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# Comparison of some physico-chemical properties of hydrophilic and hydrophobic silica aerogels

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## Abstract

Considering the possibility of long term use of silica aerogels for transparent window insulation materials, we present here the experimental results on the comparison of physico-chemical properties of hydrophilic and hydrophobic silica aerogels. In order to prepare hydrophobic aerogels, the molar ratio of tetramethoxysilane (TMOS) precursor: methanol (MeOH) solvent: water ($H_2O$): ammonium hydroxide ($NH_4OH$) as a catalyst: methyltrimethoxysilane (MTMS) as a hydrophobic reagent was fixed at optimal value = $1{:}12{:}4{:}3.6\times10^{-3}{:}\ 1.3$, respectively. After gelation, the aerogels were dried supercritically by high temperature solvent extraction method. It has been found that hydrophilic aerogels (unmodified) adsorbs water ~4–5 times of its own weight within a time period of 5 min. On the other hand, hydrophobic aerogels (modified) adsorbs $\leqslant 2\%$ water of its own weight even after putting them directly on the water surface for a time period of 1 year. It has been observed that the percentage of optical transmission is quite high (~95%) in the case of hydrophilic aerogels compared to the hydrophobic silica aerogels (~80%) at a wavelength of 900 nm for a sample thickness of 1 cm. In order to determine the thermal stability of the hydrophobic nature of the silica aerogels, both hydrophilic and hydrophobic aerogels were heat treated in air, in the temperature range between 25 and 425 °C with a heating rate of 1.5 °C /min. Anomalous weight loss (~3.3%) has been found in the case of hydrophobic aerogels around 200–210 °C which is the result of thermal decomposition of organic groups. The disappearance of the–$CH_3$ groups was confirmed from IR spectra and $^{29}$Si magic angle spinning nuclear magnetic resonance (CP/MAS-NMR) analyses of hydrophobic silica aerogels which were heat treated below and above the threshold temperature (~200 °C). © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Aerogels; Supercritical; Hydrophilic; Hydrophobic; Thermal stability

## 1. Introduction

Silica aerogels are the lightest and most transparent man made solid on earth. They possess unique properties such as high porosity (>95%) [1], large inner surface area (~600–1600 $m^2/g$) [2], low density (~5 kg/$m^{-3}$) [3], small index of refraction (1.01 to 1.10) [4], a low sound velocity (<100 $ms^{-1}$) [5], open porosity and a low thermal conductivity (~0.01 W/mK) [6]. A number of applications have been investigated including thermal insulation, support for catalysts, supercapacitors for electric cars, microfilters, adsorbents, controlled release of drugs, inertial confinement fusion (ICF) and sound attenuators; and were mentioned in the form of an application tree in the one of our recent publications [7]. Special attention is given to the possibility of CFC-free insulation for refrigerators and transparent window insulation materials (TWIM) [8]. Though these are interesting properties and practical applications, the large-scale use of silica aerogels has been limited because of their sensitivity to moisture. The concentration of water in the pores of the aerogel leads to capillary pressure, which eventually destroys the structure of the aerogels. The Si–OH groups present in the aerogel structure are the main source of hydrophilicity because they promote the adsorption of water. The replacement of the Si–OH group by hydrolytically stable Si–R (R=$CH_3$) groups inhibits the adsorption of water and, therefore, results in hydrophobic aerogels that will be unaffected by the moisture (Fig. 1). The hydrophobicity of the aerogels can be achieved by two methods: (a) surface chemical modification of the aerogels by gaseous reagents and (b) surface modification of the colloidal particles by the incorporation of certain hydrophobic reagents in the alcosol itself.

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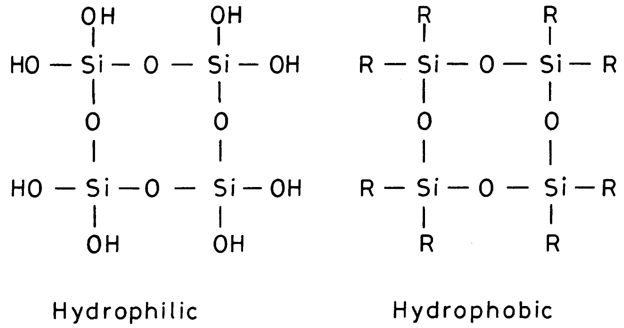


Fig. 1. Schematic diagram showing hydrophilic and hydrophobic silica aerogels.

Recently, Lee et al. [9] and Yokoyama et al. [10] reported results on the preparation of hydrophobic TMOS silica aerogels using $CO_2$ supercritical drying methods followed by methoxylation. This method of surface modification of aerogels by a methoxylation process, i.e. heating hydrophilic aerogel samples in methanol vapour at a temperature around 240 °C for 10 h. This methoxylation process not only consumes more power and methanol but time too! The desired properties for using hydrophobic silica aerogels such as transparent insulation materials for window include monolithicity, low density, and high optical transmission in the visible region and hydrophobicity stability at room temperature and at relative high humidity. However, low hydrophobicity is a significant problem for aerogels produced by $CO_2$ supercritical drying method followed by methoxylation process. Hence, in the present paper, reaction mechanism leading to the surface modifications of $-OH$ groups by water resist $-CH_3$ groups of the surface silicon atoms by incorporating methyltrimethoxysilane (MTMS) as a hydrophobic reagent in the alcosol preparation stage followed by supercritical drying of alcogels, is reported.

Comparative studies of hydrophobicity and optical transmission of both modified and unmodified aerogels have been studied and reported. Moreover, thermogravimetric analysis of the hydrophobic aerogels which were heat-treated below and above the threshold temperature (~200 °C) leading to the physico-chemical changes have also been studied and reported in the present paper.

## 2. Experimental

### 2.1. Sample preparation

Under the basic conditions, it has been observed that the hydrolysis rate of tetramethoxysilane (TMOS) is much faster than that of methyltrimethoxysilane (MTMS) [11].

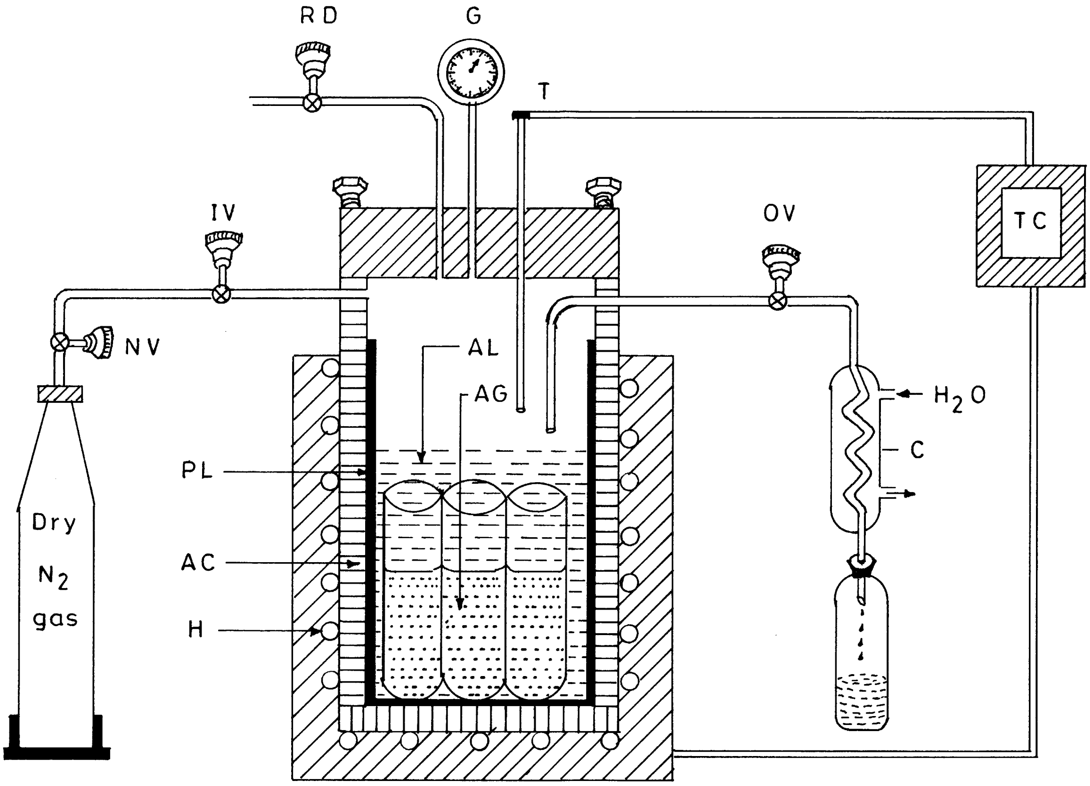
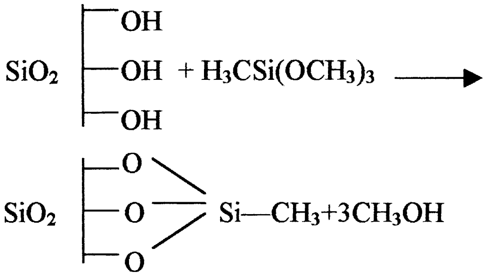


Fig. 2. Schematic representation of the supercritical drying equipment: H, heater; AC, autoclave; PL, Pyrex liner; NV, $N_2$ cylinder valve; IV, inlet valve; OV, outlet valve; C, condenser; RD, rupture disc; G, pressure gauge; T, thermocouple and TC, temperature controller.

So, in a mixture containing TMOS and MTMS, TMOS is preferentially hydrolyzed in the early stage of the reaction, during which MTMS acts as a co-solvent [12]. Hence, the core of the primary particles will not contain any alkyl group. The formation of a three dimensional solid network is achieved by the hydrolysis and polycondensation of methanolic TMOS in the presence of the ammonium hydroxide ($NH_4OH$) catalyst as per the following chemical reaction:

$$xSi(OCH_3)_4 + 2xH_2O \xrightarrow[(NH_4OH)]{MeOH} xSiO_2 + 4xCH_3OH \quad (1)$$

When a sufficient amount of TMOS gets hydrolyzed, the MTMS hydrolysis becomes faster and proceeds as follows:



(2)

In this manner the Si–OH groups react towards the formation of a permanently hydrophobic silica aerogel surface.

In order to get transparent and homogeneous alcosols and alcogels, the molar ratio of tetramethoxysilane (TMOS) precursor: methanol (MeOH) solvent: water ($H_2O$): ammonium hydroxide ($NH_4OH$) as a catalyst:

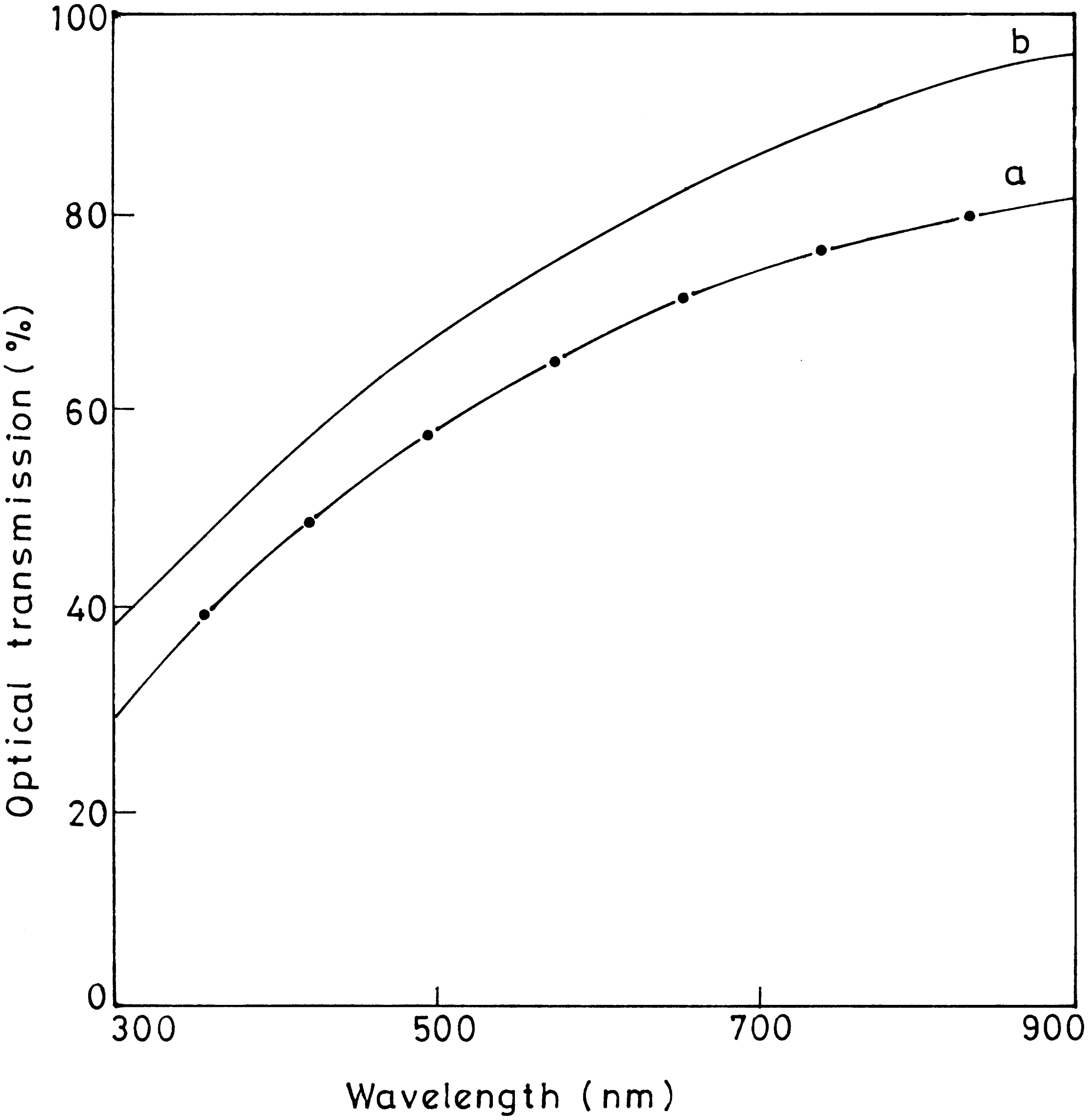


Fig. 3. Optical transmission (%) versus wavelength for: (a) hydrophobic (modified) and (b) hydrophilic (unmodified) aerogels.

methyltrimethoxysilane (MTMS) as a hydrophobic reagent was fixed at an optimal value = 1:12:4:3.6×10$^{-3}$: 1.3, respectively. The homogenous alcosol thus obtained was transferred to Pyrex test tubes of 18-mm outer diameter and 180 mm height and closed air tight to prevent the evaporation of MeOH from the sols, and kept for gelation.

### 2.2. Drying process

After gelation, the alcogels were covered with methanol in order to prevent shrinkage and cracking of the alcogels. The gelation took place at a constant temperature of 25 °C, unless otherwise specified. Silica aerogels were obtained by supercritical drying of the alcogels in an autoclave of 2 l capacity (details of the autoclave and temperature–pressure cycles are given in the one of our publication [13]) with an excess amount of MeOH and 5 bars initial pressure of dry nitrogen gas. Schematic representation of the supercritical drying equipment is as shown in Fig. 2. The temperature of the autoclave was slowly raised to 280 °C in about 10 h, which is much above the critical temperature of MeOH, and simultaneously the pressure in the autoclave was increased to 140 bars. After stabilizing the temperature and pressure for about 30 min, the alcohol was slowly released from the autoclave within a time period of 4 h. After reaching the atmospheric pressure, the autoclave was cooled to ambient temperature in about 10 h, after which the vessel is opened and the aerogels have been taken out for measurements.

### 2.3. Characterization

Hydrophobicity of the aerogels was tested by measuring the percentage of water adsorbed by the aerogels

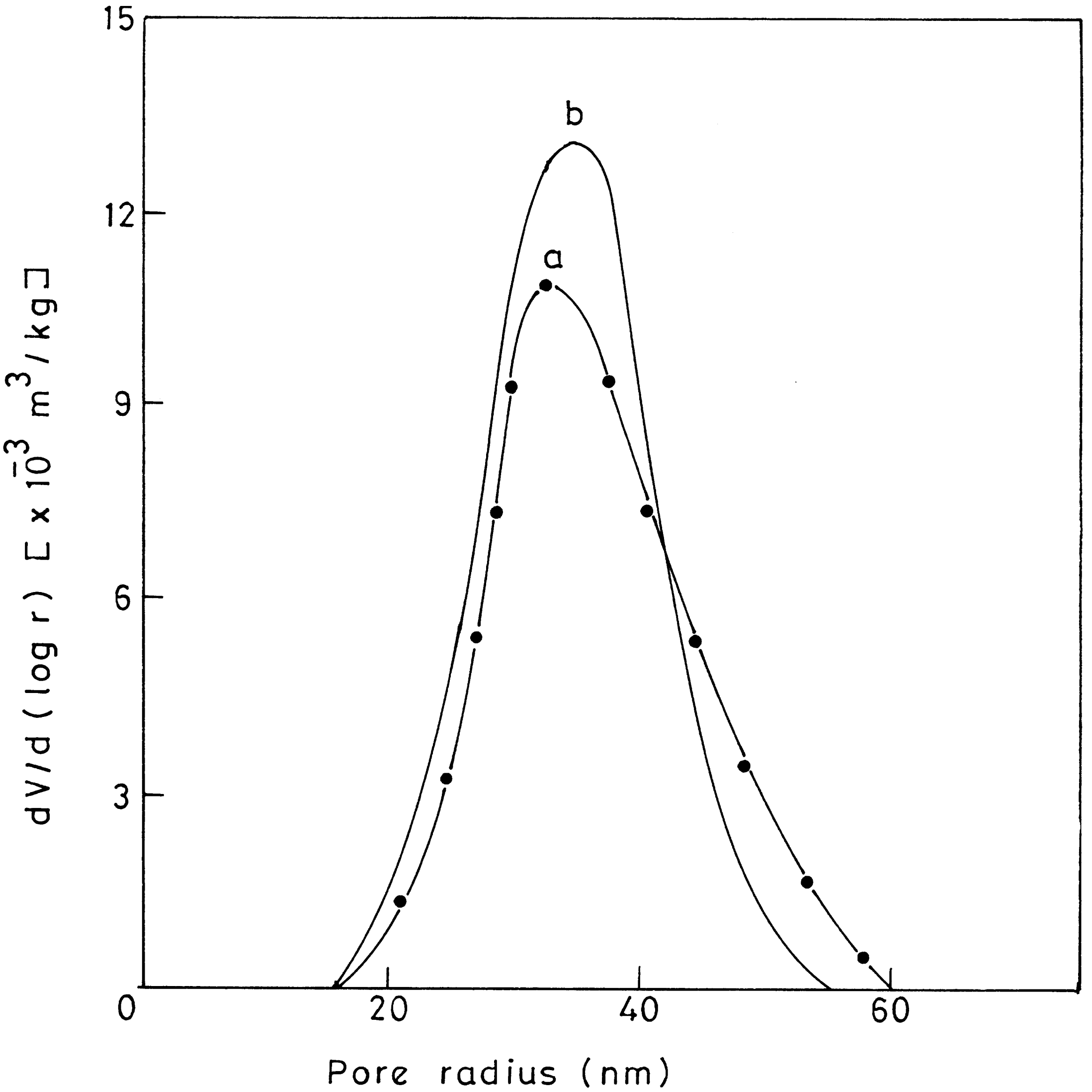


Fig. 4. Pore size distributions (PSDs) of the aerogel samples for: (a) hydrophobic (modified) and (b) hydrophilic (unmodified) aerogels.

by putting them directly in water. Water adsorption up to $\leqslant 2\%$ by weight is considered as hydrophobic and water adsorption by weight $>2\%$ is considered as hydrophilic one. The weights of the aerogels were measured using a Dhona microbalance (Model: Dhona 100 DS) having a least count of $1\times10^{-5}$ g. The percentage of optical transmission of the modified as well as unmodified aerogel (sample thickness of 1 cm) was measured in the wavelength range of 300–900 nm using a Perkin-Elmer Spectrophotometer (Model No. 783). The pore size distributions (PSDs) were measured using a multiple point nitrogen gas adsorption BET surface area analyzer (Model ASAP 2000) made by Micromeritics. A BET analysis from the amount of $N_2$ gas adsorbed at various partial pressures (five points $0.05<p/p_o<0.3$, nitrogen molecular cross sectional area = 16.2 Å$^2$) was used to determine the surface area, and a single condensation point ($p/p_o=0.99$) was used to find the pore size and pore volume. Pore size distributions were calculated from the desorption isotherms.

In order to study the thermal stability, hydrophobic aerogels were heat-treated with a controlled heating rate of 1.5 °C min$^{-1}$ using a microprocessor based Parr temperature controller (Model 4846) connected to a muffle furnace. Thermal measurements (thermogravimetric analysis, TGA) on aerogel samples of 10–20 mg in weight were carried out in a air medium, from room temperature (25 °C) up to 425 °C

Infra-red (IR) data were obtained by the transmission method on a Perkin-Elmer Spectrophotometer (Model No.783). The $^{29}$Si magic angle spinning nuclear magnetic resonance (CP/MAS-NMR) Spectra of aerogel samples were obtained on a Joel GSX270 Spectrometer at 67.9 MHz.

## 3. Results and discussion

Some authors [9,12] have subjected silica aerogels for nearly 40 days under 90–95% humid atmosphere and studied their hydrophobic nature. But in the present paper, the aerogels were directly put on the surface of water since it is the best test, of hydrophobicity) in a dust-proof closed chamber and then the weights of modified and unmodified aerogels were measured with time. It has been found that hydrophilic aerogels (unmodified) adsorbs water

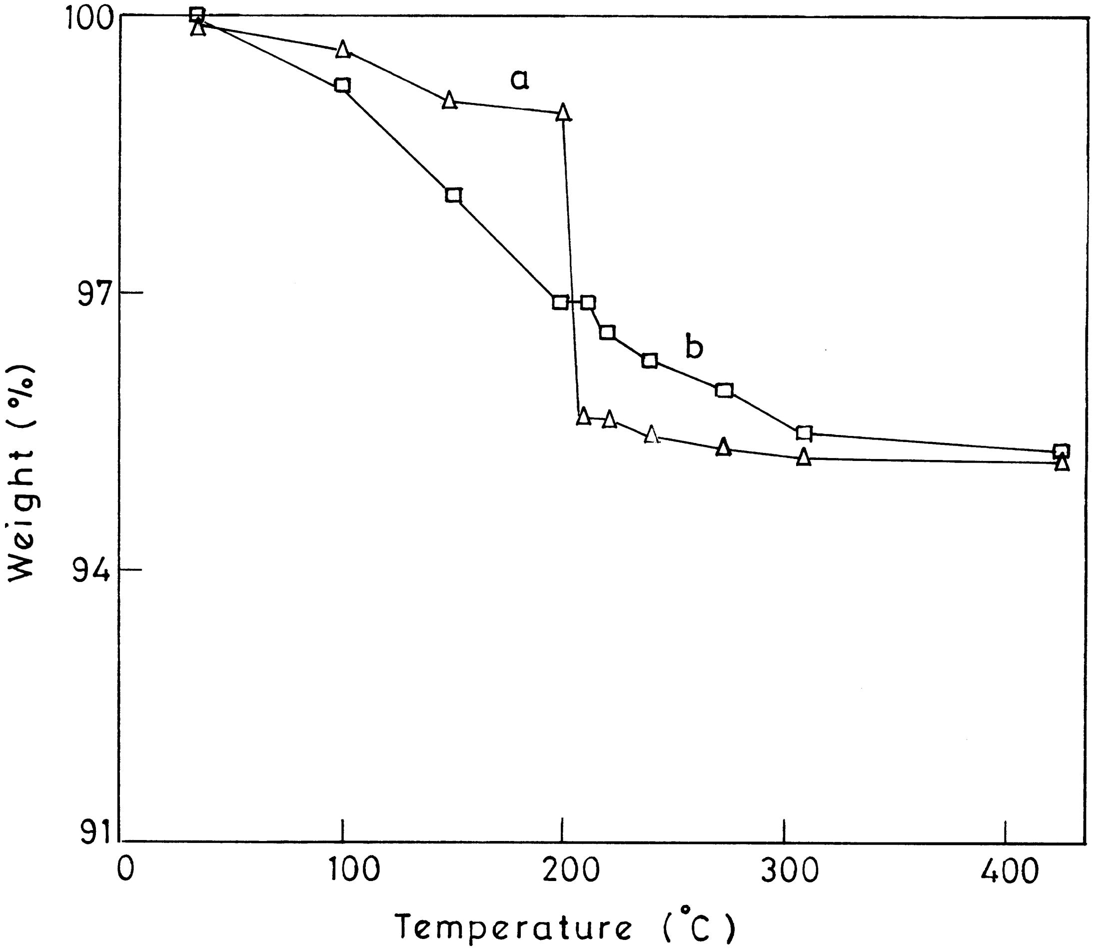


Fig. 5. Thermogravimertic analyses of: (a) hydrophobic (modified) and (b) hydrophilic (unmodified) aerogels.

~4–5 times its own weight within a time period of 5 min. On the other hand, hydrophobic aerogels (modified) adsorbs ⩽2% water of its own weight even after putting them directly on the water surface for a time period of one year. The increase in the aerogel weight (due to adsorption of water) by ⩽2% has been considered as hydrophobic and >2% as hydrophilic. The margin ~2 % was fixed due to the relative error in measuring the exact weight of the aerogel samples. Increase in weight ~4–5 times of its own weight within a time period of 5 min, in case of unmodified aerogels, is due to the fact that surface –OH group is the site where polar molecules like water get adsorbed [14]. On the other hand, in the case of MTMS modified (hydrophobic) aerogels, it has been observed that there is no weight gain after one year even after putting them on the surface of water. This is due to the fact that, incorporation of MTMS in the gel state, lead to dehydroxylation at the silica surface through the chemical reaction as described earlier [Eq. 2]. This alters drastically the physical and chemical properties of the $SiO_2$ surface.

Fig. 3 shows optical transmission (%) ~95% in the case of unmodified aerogels (Fig. 3, curve b) and ~80% in the case of modified aerogels (Fig. 3, curve a) at a wavelength of 900 nm for a sample thickness of 1 cm. Relatively low transparency of modified aerogels can be attributed on the basis of pore size distribution (PSD) (Fig. 4). PSDs are represented as $dV/d(\log r)$ plot, so that the integrated area under the plot directly corresponds to the pore volume. Here 'V' represents pore volume while '$r$' represents pore radius. It is clearly seen from the figure that the PSD for unmodified (Fig. 4, curve b) aerogels is narrow and uniform. The narrow PSD is due to simultaneous occurrence of hydrolysis and condensation which leads to formation of relatively smaller size $SiO_2$ particles and pores (SEM not shown) which results in highly transparent aerogels (~95%). The PSD for modified (Fig. 4, curve a) TMOS aerogels is little broad and shifted towards larger pore radii. This is due to the fact that the hydrolysis rate of tetramethoxysilane (TMOS) is faster than that of MTMS [11] leading to formation of a few larger size pores (SEM not shown) which results in lower transparent hydrophobic aerogels (~80%) compared to hydrophilic aerogels.

In order to study the thermal stability, hydrophobic silica aerogels were heat treated from a room temperature

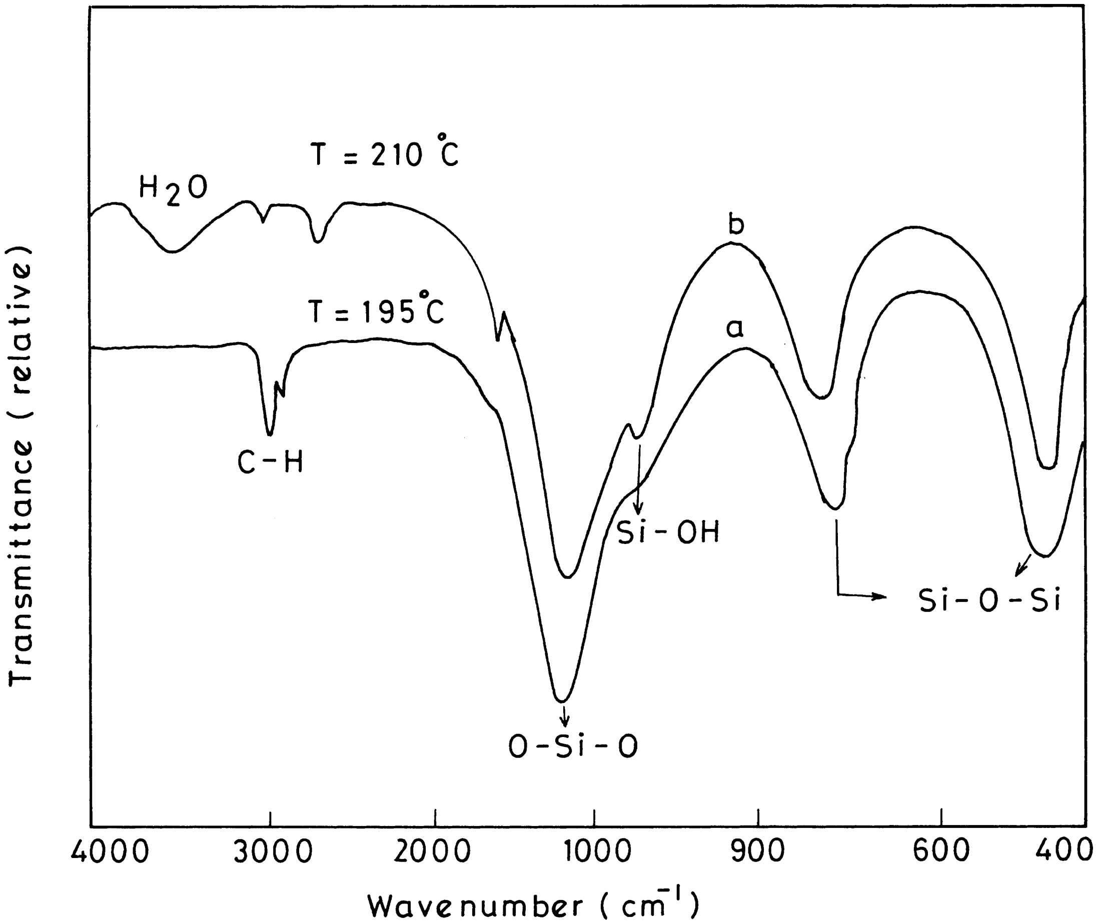
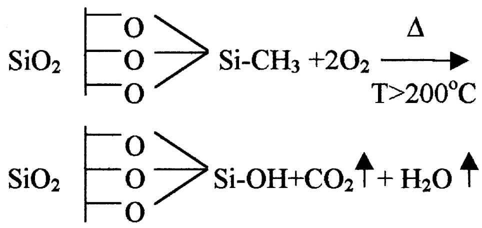


Fig. 6. Infra-red (IR) spectra of heat treated hydrophobic silica aerogels: (a) below threshold temperature ($T$ = 195 °C) and (b) above threshold temperature ($T$ = 210 °C).

(~25 °C) up to 425 °C with a heating rate of 1.5 °C min$^{-1}$ and the weight (%) loss as a function of temperature (Thermogravimetric analysis, TGA) has been recorded (Fig. 5). Of course, unmodified aerogels were also heat treated (Fig. 5, curve b). It has been observed that hydrophobic silica aerogels shows anomalous weight loss (~3.3%) between temperature range of 200 and 210 °C (Fig. 5, curve a). This weight loss is due to thermal decomposition of the organic groups (–$CH_3$ groups). Hence hydrophobicity of MTMS modified silica aerogels is guaranteed up to a threshold temperature of 200 °C above which hydrophobicity vanishes.

Fig. 6 illustrates the infra-red spectra of the hydrophobic silica aerogels which were heat treated below and above the threshold temperature (~200 °C) between wavenumber 4000 and 400 cm$^{-1}$. The absorption peak at 3000 cm$^{-1}$ corresponding to C–H bonding is quite visible in the case of hydrophobic silica aerogels (Fig. 6, curve a) which were heat treated below the threshold temperature (here $T = 195$ °C). Since incorporation of MTMS in sol leads to replacement of surface –OH groups by –$CH_3$ groups as explained earlier [Eq. (2)]. Hence, 200 °C is the approximate temperature above which hydrophobic samples become hydrophilic. Therefore, for the practical applications of hydrophobic silica aerogels as transparent window insulation materials (TWIM) or any other thermal insulation applications, hydrophobic silica aerogels (MTMS modified) are thermally stable up to a temperature ~200 °C, which is much higher than room temperature. Hydrophobic silica aerogels which were heat treated below and above the threshold temperature shows absorption bands at 1080, 800 and 460 cm$^{-1}$ are attributed to different modes of O–Si–O or Si–O–Si vibrations [15]. Moreover, it has been found that in the case of hydrophobic silica aerogels which were heat treated above the threshold temperature, Fig. (6) (curve b) shows absorption bands at 3400 and 2750 cm$^{-1}$ and are characteristics for free or adsorbed water and is accompanied by another band at 1620 cm$^{-1}$. Absorption band around 960 cm$^{-1}$ indicates the replacement of –$CH_3$ groups by –OH groups (Fig. 6, curve b) as per the following chemical reaction:



$$SiO_2(O)_3{>}Si\text{-}CH_3 + 2O_2 \xrightarrow[T>200^\circ C]{\Delta} SiO_2(O)_3{>}Si\text{-}OH + CO_2\uparrow + H_2O\uparrow \quad (3)$$

It is a well known fact that OH is the site where polar molecules like water gets absorbed i.e. leads to hydrophilic nature of aerogels [14].

Fig. 7(a) and (b) indicates the $^{29}Si$ magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra of hydrophobic aerogels which were heat treated below and above the threshold temperature respectively. For hydrophobic silica aerogels, which were heat-treated below threshold, temperature [Fig. 7(a)] shows Si peak at around −115 ppm but an additional carbon peak at 15 ppm has also been observed. This peak indicates the –$CH_3$ content of MTMS. On the other hand, hydrophobic aerogels, which were heat treated above threshold temperature, shows fall in the intensity peak at 15 ppm due to decomposition of organic (–$CH_3$) groups [Fig. 7(b)]. Hence, thermal stability of hydrophobicity is guaranteed up to the temperature ~200 °C.

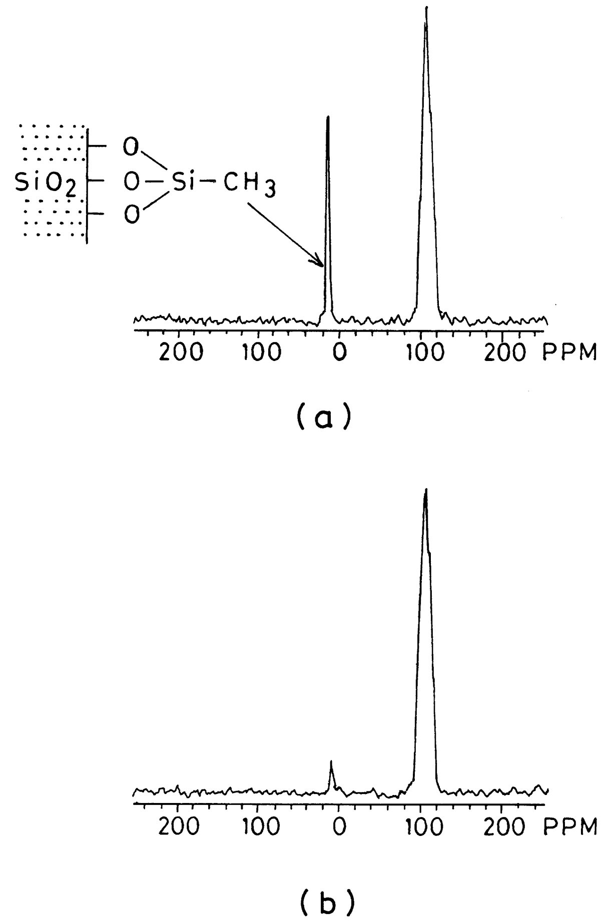


Fig. 7. $^{29}Si$ magic angle spinning nuclear magnetic resonance obtained at 67.9 MHz for the heat-treated hydrophobic silica aerogels: (a) below threshold temperature ($T = 195$ °C) and (b) above threshold temperature ($T = 210$ °C).

## 4. Conclusions

Incorporation of methyltrimethoxysilane (MTMS) at alcosol stage not only yielded monolithic, low density (0.08 g/cm$^3$) but transparent (~80%) and hydrophobic silica aerogels up to a temperature ~200 °C, by means of surface modifications of the surface silicon atoms (i.e. substitution of –OH groups by water resist –$CH_3$ groups).

Hydrophilic aerogels were found to be highly transparent (~95%) compared to the hydrophobic aerogels (~80%). Low transparency of the hydrophobic aerogels is due to the fact that MTMS acts as co-solvent and the hydrolysis rate of tetramethoxysilane (TMOS) is faster than that of MTMS leading to the formation of a few larger size pores. Hence, the pore size distribution (PSD) in the case of hydrophobic aerogels was found to be shifted towards relatively larger size pore radii compared to hydrophilic silica aerogels. From thermogravimetric analyses of hydrophobic and hydrophilic aerogels; it has been found that hydrophobic aerogels shows anomalous weight loss ~3.3% between the temperature range 200 and 210 °C which is due to thermal decomposition of organic (–$CH_3$) groups. Thermal decomposition of organic groups was confirmed by IR and CP/MAS NMR spectral analyses of the hydrophobic silica aerogels, which were heat-treated below and above the threshold temperature. Hence hydrophobicity of MTMS modified aerogels is thermally stable up to a temperature of 200 °C which is much high so far as room temperature is concerned. Studies on the hydrophobicity thermal stability to higher temperatures $\geqslant$700 °C, are in progress.

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