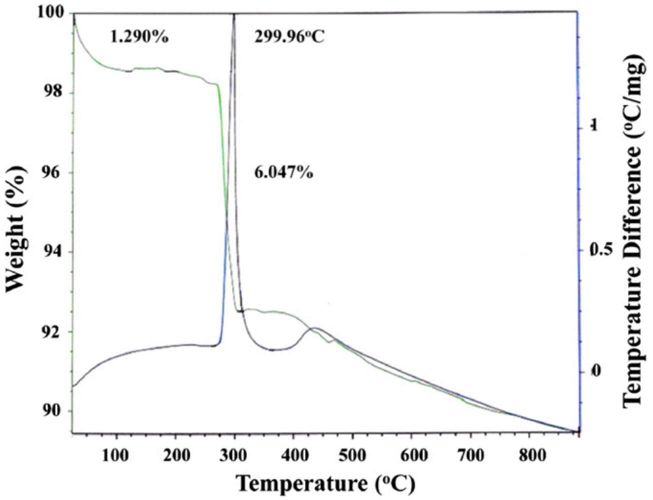


Fig. 8. TGA-DTA plot of the silica aerogel prepared using Acetonitrile::TEOS molar ratio (M) of 2.18.

4. Conclusions

The successful synthesis of optically transparent silica aerogels using acetonitrile as a diluting agent by ambient pressure drying is possible within two days. Silica aerogels with low density ~ 0.065 g/cc and low thermal conductivity ~ 0.068 W/mK were obtained using HCl (1×10^{-3}M), TBAF (0.1M) and TEOS::MeOH::H_2O(A)::H_2O(B)::Acetonitrile::TMCS molar ratio of 1::16.75::3.5::2.5::1.69::0.88 respectively. The FTIR spectrum of silica aerogels reveals that they are hydrophobic in nature with the contact angle of 150°. Further, TGA-DTA manifests the retention of the hydrophobicity in the silica aerogels up to around 300 °C. The as prepared silica aerogels can be used as thermal insulating materials.

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