Preface

Silica aerogels are well known porous materials usually derived by sol-gel process followed by supercritical drying. They have open cell structures yielding nanostructured materials with extremely high surface area (~ 1000m$^2$/g). These features lead to the unique properties such as high porosity (~95%), high optical transmission (~ 90% in the visible region), low bulk density (~0.05g/cm$^3$), low thermal conductivity (~ 0.05W/mK). Therefore, the aerogels are emerging as a new class of materials having potential scientific and industrial applications such as efficient thermal insulation for window applications, energy effective green houses and solar ponds for long term energy storage, Inertial Confinement Fusion (ICF) targets for thermonuclear fusion reactions, transparent aerogels as a media in Cerenkov radiation detectors, in radio luminescent devices, catalytic supports, capturing comet dust, hydrophobic aerogels for oil-spill clean up, silica aerogel films in ultra large scale integration circuits.

Various tetra-alkoxysilanes (such as tetraethoxysilane i.e. TEOS and tetramethoxysilane i.e. TMOS) are used as starting materials for the preparation of silica aerogels. It is seen from the literature that TMOS precursor, which is toxic, has been widely used for the preparation of silica aerogels since it gives good quality aerogels in terms of monolithicity, high optical transmission, low bulk density, less volume shrinkage etc. However, there are no detailed reports on the preparation of good quality aerogels using TEOS precursor.

Generally, the TEOS based aerogels have been produced by single step sol-gel process in which only acid catalyst is used and the aerogels obtained by
this method possesses disadvantages such as longer gelation times (minimum 3 days), higher volume shrinkage (~30%), low optical transmission (~65%) and higher densities (~0.2 g/cm³). Also, with the help of this method it is difficult to control the microstructure of the aerogel. However, in the present studies, the two step sol-gel process has been used for the preparation of TEOS based aerogels. The two step sol-gel process uses acid as well as base catalysts in proper proportions and offers an excellent control over the microstructure of the final aerogel product which is the most important aspect as far as the synthesis of monolithic and transparent aerogels is concerned.

Therefore, the present thesis is devoted for the detailed studies on the synthesis of best quality aerogels using TEOS precursor by two step sol-gel process. TEOS precursor was chosen for the present work because it is five times cheaper than TMOS and environmental friendly precursor. The attempts have also been made to obtain the low density TEOS based aerogel and to reduce the cost of the aerogel by using low cost precursor (TEOS) and the cheapest solvent i.e. methanol (MeOH). The problem of aerogel structure deterioration due to the moisture absorption has been overcome by hydrophobicizing the surface of the aerogel with various hydrolytically stable alkyl or aryl groups.

As the synthesis of the aerogels involves colloidal particle formation and condensation of these particles to form three-dimensional porous network, Chapter 1 describes some physico-chemical aspects of colloids. Also, this chapter includes fundamentals about forces between the colloidal particles and
charge on the colloidal particles, shape of the colloidal particles, etc. Molecular kinetic properties of the colloidal particles and fundamentals regarding surface tension and surface energy have also been included in this chapter.

In general, the aerogels are prepared by the sol-gel polymerization of TEOS or TMOS followed by supercritical drying. Therefore, in Chapter 2, the basic concepts underlying sol-gel process have been discussed. The difference between single step and two step sol-gel processes, gelation process and supercritical drying process are also described briefly in this chapter. The aerogels have been characterized by various sophisticated instruments such as Transmission Electron Microscope (TEM) and Scanning Electron Microscope for the nanostructure analysis of the silica aerogels, UV-VIS-NIR spectrophotometer for the optical transmission measurements, C-T meter for thermal conductivity measurements of the aerogels, Fourier Transform Infrared Spectroscopy (FT-IR), contact angle meter, etc. All these techniques have been described in the chapter 2 with the relevant theory.

Chapter 3 describes the experimental results on the synthesis of TEOS based aerogels using ethanol (EtOH) solvent by two step sol-gel process. The various sol-gel parameters such as acid and base catalyst concentrations, molar ratios of precursor, solvent and water have been optimized in order to obtain monolithic, highly transparent aerogels. The oxalic acid (A) and NH$_4$OH (B) base catalyst concentrations were varied from 0 to 0.1M and from 0.4 to 3M, respectively. The time interval (T) before base catalyst addition was varied from 0 to 72 hours. Also the molar ratios of acidic water i.e. (C$_2$H$_2$O$_4$)$_2$H$_2$O/TEOS and
basic water (NH$_4$OH) H$_2$O/TEOS were varied from 1.6 to 7 and 1.2 to 3.5, respectively. The rates of hydrolysis and condensation reactions were found to be optimum at B = 1M and A = 0.001M. The increase in the EtOH/TEOS molar ratio (S) resulted in an increase in the optical transmission of the aerogels and decrease in the volume shrinkage and hence decrease in the bulk density. The best quality TEOS based aerogels in terms of monolithicity, optical transmission (90%), low density (~0.11g/cm$^3$), low volume shrinkage (~10%) have been obtained by the two step sol-gel process for the molar ratio of TEOS:EtOH:H$_2$O(acidic):H$_2$O(basic) of 1:6.9:3.5:2.2, alongwith oxalic acid and NH$_4$OH concentrations of 0.001 and 1M, respectively. The results have been discussed by taking in to consideration the hydrolysis and condensation reactions.

The effect of methanol solvent on the monolithicity, bulk density and optical transmission of the silica aerogels has been studied in Chapter 4. The hydrolysis and condensation of TEOS proceeded in methanol with oxalic acid and NH$_4$OH as catalysts, respectively. The wet gels were supercritically dried in methanol. The advantages of methanol over ethanol are: Methanol is the cheapest solvent and it is five times less costly than ethanol. Also methanol contains smaller chain alkyl group (i.e. – CH$_3$), because of which the aerogels could be produced with higher MeOH/TEOS molar ratio (55) due to the less steric hindrance. Whereas with ethanol (EtOH) solvent, the aerogels with EtOH/TEOS molar ratio > 6.9 could not be obtained since it contains longer chain
alkyl group (-\(\text{C}_2\text{H}_5\)). The use of methanol in the two step sol-gel process resulted in the aerogels with increased optical transmission (~93%), low bulk density (~0.055 g/cm\(^3\)) and low thermal conductivity (~0.04 W/mK). The molar ratio of TEOS:MeOH:acidic\(\text{H}_2\text{O}\):basic\(\text{H}_2\text{O}\) was found to be optimum at 1:33:3.5:3.5 along with the oxalic acid and \(\text{NH}_4\text{OH}\) concentrations at 0.001 M and 1 M respectively. The aerogels have been characterized by transmission electron microscopy, optical transmission and physical properties measurements.

Chapter 5 describes the comparative studies on the hydrophobic and physical properties of the tetraethoxysilane (TEOS) based silica aerogels prepared by two step sol-gel process followed by supercritical drying. Silica alcogels were prepared by keeping the molar ratio of TEOS: Methanol (MeOH): \(\text{H}_2\text{O}\) (acidic): \(\text{H}_2\text{O}\) (basic) constant at 1:33:3.5:3.5 with oxalic acid and ammonium hydroxide concentrations fixed at 0.001 M and 1 M, respectively. In all, nine different co-precursors (C.P.) of the type \(\text{R}_n\text{SiX}_{4-n}\) have been used to hydrophobicize the surface of the silica aerogel. The surface chemical modification of silica aerogels was confirmed by the presence of C-H and Si-C peaks at 2900,1450 cm\(^{-1}\) and 840 cm\(^{-1}\), respectively, in the FTIR spectra. The microstructure of the aerogels was studied using Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) techniques. In addition to these studies, stability of the hydrophobic aerogels against organic impurity (methanol in the present studies) in water has also been studied. The surface chemical modification using phenyltriethoxysilane (PTES) resulted in
transparent (~80%) and hydrophobic aerogels (θ ~140°) with the highest thermal stability, among the all co-precursors, up to a temperature of 520°C. Whereas, the aerogels modified with the trimethylethoxysilane (TMES) showed negligible volume shrinkage with highest θ value of 148°.

Chapter 6 presents the experimental results of the studies on the transportation of water droplets using a superhydrophobic silica aerogel powder coated surface. The superhydrophobic silica aerogels were prepared using sol-gel processing of methyltrimethoxysilane (MTMS) precursor, methanol (MeOH) solvent and base (NH₄OH) catalyzed water followed by supercritical drying using methanol solvent. The molar ratio of NH₄OH/MTMS, H₂O/MTMS and MeOH/MTMS were varied from 1.7 x 10⁻¹ to 3.5 x 10⁻¹, 2 to 8 and 1.7 to 14, respectively, to find out the best quality aerogels in terms of higher hydrophobicity and high droplet velocity. A specially built device was used for the measurement of velocity of water droplet of size 2.8mm (±0.2mm) on an inclined surface coated with superhydrophobic aerogel powder. Liquid marbles were prepared by rolling water droplets on the aerogel powder and the marble(s) velocities on a non-coated inclined surface were compared with that of the water droplets. It was observed that the microstructure of the aerogel affects the droplet as well as marble velocities considerably. For an aerogel with uniform and smaller particles, the water droplet and marble velocities were observed to be maximum i.e. 144 and 123 cm/s, respectively. Whereas, for the aerogels with bigger and non-uniform particles, the water droplet and marble velocities were
observed to be minimum i.e. 92 and 82 cm/s, respectively. The results have been discussed by taking into account the contact angles and microstructural observations. Thus it has been shown that a very small quantity (from a few nano-liters to micro-liters) of liquid can be transported without mass loss, very efficiently on a surface coated with superhydrophobic silica aerogels. In addition, nano to micro liters of liquids can also be transported by coating and rolling the liquid droplets with the superhydrophobic aerogel powder.

The starting material cost being the major obstacle in the commercialization of the silica aerogels, the Chapter 7 describes the production of silica aerogels using low cost alkoxide precursor such as tetraethoxysilane (TEOS) and the cheapest solvent, methanol (MeOH), using two step sol-gel process. Moreover, the experiments on the dilution of the TEOS precursor with methanol solvent to large volumes have also been carried out, which has resulted in ultra low density TEOS based aerogels with further reduction in the overall cost of the aerogel. Monolithic and transparent (~88%) aerogels with ultra low density (~ 0.018 g/cm³) and low thermal conductivity (~ 0.05 W/mK) have been obtained for the molar ratio of TEOS: MeOH: (H₂O): basic (H₂O) at 1:99:6.25:14.58, respectively. The aerogels have been characterized by bulk density, porosity, optical transmission, volume shrinkage and thermal conductivity measurements. The microstructure of the aerogels was studied using Transmission Electron Microscopy (TEM). The results have been discussed by taking into consideration the hydrolysis and condensation reactions.
Chapter 8 describes the synthesis of flexible and hydrophobic silica aerogels using methyltrimethoxysilane (MTMS) precursor by two step (acid-base) sol-gel process followed by supercritical drying. The effects of various sol-gel parameters on the flexibility of the silica aerogels have been investigated. It was observed that Young's modulus (Y) strongly depends on the density of the aerogels. The value of Y decreased from $14.11 \times 10^4$ to $3.43 \times 10^4$ N/m$^2$ with decrease in the density of the aerogels from 100 to 40 kg/m$^3$, respectively. The aerogels are hydrophobic with contact angle as high as 142°. The hydrophobic aerogels are thermally stable up to a temperature of 480°C above which they become hydrophilic.

The general conclusions drawn from these studies and the scope for the future work, in the field of aerogels, have been presented in Chapter 9.

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