Chapter II
Mesoporous Silica Aerogels and Microspheres through Sol-Gel Subcritical Technique

2.1 Synthesis of Silica Aerogels by Varying Experimental Parameters

2.1.1 Introduction

Silica aerogels are sol–gel derived materials which possess unique properties such as large inner surface area, low density, small index of refraction, low sound velocity, low thermal conductivity and low dielectric constant. Hydrolysis and polycondensation of a multifunctional silicon alkoxide followed by supercritical drying is the well known method to prepare silica aerogels. However the supercritical drying process involves the heating and evacuation of highly flammable solvents such as alcohols, which are hazardous at high temperature and high pressures and are also not very ecofriendly. In 1984, in Sweden, the failure in a pilot plant for the production of aerogel tiles released 1000 litres of methanol and a big explosion destroyed the whole building. Problems arise from the combination of high temperatures and high pressure as well as the flammability of the solvents. In addition, the supercritical drying results in aerogels which are fragile having very low strength making it difficult for easy handling.
Ambient pressure drying has evolved as a promising technique for the synthesis of silica aerogels. Main methods adopted for ambient pressure drying include network strengthening and solvent exchange/surface modification of wet gels.\textsuperscript{46,55,56} The increase in stiffness and large pore size bring down the capillary pressure during drying, resulting in low density xerogels. Smith et al. synthesized mesoporous aerogel like materials at ambient pressures by introducing hydrophobic groups in the gel network.\textsuperscript{94} In this method also gel shrinks during drying. However gel undergoes reversible expansion at critical point and retains wet gel structure due to ‘spring back effect’. Schertfeger et al. prepared hydrophobic water glass based aerogels without solvent exchange and supercritical drying.\textsuperscript{56} Aging the precursor gel in silane solution is another approach to obtain high strength.\textsuperscript{49,48,95,96,97} Earlier reports indicate that the mechanical properties of the wet gel are improved by aging in mother liquor at different temperatures.\textsuperscript{98-99} During the aging step, the strength and stiffness of the wet gel increase due to an increased degree of condensation reactions, siloxane cross linking within the gel network, dissolution and reprecipitation of silica and attachment of unreacted oligomers from the gelation process or monomers added from the aging solution.\textsuperscript{52} Titulaer et al. found that the pore structure development on aging spherical silica gel bodies is influenced by temperature, pH and the silica to water ratio which affects the rate of silica transport.\textsuperscript{100} Chou et al. studied the
effect of aging solvent on silica gels.\textsuperscript{101} They related surface area to the polarity parameter of the aging solvent. Hdach et al. investigated the influence of aging and pH on the modulus of aerogels.\textsuperscript{102} Davis et al. reported that aging at higher pH yield lower surface area, larger pore volume and a narrow pore size distribution.\textsuperscript{103} Haereid et al. has shown that by aging TEOS-based alcogels in solutions of TEOS/ethanol the strength and stiffness can be favourably increased and thereby reduce the shrinkage during drying at ambient pressure. Low-density silica xerogels ($\rho = 0.24 \text{ g/cm}^3$) are obtained by changing aging parameters such as time and temperature.\textsuperscript{46,48,95}

Numerous studies are available in literature on the effect of processing parameters on the properties of resultant silica aerogels.\textsuperscript{104} Lee et al. studied the effect of pH on the physicochemical properties of silica aerogels prepared by an ambient pressure drying.\textsuperscript{105} Rao et al. investigated the effect of precursors, methylation agents and solvents on the properties of resultant silica aerogels.\textsuperscript{55} They prepared low density aerogels (0.14–0.3 g/cm$^3$) using TMOS and sodium silicate based recipes and TMCS or HMDS as surface modifiers. Using the TMOS precursor, TMCS; and for sodium silicate precursor, HMDS resulted in the best quality silica aerogels in terms of monolithicity, visual transparency and lowest density. Kumar et al. reported the synthesis of high surface area silica by solvent exchange in alkoxy derived silica aerogel under subcritical conditions.\textsuperscript{106} They
found that solvents of low vapour pressure and high molecular weight favour the formation of gels with high pore volume. Takahashi reported that the solvent exchange influences the pore structure of silica aerogels. However synthesis of silica aerogel at ambient conditions and its commercialization still remain a great challenge. Since various processing parameters have great influence on the structural and porosity features of the resultant aerogel, the experimental parameters has to be investigated in detail. The present study deals with the synthesis of silica aerogel at subcritical temperature and pressure by varying the synthesis conditions. This chapter includes the effect of hydrolysis temperature, gelation pH, aging pH, aging solvent and surface modification on the porosity characteristics of subcritically dried silica aerogels.

2.1.2 Experimental

2.1.2.1 Materials and Methods

Tetraethoxysilane (Fluka Chemicals) was used as the precursor for the synthesis of silica aerogel under acidic conditions. TEOS was mixed with isopropanol (SD Fine Chemicals) and kept for stirring. Acidified water (0.001 M Hydrochloric acid (SD Fine Chemicals) was added to this mixture very slowly. TEOS:isopropanol:water molar ratio was maintained as 1:4:16. The stirring was continued until a homogeneous mixture was obtained. This sol was then transferred to cylindrical moulds for gelation. After gelation, the gels were
transferred to a 1:1 mixture of isopropanol and water for 24 h. The solvent exchange was done using isopropanol. The gels were washed 5 times with isopropanol within 24 h. For aging, the gel was kept in 80% silane solution in isopropanol for different time intervals. The final step of solvent exchange of these gels was carried out with isopropanol. The gels were taken out and dried at 50 °C for one day and 70 °C for two days. Fig. 2.1.1 shows a process scheme for the synthesis of silica aerogel by subcritical drying method. For the present study hydrolysis temperature, gelation pH, aging solvent composition (isopropanol:water ratio) and aging pH (silane:isopropanol) was varied. Hydrophobic silica aerogel was synthesized by surface modification with trimethylchlorosilane.

2.1.2.2 Characterization of Aerogels

Bulk density of the rod shaped gels was calculated using mass by volume ratio. It is the density of the material including pores and interparticle voids.

\[ \text{Volume, } V = \frac{\pi d^2 h}{4} \]

where ‘d’ is the diameter and ‘h’ is the length of the gel.

Specific surface area and adsorption isotherm of the calcined aerogels were obtained using a BET surface area analyzer (Micromeritics, Gemini Model 2360). The samples were preheated in a flow of nitrogen for 3 h at 200 °C to remove all the volatiles and chemically adsorbed water from the surface.
Fig. 2.1.1. Flow chart used for the synthesis of silica aerogels

Structural characteristics of the aerogels were investigated by a Fourier Transform Infrared Spectrophotometer (Nicolet, Magna 560) in the range 4,000-400 cm\(^{-1}\) by the KBr pellet method. Thermal decomposition curves of the dried
aerogels were obtained using a Differential Thermal Analyzer (Schimadzu, DTA 50) in air at a heating rate of 10 °Cmin⁻¹. Contact angles were measured using a Tensiometer (Data Physics, DCTAT11). The increase in square of sample weight, when in contact with water was calculated using the same instrument. Porous morphology of the aerogels was observed by Scanning Electron Microscopy (JEOL, JSM 5600LV) in the secondary electron image (SEI) mode.

2.1.3. Results and Discussion

2.1.3.1 Effect of Hydrolysis-Condensation Conditions

The density measurements and BET surface area measurements are given in Table 2.1.1. Density decreased with the increase in hydrolysis temperature. The decrease in density is due to the increased porosity of the aerogels synthesized at a higher hydrolysis temperature. Surface area analysis also reveals that the aerogels possess high porosity. Surface area, average pore size and total pore volume of silica aerogels synthesized at 60 °C increased to 648 m²/g, 8.8 nm and 1.44 cc/g from 635 m²/g, 6.2 nm and 0.99 cc/g respectively.

According to Iler, polymerization of silica occurs in three stages, 1) polymerization of monomers into particles 2) growth of particles 3) linking of these particles into chains and three dimensional networks. Growth of particles (Ostwald ripening) depend on the dissolution-reprecipitation of silica.²⁶ Dissolution of silica is directly proportional to the temperature.⁶ As the
temperature is increased, small silica particles dissolve and reprecipitate on larger silica particles. Hence in the present study at higher hydrolysis temperature large number of silica particles are dissolved and reprecipitated. This will improve the strength of the gel network which in turn reduces the shrinkage during drying. Hence we could get a higher pore size and pore volume at higher hydrolysis temperature. Solubility of amorphous silica is largely dependent on the pH of the solution also. Hence gelation of silica aerogels in an NH$_3$ atmosphere enhances the dissolution-reprecipitation reactions. Necks between particles grow resulting in an increase in the average pore size of the gel. A comparatively large pore size of 18 nm and a higher pore volume of 2.04 cc/g is obtained. Dissolution-reprecipitation reactions of small silica particles are responsible for the increase in mesoporosity.

As can be seen from Table 2.1.1, the mesopore volume largely contributes to the total pore volume of the aerogels.

Fig. 2.1.2 shows adsorption isotherms of silica aerogels synthesized at different hydrolysis-condensation conditions. All the isotherms show a type IV behaviour which is the characteristics of a mesoporous material. In the case of silica aerogels synthesized under NH$_3$ atmosphere volume adsorption is lower at lower relative pressures and it shows a sudden increase at above 0.8. This is due to the increased mesopore volume. Micropores contribute more to the volume adsorption at lower relative pressures whereas mesopores are responsible for the
volume adsorption at higher relative pressures. As the temperature and pH are increased, Ostwald ripening occurs at a greater extent and the mesopore volume increases.

**Table 2.1.1.** BET surface area analysis and density measurements of silica aerogels synthesized by varying hydrolysis-condensation conditions

<table>
<thead>
<tr>
<th>Sample details</th>
<th>Density (g/cc)</th>
<th>Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Total pore volume (cc/g)</th>
<th>Mesopore volume (cc/g)</th>
<th>Micropore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrolysis (30 °C)</td>
<td>0.54</td>
<td>635</td>
<td>6.2</td>
<td>0.99</td>
<td>0.96</td>
<td>0.03</td>
</tr>
<tr>
<td>Hydrolysis (60 °C)</td>
<td>0.42</td>
<td>648</td>
<td>8.8</td>
<td>1.44</td>
<td>1.42</td>
<td>0.01</td>
</tr>
<tr>
<td>Gelation (NH₃ atm.)</td>
<td>--</td>
<td>452</td>
<td>18</td>
<td>2.04</td>
<td>2.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>

BJH pore size distribution of silica aerogels synthesized at different hydrolysis-condensation conditions are provided in Fig. 2.1.3. As the hydrolysis temperature is increased, smaller pores decreased and larger pores increased in volume. With the increase in gelation pH (NH₃ atm.) a similar trend is observed but to a greater extent. This supports our earlier observation that dissolution-reprecipitation contributes to the increase in the porosity of silica aerogels synthesized at a higher temperature and pH. Larger particles and pores are formed.
at the expense of smaller particles and pores. Hence a decrease in smaller pores and increase in larger pores.

![Graph showing adsorption isotherms of silica aerogels](image1)

**Fig. 2.1.2.** Adsorption isotherms of silica aerogels synthesized by varying hydrolysis-condensation conditions

![Graph showing BJH pore size distribution](image2)

**Fig. 2.1.3.** BJH pore size distribution of silica aerogels synthesized by varying hydrolysis-condensation conditions
2.1.3.2 Effect of Aging Solvent

Table 2.1.2 gives the surface area results of silica aerogel synthesized using different solvent composition in aging step. Average pore size, total pore volume and surface area decreases as water content is increased in the aging solvent. Silica aerogels aged in isopropanol has a surface area 641 m$^2$/g, pore volume 1.27 cc/g and pore size of 7.9 nm whereas water aged sample has a surface area 621 m$^2$/g, pore volume 0.62 cc/g and pore size of 3.9 nm.

Table 2.1.2. BET surface area characteristics of silica aerogel aged in different solvent composition

<table>
<thead>
<tr>
<th>Aging solvent</th>
<th>Surface area (m$^2$/g)</th>
<th>Average pore size (nm)</th>
<th>Total pore volume (cc/g)</th>
<th>Mesopore volume (cc/g)</th>
<th>Micropore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol (IPA)</td>
<td>641</td>
<td>7.9</td>
<td>1.27</td>
<td>1.24</td>
<td>0.03</td>
</tr>
<tr>
<td>IPA:Water (1:1)</td>
<td>635</td>
<td>6.2</td>
<td>0.99</td>
<td>0.96</td>
<td>0.03</td>
</tr>
<tr>
<td>IPA:Water (1:3)</td>
<td>630</td>
<td>4.9</td>
<td>0.89</td>
<td>0.85</td>
<td>0.04</td>
</tr>
<tr>
<td>Water</td>
<td>621</td>
<td>3.9</td>
<td>0.62</td>
<td>0.58</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The decrease in porosity is due to the shrinkage during drying. In the present case this can be attributed to the difference in surface tension of the solvent compositions. Capillary pressure, P_c exerted on the pore walls is directly
proportional to the surface tension of the pore liquid. A high surface tension liquid will generate a high capillary pressure and a greater shrinkage during drying.\textsuperscript{56} Surface tension of isopropanal and water are 23 mN/m and 72.8 mN/m respectively at 20 \textdegree C. Mixture of these solvents has surface tension in between these values. When a high surface tension liquid such as water is used capillary pressure exerted in the pores will be maximum and greater shrinkage occurs for the dried gel structure. Hence the reduction in porosity is observed. In the case of isopropanol aged samples surface tension is minimum at the pore walls and lesser shrinkage to the gel structure during drying. Hence a greater porosity is observed.

Adsorption isotherms of silica aerogels aged in different solvent composition is provided in Fig. 2.1.4. All the isotherms show type IV behaviour (mesoporous materials). At above a relative pressure of 0.6 water aged samples showed a decrease in volume adsorption. Volume adsorption at higher relative pressure are mainly due to the mesopores. Mesopore volume is decreased in the case of water aged samples. Hence the reduction in volume adsorption. Fig. 2.1.5. shows the BJH pore size distribution of silica aerogels aged in various isopropanol:water ratios. Water aged samples have a narrow pore size distribution and majority of the pores lie below 10 nm. Aging in other solvents resulted in a broader distribution. The pore size distribution of 1:3, 1:1 and isopropanol aged samples shift to the higher pore size region. This shift in pore size distribution can
be again attributed to the surface tension of the aging solvent. Low surface tension liquid will exert less capillary pressure and shrinkage during drying. Hence a greater mesopore volume is achieved with isopropanol.

![Graph 1](image1.png)

**Fig. 2.1.4.** Adsorption isotherms of silica aerogels aged in different solvent composition

![Graph 2](image2.png)

**Fig. 2.1.5.** BJH pore size distribution of silica aerogels aged in different solvent compositions
2.1.3.3 Effect of Aging pH

Table 2.1.3 provides BET surface area results of silica aerogels synthesized by changing the pH of aging solution. Surface area decreased from 607 m$^2$/g to 431 m$^2$/g where as pore volume and pore size increased from 0.88 cc/g and 5.8 nm to 1.45 cc/g and 13.5 nm respectively when the aging pH was changed from 3 to 11. Solubility of amorphous silica is proportional to pH. At lower pH, dissolution is minimum and as the pH increases solubility of silica increases. The dissolution-reprecipitation reactions increases the pore size and pore volume. In the case of silica aerogels gelled in NH$_3$ atmosphere (Table 2.1.1), a similar trend is observed. The present results show that even after long time of gelation, aging can influence the final gel structure. The high surface area at an aging pH of 3 can be attributed to small pore size of the aerogel.

Adsorption isotherms of silica aerogels synthesized by aging in different pH are provided in Fig. 2.1.6. All the isotherms show a type IV behaviour which is the characteristic of mesoporous material. For silica aerogels aged at pH ~ 11 volume adsorption is less at lower relative pressures and it is high at higher relative pressures. This shows the high mesoporosity of the samples aged at high pH which is due to the ostwald ripening of silica (Fig. 1.4).
Table 2.1.3. BET surface area characteristics of silica aerogel aged in silanes of different pH

<table>
<thead>
<tr>
<th>Aging pH</th>
<th>Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Total pore volume (cc/g)</th>
<th>Mesopore volume (cc/g)</th>
<th>Micropore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>607</td>
<td>5.8</td>
<td>0.88</td>
<td>0.86</td>
<td>0.020</td>
</tr>
<tr>
<td>7</td>
<td>583</td>
<td>7.2</td>
<td>1.05</td>
<td>1.04</td>
<td>0.007</td>
</tr>
<tr>
<td>11</td>
<td>431</td>
<td>13.5</td>
<td>1.45</td>
<td>1.44</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Fig. 2.1.6. Adsorption isotherms of silica aerogels aged in silanes of different pH

Fig. 2.1.7 shows the BJH adsorption isotherms of silica aerogels synthesized after aging at different pH. As the pH increases pore size distribution

44
becomes broad and shifts to the right. Aging at a pH of 11 resulted in larger pores and contribution from the small pores are very less. Dissolution and reprecipitation of silica occur at a greater extent at high aging pH and hence the increase in mesoporosity.

![Fig. 2.1.7. BJH pore size distribution of silica aerogels in silanes of different pH](image)

2.1.3.4 Effect of Surface Modification

Long term use of pure silica aerogel is not recommended because of the hydrophilicity of the surface hydroxyl groups of the silica. The hydroxyl groups absorb moisture and minimize the inherent properties of silica aerogel. Besides, surface modification of the hydroxyl groups will reduce the condensation during the drying and reduces collapse of the gel structure. Functionalization of these hydroxyls with organic moieties is an interesting area of research. Many research articles and reviews are available in the literature on these aspects. In the
The present study the effect of surface modification with trimethylchlorosilane in the present synthetic conditions was investigated. Fig. 2.1.8 gives the FTIR spectra of silica aerogels with and without surface modification. Both the graphs show the peak of Si-O-Si asymmetric stretching vibration at 1100 cm\(^{-1}\). The intensity of broad peak corresponding to OH stretching (~3500 cm\(^{-1}\)) decreases in the case of hydrophobic silica aerogel. There are additional absorption bands for modified silica aerogels at 2900 and 1450 cm\(^{-1}\) related to C-H bonds and at 840 cm\(^{-1}\) related to Si-C bonds.\(^{113}\)

**Fig. 2.1.8.** FTIR spectra of silica aerogels A) Hydrophilic SiO\(_2\) aerogel

B) Hydrophobic SiO\(_2\) aerogel

DTA of hydrophilic and hydrophobic aerogels are given in Fig. 2.1.9. Hydrophilic silica aerogels show an endothermic peak at around 100 °C due to the
removal of adsorbed water. Such a peak is absent for hydrophobic silica aerogel which means that adsorbed water is absent in silica aerogels treated with trimethylchlorosilane. Exothermic peak at ~500 °C corresponds to the decomposition of methyl groups. Hence silica aerogels loose hydrophobicity at ~500 °C. TGA curve of hydrophobic and hydrophilic aerogels are provided as Fig. 2.1.10. Hydrophilic silica aerogels showed an initial weight loss of ~15% due to the removal of water. This weight loss is less than 2% in the case of hydrophobic silica aerogel.

BET surface area results of hydrophilic and hydrophobic silica aerogel are given in Table 2.1.4. Surface area, average pore size and total pore volume were increased from 621 m²/g, 3.9 nm and 0.62 cc/g to 797 m²/g, 6.4 nm and 1.28 cc/g respectively for hydrophobic silica aerogel. In the case of hydrophobic aerogel surface hydroxyls are replaced with methyl groups. Hence the condensation between hydroxyls at the internal surface of the aerogel is prevented. This will reduce the shrinkage during drying and an increase in average pore size and total pore volume is observed. Spring back effect also contributes to the retention of porosity of the aerogel structure.¹⁰⁹
Fig. 2.1.9. DTA pattern A) Hydrophilic SiO$_2$ aerogel  
B) Hydrophobic SiO$_2$ aerogel

Fig. 2.1.10. TGA curve A) Hydrophilic SiO$_2$ aerogel  
B) Hydrophobic SiO$_2$ aerogel
Table 2.1.4. BET surface area characteristics of silica aerogels

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Total Pore volume (cc/g)</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic silica aerogel</td>
<td>621</td>
<td>3.9</td>
<td>0.62</td>
<td>--</td>
</tr>
<tr>
<td>Hydrophobic silica aerogel</td>
<td>797</td>
<td>6.4</td>
<td>1.28</td>
<td>87°</td>
</tr>
</tbody>
</table>

Fig. 2.1.11 (A & B) shows the behaviour of hydrophilic and hydrophobic aerogels towards water. In the Fig. 2.1.11 A, hydrophobic aerogel float on water whereas hydrophilic aerogel sinks. Fig. B shows a single water drop on a hydrophobic silica aerogel surface. Water drop attains nearly spherical shape due to the hydrophobicity of the aerogel sample. Photographs of silica aerogel monoliths synthesized by subcritical technique are provided as Fig. C. The aerogels are either transparent or translucent which are typical characteristics of silica aerogels. Scanning electron micrograph of silica aerogel (Fig. D.) shows the amorphous nature of the silica as well as uniform distribution of mesopores of size <10 nm.
2.1.4. Conclusions

1. Silica aerogels with tailored porosity were synthesized through subcritical drying technique. Tailoring of porosity was achieved by varying the experimental (hydrolysis temperature, gelation pH and surface modification) as well as aging parameters (aging pH and aging solvent).

2. Hydrolysis temperature and gelation pH influence the porosity of subcritically dried silica aerogels. This can be attributed to an enhancement in the dissolution-reprecipitation reactions of silica by an increase in temperature and pH. Pore size can be varied between 6.2 nm and 18 nm.
whereas pore volume can vary between 0.99 cc/g and 2.04 cc/g by changing the gelation pH.

3. Effect of water content in the aging solvent composition was investigated. Pore size, pore volume and surface area decrease as water content in the aging solvent is increased. The decrease in porosity is due to the high surface tension of solvent.

4. It was found that aging pH affect the porosity of subcritically dried silica aerogels. Surface area decreases from 607 m$^2$/g to 431 m$^2$/g whereas pore size and pore volume increased from 5.8 nm and 0.88 cc/g to 13.5 nm and 1.45 cc/g respectively by changing the aging pH from 3 to 11. This can be attributed to the progress in dissolution-reprecipitation reactions of the silica with an increase in aging pH.

5. Hydrophobic silica aerogel was synthesized by TMCS/n-Hexane surface modification for long term application of aerogels and compared with the properties of hydrophilic silica aerogels synthesized through subcritical drying technique. It has been found that surface modification enhances the mesoporosity of silica aerogels. However oxidation of organic group responsible for hydrophobicity occurs at ~500 °C as evidenced by DTA and hence it loses hydrophobicity above that temperature.
2.2 Synthesis of Silica Aerogel Using Organic Templates

2.2.1 Introduction

Major problems during the synthesis of low-density, high-surface-area materials at ambient pressure primarily arise from the large capillary pressure that occurs during drying (a result of the small pore sizes) and low stiffness (a result of the low-density).\textsuperscript{114} Supercritical drying reduces the capillary pressure to a minimum.\textsuperscript{39} However this technique is not recommended for the commercial synthesis of aerogels because of its expensive and hazardous nature.\textsuperscript{56,115,116} Several methods were attempted to avoid supercritical technique and synthesize aerogel at ambient conditions.\textsuperscript{55,56,57,117} One approach is based on an aging technique in which wet gels are aged in mother liquor to promote dissolution-reprecipitation of silica monomer to improve the strength and stiffness of the network.\textsuperscript{46,95,96,117,118} Another approach is the use of organic additives.\textsuperscript{114,119,120} Organic additives either act as a template or as drying control chemical additive. In both the cases it increases the porosity of silica aerogels. DCCA will reduce the differential drying stresses by minimizing the differential rates of evaporation, and ensuring a gel structure with uniform pore and particle sizes.\textsuperscript{121} DCCA can also control the rate of hydrolysis and condensation reaction, pore size distributions, pore liquid vapour pressure and drying stress. Uniform scale of structure achieved
during gelation results in uniform growth of the network during aging, which increase the strength of the gel and its ability to resist drying stress.\textsuperscript{60}

Influence of various DCCAs in the sol-gel processing of xerogels have been investigated and discussed by many authors.\textsuperscript{59,119} However, a few reports are available in the literature on the preparation of monolithic silica aerogels using DCCAs.\textsuperscript{59,60,62,119,121} Haranath et al. investigated the influence of oxalic acid, glycerol, N, N dimethylformamide and formamide on the optical transmittance and porosity features of TMOS based aerogels.\textsuperscript{121} They found that pore size distribution shifts towards smaller pore radii for acidic DCCA and larger pore radii for basic DCCAs. They also reported that DCCA/TMOS molar ratio of \textasciitilde 0.4 as the limiting value for almost all the modified aerogels, above which cracking probability of the aerogels increased drastically. Polyethyleneglycol was used by some researchers as a template for the synthesis of aerogels.\textsuperscript{62,63} Their study revealed that high concentrations of PEG weaken the solid matrix whereas small concentration of PEG strengthen the matrix. Reetz et al.\textsuperscript{64} used polyvinylalcohol and PEG as biocatalyst supports, because it was found that the lipase activity was significantly enhanced in the presence of these additives. Rao et al.\textsuperscript{122} reported the influence of N, N-dimethylformamide and glycerol on the physical properties of TEOS silica aerogels. They got a narrow and uniform distribution of pores when DCCA was used. However use of organic templates to tailor the porosity of
subcritically dried silica aerogels still remains a great challenge and many factors need to be explored. We synthesized silica aerogels using different concentrations of Polyethyleneoxide (PEO), Cetyltrimethylammoniumbromide (CTAB), Polyethyleneglycol (PEG), Hexamethylenetetramine (HMTA) and investigated their effect on the porosity features of subcritically dried aerogels.

2.2.2 Experimental

Tetraethoxysilane (TEOS, Aldrich Chemicals) is mixed with isopropanol (SD Fine Chemicals) and kept for stirring. Acidified water (0.001M Hydrochloric acid) was added to this mixture very slowly. TEOS:isopropanol:water molar ratio was maintained as 1:4:16. The stirring was continued until a homogeneous mixture was obtained. PEO (MW 80,000.00, Aldrich Chemicals) was added to the sol. Concentration of PEO was varied as 0, 0.1, 0.3, 0.5, 1 weight percentage (wt%) of silica. This sol was then transferred to cylindrical moulds for gelation. After gelation, the gels were transferred to a 1:1 mixture of isopropanol and water for 24 h. The solvent exchange was done by isopropanol. The gels were washed 5 times with isopropanol within 24 h. For aging, the gel was kept in a 80% silane in isopropanol solution for 48 h. The final step of solvent exchange of these gels was carried out with isopropanol. The gels were taken out and dried at 50 °C for one day and 70 °C for two days. Fig. 2.2.1 provides the process scheme used for the synthesis of silica aerogel. The experiment was repeated using CTAB (0.1, 0.3,
0.5, 1 wt%), HMTA (0.1, 0.3, 0.7, 1 wt%) and PEG (0.1, 1, 2, 3 wt%). CTAB, HMTA and PEG (MW 285) was purchased from SD Fine Chemicals.

Fig. 2.2.1. Flow chart for the synthesis of silica aerogel

2.2.3. Results and Discussion

2.2.3.1 Silica-PEO Aerogel

Development of ordered mesoporous structures enhanced the significance of surfactants as templates. Surfactant templated synthesis of mesoporous silica nanostructures is an area of great interest. Matos et al. demonstrated the effect of surfactants on the porosity of carbon xerogels. They found that the addition of cationic surfactant increased the pores size (2–25 nm) and the size of carbon particles whereas anionic surfactants promote larger mesopore size (2–40 nm).
nm and larger than 80 nm) and a bimodal pore size distribution. Polyethyleneoxide block polymers as well as homo polymers have been used as an organic template for the synthesis of mesoporous silica by many researchers. The present study deals with the synthesis of silica aerogels using polyethylene oxide as an organic template.

Fig. 2.2.2 provides DTA and TGA of silica and silica-PEO aerogels (Si-PEO). An endothermic peak corresponding to adsorbed water is observed in the DTA of silica and silica-PEO aerogel. An exothermic peak at around 250 °C in the case of Si-PEO is due to the thermal decomposition of polyethyleneoxide. TGA shows a three step weight loss for both the aerogels. First step corresponds to the desorption of adsorbed water in both cases. Second step of weight loss is due to the chemically adsorbed water in the case of silica aerogels. Si-PEO aerogel showed a greater weight loss at this step since the weight loss due to decomposition of polyethylene oxide overlap with that of chemically adsorbed water.

Fig. 2.2.3 provides adsorption isotherm of Si-PEO aerogels. All the isotherms show type IV behaviour which is the characteristics of mesoporous materials. Table 2.2.1 gives surface area results of silica aerogels synthesized with different concentration of PEO. Surface area, pore volume and pore size initially increases as the concentration of PEO increased from 0.1 to 0.3 wt%. Si-0.1 wt%
PEO has a surface area 731 m$^2$/g, pore size 5.8 nm and pore volume 1.07 cc/g. As the concentration increased to 0.3 wt% these values increased further to 907 m$^2$/g, 18.9 nm and 4.29 cc/g.

Fig. 2.2.2 A) DTA of Si and Si-PEO aerogel

Fig. 2.2.2 B) TGA of Si and Si-PEO aerogel
Table 2.2.1. BET surface area results and dielectric constants of Si-PEO aerogels

<table>
<thead>
<tr>
<th>PEO (wt %)</th>
<th>Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Total pore volume (cc/g)</th>
<th>Micro pore volume (cc/g)</th>
<th>Meso pore volume (cc/g)</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>635</td>
<td>6.2</td>
<td>0.99</td>
<td>0.03</td>
<td>0.96</td>
<td>2.52</td>
</tr>
<tr>
<td>0.1</td>
<td>731</td>
<td>5.8</td>
<td>1.07</td>
<td>0.048</td>
<td>1.022</td>
<td>2.33</td>
</tr>
<tr>
<td>0.3</td>
<td>907</td>
<td>18.9</td>
<td>4.29</td>
<td>0.057</td>
<td>4.233</td>
<td>2.29</td>
</tr>
<tr>
<td>0.5</td>
<td>492</td>
<td>20.8</td>
<td>2.49</td>
<td>0.036</td>
<td>2.454</td>
<td>2.34</td>
</tr>
<tr>
<td>1</td>
<td>672</td>
<td>9.6</td>
<td>1.62</td>
<td>0.047</td>
<td>1.573</td>
<td>2.38</td>
</tr>
</tbody>
</table>

The increase in surface area can be attributed to the corresponding increase in micro as well as mesoporosity. Christine et al. showed that a gradual transition occurs from microporous to micro-mesoporous with increasing PEO content in the sol-gel mixture. The present results also show a similar effect. However, surface area and pore volume decrease above 0.3 wt% of PEO. As the concentration of PEO is further increased to 0.5 wt% in the silica system, the surface area and pore volume decreased to 492 m²/g and 2.49 cc/g respectively. This means that above a
particular concentration, PEO does not increase the porosity of silica system. This is clear as even with 1 wt% PEO, pore volume shows a tendency to decrease.

![Graph](image)

Fig. 2.2.3. Adsorption isotherms of Si-PEO aerogels with different concentration of PEO

The transition from a purely microporous to a micro-mesoporous material is attributed to the solubility limit of the hydrophilic PEO in the silica matrix. Above a critical volume fraction of PEO in the sol-gel mixture, pores will increase in size until the mesopore regime is reached, which can be described by a process of unspecific nanoscale demixing. In other words, the probability of a pore being formed by more than one individual PEO chain increases with the PEO volume fraction. The macroscopic properties of silica made in presence of large amounts of PEO in the sol-gel mixture confirm the unspecific demixing of Si-PEO hybrid by being opaque, the light scattering domains being crystalline PEO.
Samples made with lower PEO volume fractions are transparent and completely amorphous.

2.2.3.2 Silica-CTAB Aerogel

Cationic surfactants (Quarternary ammonium salts) are reported to be efficient templates for the synthesis of mesoporous materials. In the present study CTAB is used as an organic template for the porosity control of mesoporous silica aerogels. Thermal analysis of the Si-CTAB aerogels were carried out using DTA and TGA. Fig. 2.2.4 provides DTA of the hybrid aerogels.

![DTA of Si and Si-CTAB aerogel](image)

DTA of Si and Si-CTAB aerogel shows an endothermic peak at around 80 °C due to the removal of adsorbed water. Many exothermic peaks are observed in the temperature range 200-400 °C due to the decomposition of organic moieties. It has been reported that cetyltrimethylammonium surfactants undergo several
decomposition steps during the calcination. The majority of the surfactants first break down to form hexadecane and a trimethylamine species in the temperature range of 100 to 220 °C.\textsuperscript{131} Upon heating at high temperatures the carbon chain fragments are eliminated and the available surface becomes hydrophilic. Fig. 2.2.5 shows the TGA of Si and Si-CTAB aerogel.

![TGA of Si and Si-CTAB aerogel](image)

**Fig. 2.2.5.** TGA of Si and Si-CTAB aerogel

Both the curves show a three step decomposition pattern. First step is due to the loss of adsorbed water. Weight loss due to adsorbed water is lower in the case of Si-CTAB aerogel. Silica aerogels showed ~20% weight loss at this step whereas Si-CTAB aerogels showed only 12%. This can be attributed to the partial hydrophobicity of Si-CTAB aerogels.\textsuperscript{131} Second step of weight loss which starts from 200 °C is due to the removal of chemically bonded water in the case of silica aerogel. A similar weight loss is observed for Si-CTAB aerogel at this temperature.
range corresponding to the decomposition of organic moieties in the DTA curve. Third step of weight loss corresponds to the dehydroxylation in both the cases.

Fig. 2.2.6 represents adsorption isotherms of Si-CTAB aerogels with different concentration of CTAB. All the isotherms are of type IV which show the mesoporous nature of the resultant aerogels. Table 2.2.2 provides the BET surface area results of Si-CTAB aerogels. Silica aerogel has a surface area of 635 m$^2$/g, pore size 6.2 nm and pore volume 0.99 cc/g. As the concentration of CTAB is increased surface area decreases and pore size and pore volume increases. Si-0.1 wt% CTAB has a surface area 545 m$^2$/g, pore size 8.1 nm and pore volume 1.04 cc/g. As the concentration of CTAB is increased to 1 wt% surface area decreases to 501 m$^2$/g, and pore size and pore volume increase to 19.5 nm and 2.45 cc/g respectively. Intermediate concentrations also showed similar trend. Matos et al. has reported that addition of cationic surfactant increases the pores size (2–25 nm) and the size of particles in the case of carbon xerogels. The decrease in surface area is due to the increase in pore size. Smaller pores have a greater surface area compared to the larger pores. The increase in pore size with respect to the concentration of surfactant is related to the elimination of surfactant upon calcination. Combustion of larger number of organic molecules enhances the porosity of the inorganic matrix.
Fig. 2.2.6. Adsorption isotherms of Si-CTAB aerogels with different concentration of CTAB

Table 2.2.2. BET surface area characteristics of Si-CTAB aerogels

<table>
<thead>
<tr>
<th>CTAB (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>635</td>
<td>0.99</td>
<td>6.2</td>
</tr>
<tr>
<td>0.1</td>
<td>545</td>
<td>1.04</td>
<td>8.1</td>
</tr>
<tr>
<td>0.3</td>
<td>511</td>
<td>1.91</td>
<td>14</td>
</tr>
<tr>
<td>0.5</td>
<td>508</td>
<td>2.21</td>
<td>17.4</td>
</tr>
<tr>
<td>1</td>
<td>501</td>
<td>2.45</td>
<td>19.5</td>
</tr>
</tbody>
</table>
2.2.3.3 Silica-HMTA Aerogel

HMTA is reported as an organic template and cross linking agent for the synthesis of mesoporous materials. Wu et al. has used HMTA as a crosslinking agent for the synthesis of carbon aerogel. They reported that HMTA works not only as a catalyst but also as a cross-linking reagent, which will affect the size and stacking of the organic particles and thus improve the strength of the alcogel network. In the present study we used HMTA as a template for the synthesis of silica aerogels at ambient conditions. Fig. 2.2.7 is the DTA pattern of Si and Si-HMTA aerogel where as Fig. 2.2.8 is the TGA curve of the same.

![Fig. 2.2.7. DTA of Si and Si-HMTA aerogel](image)

An endothermic peak at around 90 °C in the DTA is due to the removal of adsorbed water and is present in Si and Si-HMTA aerogel. This corresponds to ~12.5 wt% loss in the TGA curve. However Si-HMTA aerogel showed a slight
decrease in weight loss (~11 wt%) at this range. The phenomena may be due to the presence of organic groups on the surface of the silica which inhibits the adsorption of water. An exothermic peak at around 250 °C is due to the decomposition of methylene group in Si-HMTA aerogel. This weight loss is observed in the range 200-300 °C in the TGA and it is ~2.5 wt%. The rest of the weight loss in this temperature range corresponds to the removal of chemically bonded water and is observed in the silica aerogel also. Third step of weight loss at above 500 °C corresponds to dehydroxylation.

Fig. 2.2.8 TGA of Si and Si-HMTA aerogel

Table 2.2.3 provides BET surface area results of Si and Si-HMTA aerogels. Surface area, pore size and pore volume increase initially with increase of HMTA concentration and then it decreases. Silica aerogel has a surface area 635 m²/g.
pore size 6.2 nm and pore volume 0.99 cc/g which increased to 884 m²/g, 10.4 nm and 2.3 cc/g with an addition of 0.7 wt% HMTA. The increase is steady up to 0.7 wt%, but it decreases on further addition of HMTA. It has been reported that cross-linking with HMTA enhances the strength of the gel network. Hence a decrease in shrinkage during drying and an increase in porosity of the resultant aerogels. Fig. 2.2.9 provides adsorption isotherms of Si-HMTA aerogel. Isotherms exhibit type IV behaviour indicating the mesoporous nature of the aerogels.

Table 2.2.3. BET surface area results of Si-HMTA aerogels

<table>
<thead>
<tr>
<th>HMTA (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>635</td>
<td>0.99</td>
<td>6.2</td>
</tr>
<tr>
<td>0.1</td>
<td>648</td>
<td>2.06</td>
<td>12.7</td>
</tr>
<tr>
<td>0.3</td>
<td>884</td>
<td>2.3</td>
<td>10.4</td>
</tr>
<tr>
<td>0.7</td>
<td>860</td>
<td>1.84</td>
<td>8.5</td>
</tr>
<tr>
<td>1</td>
<td>648</td>
<td>0.87</td>
<td>5.4</td>
</tr>
</tbody>
</table>
2.2.3.4 Si-PEG Aerogel

PEG has been widely used as a DCCA for the synthesis of mesoporous silica. PEG forms hydrogen bonds both with water and the silanol groups and helps to reduce the capillary pressure during drying.\textsuperscript{133-134} We have adopted PEG as an organic template for the synthesis of silica aerogel at ambient conditions. DTA of Si and Si-PEG aerogel is provided as Fig. 2.2.10. An endothermic peak corresponding to the adsorption of water is observed at ~100 °C in both the case. The exothermic peak at ~300 °C is due to the oxidation of organic compounds.

Table 2.2.4 demonstrates surface area results of Si-PEG aerogels. Surface area increases with increase in concentration of PEG. Si-1 wt% PEG has a surface area of 697 m\textsuperscript{2}/g, pore volume 0.827 cc/g and 4.7 nm which increased to 762 m\textsuperscript{2}/g, 0.982 cc/g and 5.1 nm respectively as the concentration of PEG increased to 3
wt%. The increase in surface area and porosity can be attributed to the removal of organic template upon calcination. Fig. 2.2.11 provides adsorption isotherms of Si-PEG aerogels. All the isotherms are of type IV (mesoporous characteristics).

![Fig. 2.2.10. DTA of Si and Si-PEG aerogel](image)

**Table 2.2.4. BET surface area results of Si-PEG aerogels**

<table>
<thead>
<tr>
<th>PEG (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Total pore volume (cc/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>635</td>
<td>0.99</td>
<td>6.2</td>
</tr>
<tr>
<td>1</td>
<td>697</td>
<td>0.827</td>
<td>4.7</td>
</tr>
<tr>
<td>2</td>
<td>718</td>
<td>0.767</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>762</td>
<td>0.982</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Fig. 2.2.11. Adsorption isotherms of Si-PEG aerogels with different concentration of PEG

2.2.4 Conclusions

1. Silica aerogels were synthesized at ambient conditions using different organic templates such as PEO, CTAB, HMTA and PEG, and investigated the effect of its concentration on the porosity features of resultant aerogels.

2. The pore size could be tailored well and so also pore volume and surface area, by varying the concentration of organic additives. All the aerogels showed type IV adsorption isotherms which are the characteristic of mesoporous materials.

3. Thermal analysis of silica aerogels with organic additives showed that decomposition of organics starts at ~200 °C and completes at ~400 °C. Hence 400 °C was selected as the calcination temperature to eliminate organic templates and attain porosity.
4. Use of PEO (0.3 wt%) as template resulted in a surface area as high as 907 m²/g, pore size 18.9 nm and pore volume 4.29 cc/g. The dielectric constant of the aerogel is found to be 2.29 at 13 MHz.

5. Si-CTAB aerogels showed relatively lower surface area (501-545 m²/g) compared to other organic additives. However we could get a total pore volume of 2.45 cc/g and 19.5 nm for Si-1 wt% CTAB.

6. Si-HMTA aerogels possessed a maximum surface area of 884 m²/g, pore volume 2.3 cc/g and average pore size 10.4 nm for 0.3 wt% HMTA.

7. Si-PEG aerogels possess a lower pore size (4.2 nm-5.1 nm) compared to other silica aerogels. Maximum surface area obtained was for Si-3 wt% PEG and is 762 m²/g. It had a total pore volume of 0.982 cc/g and an average pore size of 5.1 nm.

8. Correlation of the molecular weights of the polymers (PEO and PEG) with the surface area results we could say that molecular weight of the polymers affect the porosity of resultant aerogels. Low molecular weight polymer (PEG, Mw ~ 285) resulted in a lower pore size, pore volume and surface area whereas high molecular weight of the polymer (PEO, Mw ~80,000,00) resulted in a greater pore size, pore volume and surface area.
2.3 Synthesis of Silica Microspheres through Sol-Emulsion-Gel Technique

2.3.1 Introduction

Synthesis of mesoporous materials having regular geometries has been of considerable interest in recent years owing to their great potential in catalysis, adsorption, separation, sensing, medical use, ecology and nanotechnology.\textsuperscript{135-140} Microspheres are widely employed as a feed material for plasma sprayed coatings, as thermal insulators, light weight filler in composites, internal confinement fusion of nuclear material, substrates for controlled drug release and gas storage materials.\textsuperscript{141-144} Microspheres are generally synthesized by the dual nozzle hollow drop generation\textsuperscript{145}, spray pyrolysis\textsuperscript{146}, emulsion–evaporation\textsuperscript{147}, melting in dc plasma\textsuperscript{148}, or sol–emulsion–gel techniques.\textsuperscript{149-152} The sol–emulsion–gel method is widely practiced for the preparation of ceramic microspheres. Mesoporous silica microspheres find application in diverse fields including clinical, pharmaceutical, electronic packaging, selective adsorption, chemical sensing, controlled drug delivery and also in the preparation of silica glass, structural ceramics and chromatographic columns.\textsuperscript{153-154} Artificial opals are SiO\textsubscript{2} microspheres synthesized by self assembly methods to form a close packed structure.\textsuperscript{155} Silica microspheres have been used as an immobilization matrix for several molecules.\textsuperscript{143,144,156} Spherical silica particles with modified surface properties are important in composite materials, adsorbents, pigments, detergents, cosmetics and
pharmaceuticals. Functionalization of the silica particle surface can be used to enhance or control the overall properties. In the present work, a modified sol–emulsion–gel process was developed for the synthesis of hydrophobic silica microspheres. Hydrophobicity was induced by surface modification using trimethylchlorosilane. The sol–emulsion–gel process involves silica sol generated from TEOS as aqueous phase, n-Hexane as the oil phase and sorbitanmonooleate (Span 80) as the surfactant to enhance the emulsion formation. Effect of surfactant concentration, aging time and viscosity of the silica sol on microsphere formation is investigated.

2.3.2 Experimental

The water in oil emulsion was prepared using silica sol as the aqueous phase and n-Hexane (SD Fine Chemicals) as the oil phase. Silica sol was obtained by hydrolyzing tetraethylorthosilicate (Sigma Aldrich Chemie) with $10^{-3}$ M hydrochloric acid (SD Fine Chemicals) using isopropanol (SD Fine Chemicals,) as the homogenizing solvent. The tetraethylorthosilicate:isopropanol:water ratio was kept as 1:4:16. In a typical synthesis of silica microspheres, 20 ml hexane was mixed with 5 ml silica sol and Span 80 (SD Fine Chemicals) was added under stirring (500 rpm). The effect of surfactant concentration on microsphere properties was studied by varying the concentration of surfactant as 0.5, 1, 1.4, 1.8, and 2 volume percentage. Constant stirring for 20 minutes resulted in silica
microspheres. The spheres were decanted, then solvent exchanged (five times) with hexane and the product divided into two parts. One part was made hydrophobic by treating with trimethylchlorosilane (TMCS) (Sigma Aldrich Chemie) for a period of 24 h and the other part was dried at 70 °C. The hydrophobic spheres were solvent exchanged with hexane (five times) after functionalization and dried at 70 °C. The flow chart for microsphere synthesis is provided in Fig. 2.3.1. In order to study the effect of viscosity, silica sols aged for different time periods (2, 5, 8, 11, and 17 h) were used for the preparation of the microspheres.

Fig. 2.3.1. Flow chart for the synthesis of silica microspheres
Rheological behaviour of the precursor sol was monitored using a rheoviscometer (Anton Paar GmbH) employing the cylinder and bob method. Structural characteristics of the microspheres were investigated by a Fourier Transform Infrared spectrophotometer (Magna 560, Nicolet) in the range 400–4,000 cm$^{-1}$ by the KBr pellet method and thermal decomposition curves of the dried microspheres were obtained using a Differential Thermal Analyzer (DTA 50, Shimadzu) in air at a heating rate of 10 °C min$^{-1}$. Specific surface area and adsorption isotherm of the samples were obtained using a BET surface area analyzer (Gemini 2360, Micromeritics). Contact angles were measured using a Tensiometer (DCAT11, Data Physics) under dynamic mode. The increase in square of sample weight, when in contact with water was calculated using the same instrument. Microsphere morphology was observed using an Optical Microscope (MZ16 A, Leica) in transmission mode and by Scanning Electron Microscopy (JSM 5600LV, JEOL) in the secondary electron image (SEI) mode.

2.3.3 Results and Discussion

2.3.3.1 Effect of Surfactant Concentration

In a sol–emulsion–gel process, an aqueous sol phase is dispersed in a nonpolar oil phase to form the emulsion. The high interfacial tension between the aqueous phase and the oil phase is reduced by the addition of an amphiphilic surfactant making the emulsion kinetically stable.$^{163-164}$ Mechanical agitation
provides the energy to overcome the interfacial tension and disperse the aqueous phase to form the emulsion. Surfactant concentration and viscosity of the sol droplets control sphere formation in a sol–emulsion–gel process,\textsuperscript{149-150} and although these influences have been observed in alumina and other systems there are few reports on their effect for silica.\textsuperscript{164} Hence in the present study the effect of surfactant concentration (Span 80), effect of aging time, and sol viscosity on the synthesis outcome have been investigated.

Alterning the concentration of Span 80 modified the morphology, diameter, and uniformity of the resultant silica microspheres (Fig. 2.3.2). For this study, silica sol as prepared (without aging) was used. When 1 vol% surfactant was used, mostly irregular particles were obtained, as sphere formation was incomplete. Probably the concentration of surfactant was inadequate to form a monodispersed emulsion. On increasing the Span 80 concentration to 1.4 vol% smaller and more uniform particles (50 µm) resulted (Fig. 2.3.3). For a surfactant concentration of 1.8 vol% clustering and aggregation was observed while a further increase to 2 vol% yielded larger spheres and many spheres collapsed. The critical micelle concentration (CMC) of the surfactant in the continuous liquid phase controls emulsion stability and hence sphere formation.
Fig. 2.3.2. Optical micrographs of silica microspheres synthesized by varying concentration of Span 80 a) 1 vol% b) 1.4 vol% c) 1.8 vol% d) 2 vol%

Fig. 2.3.3. Scanning electron micrograph of silica microspheres synthesized using 1.4 vol% Span 80

Fig. 2.3.4 shows the variation of surface tension of n-hexane with Span 80, where the discontinuity gives the CMC as between 1 and 1.5 vol%. In a surfactant-hydrophobic solvent system, the surfactant molecules tend to reduce...
unfavorable interactions by minimizing exposure of the hydrophilic end to the hydrophobic solvent molecules by locating at the interface at low concentrations and forming assembled structures at higher concentrations. The minimum concentration required to form assembled structures coincides with the CMC. In an emulsion, when the surfactant concentration is above CMC destabilization of the emulsion, flocculation will ultimately occur, a phenomenon exploited in the fractionation technique of Bibette.\textsuperscript{165} Aggregated and deformed structures result when flocculated emulsion droplets undergo gelation.

![Graph of surface tension of n-Hexane with different concentration of Span 80.](image)

**Fig. 2.3.4.** Surface tension of n-Hexane with different concentration of Span 80

The surface area of the microspheres decreases when the concentration of Span 80 increases (Table 2.3.1). For 1 vol% Span 80 a surface area of 363 m$^2$/g was obtained and it decreases to 296 m$^2$/g for 1.8 vol%. Sol–gel condensation of
silica results in a highly porous gel network which collapse partially during drying, due to stress. The high surface area values are a clear indication of the porous nature of the spheres. The slight increase in average pore diameter with surfactant concentration arises from agglomeration observed for high surfactant concentrations. In the adsorption isotherms (Fig. 2.3.5) spheres prepared at lower surfactant concentrations (1–1.4 vol% Span 80) show a plateau at high pressures that is absent at higher concentrations. This indicates a greater contribution from larger pores (>50 nm) in latter material due to agglomeration. When the contribution to the pore volume from larger pores increases the surface area decreases.

Table 2.3.1. BET surface area results of silica microspheres

<table>
<thead>
<tr>
<th>Span 80 (vol%)</th>
<th>Surface area (m²/g)</th>
<th>Average pore size (nm)</th>
<th>Total pore volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>363</td>
<td>8.3</td>
<td>0.76</td>
</tr>
<tr>
<td>1.4</td>
<td>319</td>
<td>8.5</td>
<td>0.78</td>
</tr>
<tr>
<td>1.8</td>
<td>296</td>
<td>9.4</td>
<td>0.93</td>
</tr>
</tbody>
</table>
2.3.3.2 Effect of Viscosity of Silica Sol

Viscosity of polymeric silica sol varies with time. Kim et al. observed the influence of viscosity of silica sol on sphere formation in a hollow drop generation method for preparing hollow silica spheres. Silica sol aged for different times of 5–17 h were used at a surfactant concentration of 1.4 vol%. Optical microscopy showed that 8 h aging gives more uniform spheres of size ~50 µm (Fig. 2.3.6), with longer times (11 and 17 h) resulting in aggregated and deformed spheres. During aging, condensation reactions proceed in the silica sol and networked clusters start to form. After gelation has proceeded considerably, it will be difficult to form spherical droplets of uniform size and shape from the sol. The optimum
viscosity to obtain uniform spheres represents the balance between the extent of gelation and the droplet sizes achievable for the particular surfactant concentration, volume ratio (discontinuous phase/continuous phase), and shear rate. The viscosity of silica sol aged for different times shows the direct correlation between increasing viscosity and the degree of polymerization between silica particles (Fig. 2.3.7). Under mechanical agitation this polymer network breaks down at higher viscosities.

**Fig. 2.3.6.** Optical micrographs of silica microspheres synthesized after aging the sol for different time intervals (1.4 vol% Span 80) a) 5 h b) 8 h c) 11 h d) 17 h
Fig. 2.3.7. Viscosities of silica sol aged at different time intervals

2.3.3.3 Hydrophobic Silica Microspheres

Fig. 2.3.8 shows the FTIR spectra of silica microspheres with and without surface modification using trimethylchlorosilane. A broad peak at 3449 cm\(^{-1}\) observed for the unmodified and modified microspheres can be ascribed to isolated hydrogen bonded Si–OH groups.\(^6\) Peak intensity is lower in the latter case due to the replacement of Si–OH groups by the organic group leading to reduced hydrophilicity. Silanol hydroxyls undergo silanization with chlorosilane thereby replacing the hydroxyl groups by methyl groups. The peak at 1639 cm\(^{-1}\) corresponds to the deformation mode of adsorbed water molecules in the unmodified sample, and is very weak in the modified sample. The features at 840 and 1275 cm\(^{-1}\) correspond to the Si–C bond present in the hydrophobic silica.
microspheres, while the CH$_2$ stretching vibration is located at 2959 cm$^{-1}$ in the hydrophobic silica microspheres. A schematic representation of the formation of hydrophobic silica microspheres is provided as Fig. 2.3.9.

![Fig. 2.3.8. FTIR spectra of silica microspheres](image)

a) With surface modification b) Without surface modification

Contact angles of different silica microspheres heated at 70 and 350 °C are provided in Table 2.3.2. The increase in weight of the sample when in contact with water is also given. Surface modification with trimethylchlorosilane resulted in contact angle of 90° and in very low weight gain (0.00003 g/s). Spheres without modification showed a contact angle of 84° with an increase in weight per second of 0.00256 g/s and shows that surface modification with trimethylchlorosilane is effective in making the microspheres hydrophobic. Contact angle of unmodified silica decreases to 37° after heating at 350 °C where as contact angle of hydrophobic silica microspheres remains the same. The decrease in contact angle
can be attributed to the removal of some Span 80 that were not washed off by the solvent exchange.

**Fig. 2.3.9.** A schematic representation of formation of hydrophobic silica microspheres

**Table 2.3.2.** Contact angle measurements of silica microspheres

<table>
<thead>
<tr>
<th>Sample details</th>
<th>Contact angle (°)</th>
<th>Increase in weight per second (g²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheres (TMCS modified)</td>
<td>90</td>
<td>0.00003</td>
</tr>
<tr>
<td>Spheres (Unmodified)</td>
<td>84</td>
<td>0.00256</td>
</tr>
</tbody>
</table>

83
Hydrophilic microspheres show strong endothermic peak at ~120 °C due to the removal of adsorbed water, while an exothermic peak is due to removal of residual surfactant at 345 °C (Fig. 2.3.10). The endothermic peak at 120 °C is absent in the case of hydrophobic microspheres as expected. A sharp exothermic peak at 442 °C reflects the decomposition of the methyl groups and so hydrophobicity is retained up to that temperature.

![DTA spectra of silica microspheres A) With modification B) Without modification](image)

**Fig. 2.3.10** DTA spectra of silica microspheres A) With modification B) Without modification

### 2.4.4 Conclusions

1. Silica microspheres (~50 µm) were synthesized through a sol–emulsion–gel technique using Span 80 as the surfactant in silica sol/n-Hexane water in oil emulsion system.
2. Concentration of surfactant and viscosity of silica sol are found to be important factors in the synthesis of SiO$_2$ microspheres. It can be concluded that there is an optimum surfactant concentration and aging time for the silica sol to obtain uniform spheres, below which clustering, aggregation, and structural collapse occur. A surfactant concentration of 1.4 vol% yielded highly regular spheres with a surface area of 319 m$^2$/g and a pore size of 8.5 nm. Silica sol aged for 8 h gave the most uniform spheres when the aging time was varied in the preparation of microspheres.

3. Surface modification by trimethylchlorosilane resulted in hydrophobic microspheres with a contact angle of $\sim$90°. Differential thermal analysis shows that the decomposition of organic moieties responsible for hydrophobicity occur around 440 °C and hence it can be concluded that hydrophobicity is retained up to that temperature.