Chapter 1

Introduction

During the first half of the twentieth century the concept of porosity took a hairpin turn and ceased its existence as a ‘nuisance to ceramic scientists and metallurgists’. Pores became a material in itself and an object to be engineered. One of the earliest materials to base its existence on porosity is unarguably, aerogels. Ever since Kistler demonstrated the supercritical drying to remove solvent from a wet gel without shrinkage, researchers have stretched the limits of human imagination of low density solids.\textsuperscript{1,2} In 1992 Mobil scientists engineered the first crystalline porosity or ordered porosity in silica gels.\textsuperscript{3} This in turn developed in to an upsurge in research on porous materials and further fuelled the interest in highly porous materials. Simultaneously the concept of Metal Organic Frameworks developed to extend the nano engineering of porosity to the microporous regime.\textsuperscript{4} The scopus database cites 7453 articles in the interval 1980-1989, 14,775 for the years 1990-1999 and 25,369 for the year 2000-2009 for the search with the word ‘porous’ in the title. This is a suitable reflection of the rise in the interest on porous materials during these three decades. Even though pores in the whole range from nm to \(\mu\)m are hot topics of research we would limit our description to the nanometre regime, since it is more applicable to the topic of this thesis.

Materials are porous if they contain cavities, channels or interstices that are deeper than they are wide.\textsuperscript{5} The pores may be regularly arranged as in molecular sieves. However, the more common situation is an irregular pore structure, as obtained by cross-linking of polymer chains, aggregation or agglomeration of small particles or selective removal of elements of a solid (e.g. by etching or pyrolysis). The physical properties of a porous solid and its reactivity are effectively influenced by the kind, shape and size of the pores.

Applications of porous materials are limited only by imagination. A large variety of fields depend on porosity for their technological advance. Porous silicon is poised to
take centre stage in the biosensor development efforts owing to its tunable pore size and porosity.6 Further these materials have also found application in drug delivery systems.7 Utilization of a porous medium for combustion of liquid fuels is proving to be a promising approach for future applications. The porous medium burner for liquid fuels is more advantageous than the conventional open spray flame burner for several reasons; these include enhanced evaporation of droplet spray owing to regenerative combustion characteristics, low emission of pollutants, high combustion intensity with moderate turn-down ratio and compactness.8 Porous polymers are the new generation polymers which are particularly investigated for applications in fuel cell membranes, as electrode materials for batteries, for gas storage and also for sorption materials/chromatography.9,10 As the concern over global warming grows the need for renewable and clean energy sources have lead to biofuels. The conversion of biomass to biofuel requires porous materials as catalysts and improving their catalytic activity is an active area of interest.11 Applications of inorganic porous materials in medical science have been reviewed by Wang et al. and include applications like enzyme immobilizing, enzyme simulation, biological sensors, controlled release drug carrier etc.12 Zeolites are complex, highly porous crystals veined with tiny channels made of silicon, aluminium and oxygen and several additional elements. The very small sizes of the pore channels (~1 nm) make them very good molecular sieves and catalysts. Similar properties have been observed for mixed-valent manganese oxides and are now commonly addressed as octahedral molecular sieves (OMS).13 One of the earliest applications of porous materials has been thermal insulations. In thermal insulation panels, the loss of heat by convection can be prevented by the presence of pores in the nanometer regime. When the pore sizes are lower than the mean free path of the gas molecules filling the pores, the gas molecule collides with the pore walls before encountering another gas molecule and the transfer of heat between the molecules is prevented. Materials scientists have nearly exhausted the list of dense materials for achieving low dielectric constants which is very much required for the next generation microelectronics. Porosity is the only alternative to achieve low dielectric constants (k<2).14
**Classification of Porous Materials**

Pores can be considered as cavities extending throughout a solid. Pores can be inherent, be part of the crystal structure as in zeolites or can be engineered as in MCM materials or formed during the preparation process as in sol gel derived silica gels. The pores can be classified as open and closed as applicable to material scientists. Open pores have access to the external surface of the solid where as closed pores are inaccessible. Closed pores are usually formed during processing and by uneven mass transport during thermal treatment.

A convenient classification of pores is according to their average width and is accepted by the IUPAC. Accordingly micropores have width <2 nm, mesopores have average pore width in the range 2-50 nm and above 50 nm, pores are termed as macropores. Unless chemically controlled, porous materials can have pores in the wide range mentioned. Porosity is the ratio of the volume of open pores to the total volume of the solid.

In a porous solid, the surface accessible to a guest molecule will be many times higher than that expected from the simple geometrical dimensions of the individual particles and brings in, the concept of specific surface area. It is the surface area of one gram of solid and values ranging from <<1 - >2000 can be seen in the literature. Adsorption of gases on a solid surface is a direct consequence of surface area. Valuable information regarding surface area and porosity can be obtained from the adsorption isotherm of a gas-solid system. In practice the range of suitable adsorptives are quiet narrow and nitrogen at its boiling point, 77 K is by far the most common adsorptive used to obtain information of specific surface area and porosity. The adsorption behaviour of gases on solid surfaces can be generally grouped into a few types of isotherms.

**Adsorption in Porous Materials**

There are mainly four types of isotherms according to the widely accepted classification of Brunauer, Deming, Deming and Teller classification.
Type I isotherms are characteristic of microporous solids. Here the pores are no more than a few diameters in width and the potential fields from neighbouring walls overlap and the interaction between the gas and solid will be enhanced. The consequence is that the pore filling will take place at a relatively low pressure observed as the increased absorption at low relative pressure of the isotherm. The adsorption approaches a plateau and usually no hysteresis is observed. The plateau corresponds to the complete filling of the pores according to the classical view. If the isotherm us with a sharp knee and a horizontal plateau then the uptake at a point close to saturation pressure can be considered as the total pore volume.

The Type II isotherms are observed when gases are adsorbed on a non porous solid. Since there is no pores to fill it is possible evaluate the monolayer capacity of a solid from the Type II isotherm. The Brunauer Emmett Teller (BET) model is the most successful quantitative model available for the determination of surface area from a Type II adsorption isotherm. The BET model is based on the kinetic model of Langmuir and the surface of the solid is considered as an array of adsorption sites. A state of dynamic equilibrium is assumed where the rate at which molecules arriving from the gas phase and condensing on to the base sites is equal to the molecules evaporating from the occupied sites. While Langmuir adsorption assumes that adsorption occurs only on a single layer, BET model accounts for multiple layers. The assumptions used to include multiple layers are as follows. In all layers except the first layer, the heat of adsorption is equal to the molar heat of condensation ($q_L$). In all layers except the first the evaporation-
condensation conditions are identical. At saturation pressure of the adsorptive, it condenses to a bulk liquid on the surface of the solid, or the number of layers becomes infinite. The BET equation is given as

\[
\frac{n}{n_m} = \frac{c(p / p^\circ)}{(1 - p / p^\circ)(1 + c - 1p / p^\circ)}
\]

where \( \frac{n}{n_m} \) is the occupied fraction of the monolayer capacity, \( p / p^\circ \) is the relative pressure of the adsorptive and \( c \) is given by \( c = e^{(q_1 - q_L)/RT} \) where \( q_1 - q_L \) is the net heat of adsorption. Statistical mechanical treatments show that the parameter ‘\( c \)’ has significance more that that assumed by the BET model. Now ‘\( c \)’ also involves entropic terms as well as energetic terms. When \( n / n_m \) is plotted against \( p / p^\circ \) the curve will have the shape of a Type II isotherm as long as ‘\( c \)’ exceed 2. The shape of the knee depends on the value of ‘\( c \)’ and become sharper as the value becomes greater. When ‘\( c \)’ is less than 2 and still positive the BET equation give rise to a curve having the general shape of a Type III isotherm. As long as ‘\( c \)’ exceeds 2 the BET isotherm has a point of inflection; this point is close to, but not necessarily coincident with the BET monolayer capacity. Actually the value of \( n / n_m \) at the point of inflection may deviate from unity. At the value \( c=9 \) the \( n / n_m \) has been seen to have the value 1, but for values between 9 and infinity the adsorption at the point may exceed the BET monolayer capacity by as much as 15 percent and for values of ‘\( c \)’ below 9 the two quantities deviates more and more widely till at \( c=2 \), the point of inflection disappears.

In practice the Type II isotherm display a rather long straight portion after the ‘knee’. The point where this linear portion begins was taken by Emmett and Brunauer to indicate the completion of the monolayer capacity. The estimation of the monolayer coverage is obtained by applying the BET equation over a range of the isotherm which contains this point.

Type III and Type V isotherms are characterized by convexity towards the relative pressure axis commencing at the origin. The convexity persists through out the
length of the isotherm. These isotherms are characteristic of weakly interacting gas and solid. Type III is in fact given by non porous or macroporous solids while Type V is given by mesoporous or microporous solids. The weak interaction between the adsorbent and adsorbate cause the uptake at relatively low pressures to be small; but once the adsorption starts the adsorbed molecules will promote further adsorption and the isotherm become convex to the pressure axis. Water exhibits Type III adsorption, because the dispersion contribution to its over all interaction energy is unusually small compared to the polar contribution.

The pore size that gives rise to a Type IV isotherm is usually considered mesoporous. The characteristic feature of the Type IV isotherm is the hysteresis loop. The exact shape of the loop varies from one adsorption system to the other, but the amount adsorbed is always greater at any point on the desorption curve than on the adsorption curve.

The hysteresis loop on a Type IV isotherm can be understood based on the capillary condensation theory. According to the Kelvin equation, on thermodynamic grounds, the equilibrium vapour pressure, ‘p’ over a concave meniscus of liquid, must be less than the saturation vapour pressure, ‘p°’, at the same temperature. This implies that the vapour will condense to a liquid in the pores of a solid even when the relative pressure is less than unity. The Kelvin equation is given by

$$\ln \frac{p}{p°} = \frac{-2\gamma/V_L}{RT} \frac{1}{r_m}$$

Here ($p / p°$) is the relative pressure of vapour in equilibrium with a meniscus of radius of curvature $r_m$ and $\gamma$ and $V_L$ are the surface tension and molar volume respectively of the liquid adsorptive. At the inception of the hysteresis loop capillary condensation commences in the finest pores. As pressure increases wider pores are filled until saturation, when the entire system is full of the condensate. If one assumes that the pores are cylindrical and the angle of contact to be zero so that the meniscus is hemispherical the mean radius of curvature $r_m$ will be equal to the radius of the pore less the thickness of the adsorbed film on the walls. By applying the Kelvin equation it is therefore possible
to calculate the minimum radius of pores in which capillary condensation can take place from the relative pressure at the commencement of the hysteresis loop. This minimum radius varies with system but is rarely below 1 nm. The upper limit of the applicability of the Kelvin equation is ~25 nm and is set by the practical difficulty in measuring very low lowering of vapour pressure. So the mesopore range is practically defined by the applicability of the Kelvin equation.

Calculation of pore size from the Type IV isotherm uses the Kelvin equation in the region of the isotherm where the hysteresis occurs. Considering idealised geometries for the pores it can be shown that capillary condensation and evaporation occurs in a cylindrical pore closed at one end and open at the other, at the same relative pressure and there is no hysteresis. But if the cylinder is open at both ends then condensation occurs at a relative pressure different from that of evaporation and hysteresis occurs. The mean radius calculated from the desorption branch using the Kelvin equation will be equal to the core radius (radius of the pore - thickness of the adsorbed film) and twice that of the core radius if calculated from the adsorption branch. Now if a pore is considered with a body which has radius less than twice the core radius of the neck then condensation occur at the base of the pore at a relative pressure different from that required at the neck and if \( r_b/r_n < 2 \) condensation will commence at the base of the pore and will fill the whole pore and neck at the relative pressure where condensation starts in the pore of radius \( r_b \). But evaporation will commence from the hemispherical meniscus at the neck at a relative pressure required for condensation in a pore of radius \( r_n \) and will continue till the core of the body is emptied since the pressure will already be lower than the equilibrium value required for the evaporation from the body. Here the calculation of the mean radius from the adsorption branch leads to the values of the core radius of the body and the desorption branch to the values of the core radius of the neck. A new set of pores that has come to prominence in recent years is slit shaped pores. In such pores, the mechanism of pore filling and emptying are different, pore filling happens by multilayer formation and emptying by capillary evaporation. The difference in hysteresis loops can be usually associated to the pore shape. A new classification of hysteresis loops have been
recommended by the IUPAC and are designated H1, H2, H3 and H4 (figure 1.2.). H1 loops are often obtained for agglomerates or compacts of spheroidal particles of uniform size and array. Corpuscular systems tend to give H2 loops, here pore size and shapes are not well defined. H3 and H4 are obtained with adsorbents with slit shaped pores.

![Figure 1.2.: Types of hysteresis loops](image)

**Synthesis of Porous Solids**

Synthesis of porous solids requires different techniques for pores of different sizes. Pores in the nanometer regime are usually prepared using the templating method. Zeolites are typically synthesized from solutions containing the pore directing agent. Various pore arrangements can be achieved by varying the templating agent. Mesoporous materials are easily achieved by sol gel synthesis. Ordered mesoporous materials are usually prepared by templating using self assemblies of amphiphilic molecules. Porous silicon is prepared by electrochemical dissolution. Macroporous ceramics can be made of either reticulate or foam structure. Reticulate structure is made by burning out a polymeric sponge impregnated with a ceramic slurry. The foam structure is made by producing a foam from evolved gas. The polymer carrier is burnt out leaving a porous ceramic. But sol-gel method is the most versatile due to its application in preparing porous materials with pore sizes ranging from nanometres to micrometers.

**Sol-Gel Synthesis**

Sol-gel synthesis is the widely practiced synthesis technique for the preparation of porous materials. Many variations of the technique can be seen in the literature and
modified techniques are still prevalent in synthesis of a wide range of nano particles. Sol-gel process is a colloidal route used to synthesize ceramics with an intermediate stage of a sol or a gel state. It generally consists of the preparation of a colloidal suspension of a solid into liquid; viz (a sol) and then three dimensional structures of solid enclosing the liquid (gel). The gel on further removal of liquid results in the final material which will be in the hydroxylated state.\textsuperscript{18,21} The starting material used in the preparation of the sol is usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension or sol. The sol undergoes gelation to form a monolithic gel. With further drying and heat treatment, the gel is converted into porous or dense ceramics or glass articles. If the liquid in a wet gel is removed under supercritical conditions, a highly porous and extremely low density material called aerogel is obtained. Applying sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms, ultra fine or spherical shaped, powders, thin film coatings, ceramic fibres, microporous inorganic membranes, monolithic ceramics and glasses or extremely porous aerogel materials.

**Sols & Gels**

A sol is a stable suspension of colloidal solid particles within a liquid.\textsuperscript{22} Particles of a sol are small enough to remain suspended indefinitely by Brownian motion. Sols are classified as lyophobic if there is a relatively weak solvent-particle interaction and lyophilic if the interaction is relatively strong. Lyophobic sols exhibit well defined Tyndall effect. In lyophilic sols the particles are largely solvated and this lowers the differences in refractive indices of two phases. The Tyndall effect is due to the scattering of light from the surface of colloidal particles.

Sol particles are held by Van der Waals forces of attraction or dispersion energy. Van der Waals force is proportional to the polarisabilities of the atoms and inversely related to the sixth power of their separation. This Van der Waals force results from
transitory dipole-transitory dipole interactions (London forces). It is this London forces that produce long range attraction between the colloidal particles.

The attractive potential for two infinite slabs separated by distance, ‘h’ is given by

\[ V_A = -\frac{A}{12\pi h^2} \]

\[ V_A \propto -\frac{1}{h^6} \]

for atoms. ‘A’ is a material property called Hamaker’s constant. Since this attractive force extends over distances of nanometers, sols are thermodynamically unstable.\(^2\) Aggregation can be prevented by erecting necessary barriers of comparable dimensions. Electrostatic and steric stabilization are generally used to make the sols meta stable.

**Figure 1.3.: Diffused double layer**

Electrostatic stabilization is explained by DLVO theory. According to this theory the net force between particles in suspension is assumed to be the sum of the attractive Van der Waals forces and electrostatic repulsion created by charges adsorbed on particles. The repulsive barrier depends on two types of ions that make up the double layer, charge determining ions that control the charge on the surface of the particle and counter ions that are in solution in the vicinity of the particle.\(^1\) For hydrous oxides the charge
determining ions are H⁺ and OH⁻ which establish the charge on the particle by protonating or deprotonating the MOH bonds on the surface of the particle.

\[
\begin{align*}
M\text{-OH} + H^+ & \rightarrow M\text{-OH}_2^+ \quad (1) \\
M\text{-H} + OH^- & \rightarrow M\text{-O}^- + H_2O \quad (2)
\end{align*}
\]

The ease with which the protons are added or removed from the oxide depends on the metal atom. The pH at which the particle is neutrally charged is called the Point of Zero Charge (PZC). At pH greater than PZC equation (2) predominates and the particle is negatively charged, whereas at pH less than PZC equation (1) gives the particle a positive charge. The magnitude of the surface potential depends on the departure of the pH from the PZC, and that potential attracts oppositely charged ions (counter ions) that may be present in the solution.

According to the standard theory, potential drops linearly through the tightly bound layer of water and counter ions, called the stern layer. Beyond the Helmholtz plane ‘h = H’, that is, in the Gouy layer, the counter ions diffuse freely. In this region the repulsive electrostatic potential of the double layer varies with distance from the particle, ‘h’, approximately according to

\[V_R \propto e^{\kappa(h-H)}, h \geq H\]

Where 1/κ is called the Debye-Huckel screening length. When the screening length is large (i.e. κ is small) the repulsive potential extends far from the particle. This happens when the counterion concentration is small. When counterions are present, the potential drops more rapidly with distance. Since the repulsive force, \(F_R = \frac{dV_R}{dh} \propto \kappa e^{-\kappa(h-H)}\) is proportional to the slope of the potential, the repulsive force increases with small additions of electrolyte. (i.e \(F_R\) increases with \(K\)). Large amounts of counter ions collapse the double layer. As the concentration of counter ions increases, the double layer is compressed because the same numbers of charges are required to balance the surface charge and they are now available in a smaller volume surrounding the particle. On further increase in the concentration of counter ions the double layer repulsions are
reduced to the point that net particle potential is attractive and the colloid will coagulate immediately.

When an electric field is applied to a colloid, the charged particles move towards the electrode with the opposite charge. This phenomenon is called electrophoresis. When the particle moves, it carries along the adsorbed layer and part of the cloud of counter ions, while the more distant portion of the double layer is drawn towards the opposite electrode. The slip plane or plane of shear separates the region of fluid that moves with the particle from region that flows freely. The rate of movement of particles in the field depends on the potential at the slip plane known as zeta potential. The pH at which zeta potential is zero is called the isoelectric point (IEP). The stability of the colloid correlates with zeta potential to be around 30-50 mV.

Sols can be stabilized by providing steric hindrance. An example is short chain polymers adsorbed on to the surface of particles. There are two components to this stabilization energy. As the sol particles approach one another, the adsorbed polymer loses configurational entropy. This raises the Gibb’s free energy of the system, which is equivalent to the development of a repulsive force between the particles. In addition, as the polymer layers overlap the concentration of the polymer in the overlap region increases. This leads to local osmotic pressure and a repulsive force between the particles.24

A gel is a porous three dimensionally inter-connected solid network that expands in a stable fashion throughout the liquid medium and is only limited by the size of the container.25 Gel results when the sol loses its fluidity. An important criterion for gel formation is that at least part of the solvent is bound. If the solid network is made up of colloidal particles, the gel is said to be colloidal (particulate). If the solid network is made up of sub colloidal chemical units the gel is called polymeric. In particulate gels, the sol gel transition is caused by physio-chemical effect and in the latter by chemical bonding.

Advantages and General Applications of Sol-Gel Approach

General advantages of sol-gel method that has made it so prominent are,
(1) Increased chemical homogeneity in multicomponent system.
(2) High surface area for the gels or powders that are obtained.
(3) High purity can be maintained because of the absence of grinding and pressing steps.
(4) A range of products in the form of fibers, powders, coatings and spheres can be prepared with relative ease, starting from simple solutions.
(5) Low temperatures for sol-gel process, saving energy and minimizing evaporation losses.
(6) Gels can be moulded in the shape of the final desired object, with dimensions enlarged to allow for shrinkage during drying and sintering.

The most prominent disadvantages of the process are the long processing times, cracking during drying and the expensive alkoxide precursors required for obtaining high purity.

**Solution Chemistry of Silicon alkoxides**

Sol-gel synthesis uses metal alkoxides or salts as the precursor. When the synthesis is done using metal alkoxides it is usually an aqueous based process while the use of metal alkoxides requires a non aqueous medium. In water the metal ions $M^{2+}$ are solvated by water molecules and charge transfer occurs from the filled bonding orbital of water to the empty ‘d’ orbitals of the transition metal. This in turn increases the partial charge on hydrogen and the acidity of water increases. Depending on the acidity of water i.e. the magnitude of charge transfer the following equilibria is established.

$$[M(OH_2)]^{z+} + H^+ \rightleftharpoons [M-OH]^{(z-1)+} + H^+ \rightleftharpoons [M=O]^{(z-2)+} + 2H^+$$

This is generally defined as hydrolysis. In general, hydrolysis is facilitated by increase in charge density on the metal ion, the number of metal ions bridged by the hydroxo(OH) or oxo (-O-) ligand and the number of hydrogen contained in the ligand.\textsuperscript{26}

The hydrolyzed precursors can undergo condensation reactions by either a nucleophilic substitution (1) or through a nucleophilic addition reaction (2).
Near isoelectric point, neutral precursors are able to condense indefinitely to form metal hydroxide or oxyhydroxide products depending on $\delta$ (H$_2$O). When $\delta$ (H$_2$O) <0, hydroxide products are isolated and when $\delta$ (H$_2$O) >0, oxyhydroxides are formed as metal stable intermediates to fully condensed oxides. Whether precipitation or gelation occurs depends on the processing factors like pH, temperature, speed of mixing and also on condensation kinetics.

In non aqueous processing the metal alkoxides undergo the hydrolysis-condensation reactions. The most commonly used alkoxide precursor is silicon alkoxide and they are far more stable and easy to handle than transition metal alkoxides. The solution chemistry of silicon alkoxide can be summarized as follows.

\[
\begin{align*}
\text{Hydrolysis} & : \quad \equiv \text{Si-OR} + H_2O \quad \xrightarrow{\text{Esterification}} \quad \equiv \text{Si-OH} + \text{ROH} \\
\text{Condensation} & : \quad \equiv \text{Si-OR} + \equiv \text{Si-OH} \quad \xrightarrow{\text{Alcoholysis}} \quad \equiv \text{Si-O-Si} \equiv + \text{ROH} \\
\text{Hydrolysis} & : \quad \equiv \text{Si-OH} + \equiv \text{Si-OH} \quad \xrightarrow{\text{Hydrolysis}} \quad \equiv \text{Si-O-Si} \equiv + \text{ROH}
\end{align*}
\]

Hydrolysis occurs by the nucleophilic attack of the oxygen contained in water on the silicon atom. Hydrolysis can happen in acid or base catalyzed conditions. Under acidic conditions alkoxide group is protonated in a rapid first step. Electron density is withdrawn from silicon making it more electrophilic and thus more susceptible to attack by water. The water molecule attacks from the rear and acquires a partial positive charge. The positive charge of the protonated alkoxide is correspondingly reduced making alcohol a better leaving group. The transition state decays by displacement of alcohol, accompanied by the inversion of silicon tetrahedron. The hydrolysis rate is increased by substituents that reduce steric crowding around silicon. Electron providing substituents
that help to stabilize the developing positive charges also increase the hydrolysis rate. In base catalyzed hydrolysis, water dissociates to form hydroxyl anions. The second step involves an $S_{N2}$–Si mechanism in which OH displaces OR with inversion of the silicon tetrahedron. The mechanism is affected by both steric and inductive factors; however steric factors are more important since silicon acquires little charge in the transition state.

Polymerization to form siloxane bonds occurs by either 1) an alcohol producing condensation reaction or 2) by water producing condensation reaction. The overall condensation rate is found to be minimized at around pH 1.5 and maximised at intermediate pH. Protonated and deprotonated silanols are involved in the acid and base catalyzed condensation mechanisms at pH<2 and pH>2 respectively. Under conditions in which depolymerization is suppressed, condensation may lead to molecular networks, whereas in which depolymerization is promoted, restructuring occurs ultimately resulting in the formation of highly condensed colloidal particles.

It is generally accepted that base catalyzed condensation, occurs by an $S_{N2}$-Si mechanism involving a penta or hexa coordinated silicon intermediates or transition states as in the case of the polymerization of silicic acid. The acid catalysed condensation mechanism involves a protonated silanol species. Protonation of silanol makes the silicon more electrophilic and they are more susceptible to nucleophilic attack. The most basic silanol species contained in monomers or weakly branched are the most likely to be protonated. Therefore condensation reactions may occur preferentially between neutral species and protonated silanols situated on monomers, end groups of chains etc. Acid catalysed condensation is a slower transformation than hydrolysis. However silanols protonate more easily when it is at the end of a polymer chain. The polymers obtained are therefore linear with scarcely any branching points.

The hydrolysis and condensation reactions continue and the resultant clusters grow by condensation of polymers or aggregation of particles until the links form between the clusters to produce a single giant cluster, gel. Nuclear magnetic resonance spectroscopy, Raman and infrared spectroscopy and X-ray, neutron and light scattering are the different methods for determining the structural evolution during sol-gel transition.
Sol-gel transition can also be followed by rheological characterization. In the microanalysis, the gel point is defined as the time at which the viscosity is observed to increase abruptly. The structural evolution in the silicate species in solution is explained in scales of different length. On the short length scale, the nearest neighbour of silicon may be an alkoxide group, a hydroxyl group or bridging oxygen (O-Si). On intermediate length scales, oligomeric species (dimers, trimers, tetramers etc) may be linear, branched or cyclic. On length scales large with respect to monomers and small with respect to polymers, structures may be dense with well defined solid-liquid interface, uniformly porous or tenuous network.

There are both equilibrium growth models and kinetic growth models to describe the gelation process. Flory-Stockmayer is the first among the equilibrium growth models which attempted to describe diverges in cluster and mass and average radius accompanying the gelation. This model is qualitatively successful as it correctly describes the emergence of an infinite cluster at some critical extent of the reaction and provides good prediction of gel point. However it does not provide an entirely realistic picture of polymer growth.

Kinetic growth process produces objects with self-similar fractal properties. Schafer and Keefer postulated kinetic models for the growth of gel network based on SAXS data. Two most important models are shown in figure.

Figure 1.4.: Kinetic growth models for silica polymerization
The pH value is the decisive parameter for the relative rates of hydrolysis and condensation of tetra alkoxy silanes [Si (OR)₄]. Under acidic conditions (pH 2-5) hydrolysis is favoured, and condensation is the rate determining step. A great number of monomers or small oligomers with reactive Si-OH groups are simultaneously formed. Under these conditions, reactions at terminal silicon atoms are favoured for electronic reasons. This results in polymeric gels which are formed from chains with few branches; which means in other words, small clusters condense to give a polymer like network with small pores. This process is called reaction limited cluster aggregation (RLCA). In contrast, hydrolysis is the rate-determining step under basic conditions. Due to different mechanism, reaction at the central silicon atoms of an oligomer unit is not favoured. The resultant network is characterized by big particles and large pores (“colloidal” gels). Hydrolysed species are immediately consumed because of the faster condensation. Condensation of clusters with each other is relatively unfavourable because it requires inversion of configuration at one of the silicon atoms involved in the reaction. There, the clusters grow mainly by condensation of monomers. This model is called reaction limited monomer cluster growth (RLMC) or Eden growth.

**Aging of Gels**

The composition, structure and properties of gels continue to change with time even after the gel point, in a process called aging. The subsequent drying of the gel is strongly influenced by the structure developed during aging. Particulate or polymeric gels are aged essentially to increase their strength prior to drying in order to avoid cracking and/or to alter the microstructure of the wet gels and subsequently the xerogel.

Process involved in aging are categorized as

a) Polymerization i.e. increase in connectivity of the gel network

b) Syneresis i.e. spontaneous shrinkage of the gel with the expulsion of solvent

c) Coarsening i.e. increase in pore size and reduction in surface area through dissolution and re-precipitation.
In silica gels made from hydrolysis of alkoxides, it has been shown by NMR and Raman spectroscopy that the number of bridging bonds increases long after gelation. The condensation reaction, proceeds, because of the large concentration of the silanol groups. As new bonds are formed the flexibility of the network decreases. Further hydrolysis and re-esterification can also occur.\(^{18}\)

As condensation reaction proceeds, the increase in bridging bonds causes contraction of the gel network. The shrinkage of the gel and the resulting expulsion of liquid from the pores are called syneresis. The same condensation reaction that produces gelation leads to syneresis. This type of syneresis is called macrosyneresis while microsyneresis is the process of phase separation in which the polymers cluster together creating regions of free liquid and the driving force for this is the greater affinity of polymer for itself than the pore liquid. In organic polymers more syneresis produces turbidity owing to the scattering of light by separate phase. The porosity in dried organic gels is attributed to microsyneresis.

Coarsening is a process of dissolution and reprecipitation driven by difference in solubility between surfaces of different radii of curvature. The result of dissolution-reprecipitation is to reduce the net curvature of the solid phase, small particles disappear and small pores are filled in. So the interfacial area decreases and the average pore size increases. However this will not produce any shrinkage because the centres of particles do not move towards one another.

Dissolution and reprecipitation causes growth of necks between particles, increasing the strength and stiffness of the gel. Under aqueous conditions the particle growth is such that the initial aggregates restructure through dissolution-reprecipitation to form larger, more stable particles, thereby consuming the small primary particles. The mechanism by which this occurs is termed as Ostwald ripening mechanism.

The rate of coarsening is affected by factors that affect solubility such as temperature, pH, concentration and type of solvents. The amount of shrinkage that occurs during drying is dependant on the stiffness of the network.
**Drying of Gels**

The gel consists of a solid network enclosing a continuous liquid phase. Initially the liquid/vapour interface (meniscus) is flat. Evaporation of liquid from the pores of a gel exposes the solid phase. Since the solid/vapour interfacial energy ($\gamma_{SV}$) is larger than the solid/liquid interfacial energy ($\gamma_{SL}$), the liquid tends to squeeze out from the interior of the gel to cover the exposed solid. As the liquid stretches to cover the solid, tensile stress develops in the liquid and compressive stress is imposed on to the solid phase. The meniscus begins to develop a curvature; the pressure in the liquid at the exterior surface (Pc) is related to the radius of curvature of the meniscus (r) by,

$$P_c = \frac{2(\gamma_{SV} - \gamma_{SL})}{r}$$

Initially the gel is so compliant that the compressive stress causes viscoelastic deformation of the solid, drawing it under the surface of the liquid. The network shrinks as fast as the liquid evaporates, and the liquid/vapour meniscus remains at the exterior surface of the gel. This is known as the constant rate period.18

As the gel shrinks its stiffness increases, because the solid network becomes more tightly packed and the aging process occurs concurrently. As the gel stiffens, the pressure (Pc) at the surface of the liquid rises until the meniscus reaches its maximum curvature, and the capillary pressure,

$$P_r = \frac{(\gamma_{SV} - \gamma_{SL})S_p}{V_p}$$

Where $S_p$ and $V_p$ are the surface area and volume of the (liquid filled) pore space. When the gel is too stiff to contract under the pressure, shrinkage stops. This is known as the leather hard point. The amount of shrinkage that occurs up to that point depends on the amount of aging. After the Leather hard point the shrinkage drops abruptly. The leather hard point is also referred to as critical point of drying, as the chance of cracking of the gel is high at this point. The extent of shrinkage, collapse of gel structure and
structural changes during drying of a gel greatly depends on the initial gel structure, the aging steps involved before drying, the nature of pore fluid and the method of desiccation.

Aging helps to reduce cracking of gels. However, there are other approaches, including surfactants, drying control chemical additives, hypercritical drying and dialysis. Surfactants reduce the interfacial energy and drying control chemical additives (DCCA) like formamide and oxalic acid produce larger and uniform pores. DCCAs also improve the strength of the gel.

Supercritical drying is the method by which the shrinkage of the gel network can be avoided completely. Liquid phase cannot exist above supercritical point. The interfacial tension between a solid and a gas is very small compared to that between liquid and the solid. So, when a wet gel is subjected to temperature and pressure above the supercritical point of the pore liquid, it is converted to the gas phase and the gas can be evacuated without developing any sort of drying stress. This technique leads to the formation of aerogels where the gel network is maintained as such, even after drying.

**Aerogels**

The main component of this material is air which is surrounded by a very filigrane, solid network. The network is highly porous and has a density that is only three times that of air. SiO₂ aerogels have a high transparency that is close to that of glass, a thermal conductivity corresponding to that of polystyrene or polyurethane foams, or very high specific surface areas, like in charcoal. Combination of these physical properties, related to different chemical compositions, in one material define the uniqueness of aerogels. Important aspects for various applications are thus combined, for example, for heat insulation, optical applications, sensors, catalysts, or catalyst carriers. Aerogels can be defined as materials in which the typical structure of the pores and the network is largely maintained while the pore liquid of a gel is replaced by air.

The structures of aerogels are characterized by well accessible, cylindrical, branched mesopores. Aerogels are unique among mesoporous materials owing to their extremely high porosity (low density), high specific surface area, and the possibility of
making monoliths. Aerogels can also be obtained as granulates or powders. The bulk density of aerogels is in the range of 0.004 - 0.500 g cm\(^{-3}\) owing to the high porosity.

Formation of the highly porous three-dimensional network is one of the key steps in the preparation of aerogels. This can be achieved for inorganic, inorganic-organic, and purely organic systems under controlled conditions. Network formation demonstrates the influence of chemical parameters, in particular the kind of precursors and the reaction conditions, on the resulting microstructure. The microstructure influences the macroscopic properties of the resulting solid. This is of particular interest to aerogels since the network is preserved throughout the drying process. To derive information on structure of aerogels one requires methods which cover the length scale from the lower nanometer (structure of the primary particles) to the micrometer range (linking of the particles).\(^{30}\)

**Synthesis**

Sol-gel synthesis is the irreplaceable part in aerogel synthesis. A detailed discussion of the process has been presented in the previous sections. Modifications to the precursor or incorporation of foreign compounds can be added to the general sol-gel procedure.

The added role of the solvent in aerogel synthesis has to be emphasized. In general sol gel solvent act as the homogenizing agent and chelating agent; and also influences the network formation. Since gelation results in only a marginal change in volume and the drying process during the aerogel production, the volume of the aerogel body (and thus its density) is determined by the volume of the reaction solution. Therefore, the density of aerogels is simply modified by varying the precursor concentration in the starting solution.

Nearly all metal or semimetal oxides are known to form gels, and many served for the production of aerogels. Originally Kistler used water glass for his preparation of aerogels.\(^1\) But the process was time consuming due to the need for ion exchange and subsequent solvent exchange. The use of alkoxide precursor in the synthesis of aerogel was first introduced by Teichner.\(^{31}\) Tetramethoxysilane in ethanol was used as the
precursor. The pore liquid now mainly consisted of alcohol, and therefore the wet alcogels could be dried supercritically without solvent exchange. The preparation of aerogels from polymeric gels is more difficult, because diffusion processes are strongly inhibited by the smaller pores. Complete removal of the pore liquid is therefore more difficult and results in greater shrinkage upon drying. For this reason SiO$_2$ aerogels are usually prepared by base-catalyzed reaction of tetramethoxysilane (TMOS) or tetaethoxysilane (TEOS), usually with ammonia as the catalyst. Brinker first prehydrolyzed the alkoxide with a small amount of water under acidic conditions. This results in the formation of small clusters of silicic acid. In a second step a defined amount of aqueous acid or base is added. Networks formed by this two step procedure have a structure similar to that of the reaction limited cluster aggregation model; that is, they have polymeric character. The probable explanation is that the reactive clusters formed in the first step as structure-forming units are strongly responsible for the formation of the network, independent of the kind of catalyst used in the second step. The main difference caused by base or acid catalysis in the second step is the stiffness of the resulting network. The former results in a stiffening which stabilizes the gels. With this two-step procedure a more deliberate control of the microstructure and thus the particle and pore sizes of the SiO$_2$ gels is possible. The group of Hrubesh used the two-step sol-gel process to vary the density of aerogels within a larger range. When aerogels are made by simple base-or acid-catalyzed reactions, their density is restricted to 0.030-0.300 g/cm$^3$ because the alcohol formed during hydrolysis shifts the equilibrium towards species with alkoxy groups. This results in long gelation times. Tillotson and Hrubesh removed the alcohol by distillation after the first step and replaced it by an aprotic solvent (e.g. acetonitrile). Deliberate dilution, base-catalyzed hydrolysis of the remaining Si-OR groups, and condensation of the SiO$_2$ particles resulted in the formation of a three dimensional network and a solid with a density of only 0.004 g/cm$^3$. Pajonk on the other hand synthesized oligomeric polyethoxysiloxanes of a certain size from TEOS by adding an exact amount of water and used these defined oligomers as precursors for sol-gel processing to form the three-dimensional network. BASF, Hoechst, and others
developed a procedure in which a solution of aqueous sodium silicate is ion-exchanged and then hydrolyzed under acidic conditions. For the production of Basogel, the aerogel product of BASF, a two step-procedure was applied. A solution of sodium silicate is mixed with sulfuric acid in the first step. Small hydrogel or aquagel droplets are formed by spraying. The metal salts are then extracted, and the water is exchanged for an organic solvent. The gel droplets are then supercritically dried.

Tetramethoxysilane (TMOS) undergoes a more rapid hydrolysis than tetraethoxysilane (TEOS) and Wagh has compared the aerogels obtained from three different precursors: TEOS, TMOS and PEGS (polyethoxydisiloxane) and claimed that TMOS yields narrow and uniform pores and higher surface area than TEOS. Aerogels have also been prepared from unusual precursors like rice hull ash.

Schwertfeger revisited the use of waterglass as a cheaper silica source for aerogel synthesis and Einarsrud confirmed that waterglass, produced aerogels with the highest degree of monolithicity because these gels had the highest stiffness and the largest pore size.

The choice of alcohol as a solvent in the sol-gel process is due to the solubility of water and alkoxide in it. But it is also a byproduct of the reaction and can increase the rate of the esterification reaction, the backward reaction. Zhang used methylene chloride to dissolve MTES and Dai promoted ionic liquids. Einarsrud dissolved the acid catalyst in ethylacetoacetate and added this mixture to PEDS.

**Aerogels of oxides other than silica**

The principles for network formation of SiO₂ gels also hold for non-silicate inorganic gels and aqueous solutions of salts or molecular precursors in organic solvents can be employed for sol-gel processing. Metal alkoxides of titanium, zirconium, tin, or aluminum are much more reactive towards water than alkoxyilanes. This is due to the lower electronegativity and higher Lewis acidity as well as the possibility of increasing the coordination number. The reactivity towards water is so high for many of these alkoxides that precipitates are spontaneously formed. Hence the reaction rates of metal alkoxides must be reduced to obtain gels instead of precipitates. The most common
method is the addition of a ligand like acetic acid or acetylacetone to the precursor solution. Compared to aerogels with a silicate network, one of the most important differences of metal oxide aerogels is the possibility of forming crystalline primary particles. Alumina aerogels are one of the most extensively studied metal oxide aerogels particularly for catalytic applications. TiO₂ and ZrO₂ aerogels are mostly prepared from alkoxide precursors. TiO₂ aerogels can be prepared totally amorphous or with a network of anatase primary particles. Similar attempts have been successful with V₂O₅, Cr₂O₃, Fe₂O₃, MoO₂, Nb₂O₅. Binary and ternary oxide aerogels of mixed oxide systems have also been reported. Metal impregnated aerogels are another group of aerogels that has profound catalytic applications.

**Organic aerogels**

Organic polymers starting from organic monomers can be supercritically dried to give a new class of monolithic aerogels. The most extensively studied of these materials are the resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF) aerogels. They can be prepared by polycondensation of resorcinol or melamine with formaldehyde in a slightly basic aqueous solution, often with sodium hydroxide or sodium hydrogen carbonate as the gelation catalysts. Small clusters of approximate size 2 nm are first formed. The structure can be considered as branched polymeric species characterized by a mass fractal dimension. These clusters aggregate and form particles 4-7 nm which show a surface fractal dimension. The structure is then fixed by gelation, in a temperature range from 238 to 333 K. Finally the particle surface is smoothed out by aging. Other precursors used to make organic aerogels include phenolic-furfural (PF) mixtures with poly- (dimethylsiloxane) (PDMS), 2,3-didecyloxyanthracene (DDOA) with ethanol or supercritical CO₂ as the solvent, polyacrylonitrile (PAN) or polyisocyanates. The organic aerogels reported are non transparent. Bulk densities are of the order of 0.24 g cm⁻³ and a specific surface area of approximately 300 m² g⁻¹. Pyrolysis of organic aerogels, at temperatures above 500 °C, produces an electrically conductive carbon network. These networks retain the high specific surface area (400-800 m² g⁻¹), the large specific mesopore volume (>0.55 cm³ g⁻¹), and the isotherms with a hysteresis loop of their parent
organic aerogel.\textsuperscript{70,71} These materials are called carbon aerogels and are of extreme interest in energy research for super capacitor applications.

**Organic Inorganic Hybrids**

The possibility of combining the properties of organic and inorganic compounds in a unique material is an old challenge that started with the beginning of the industrial era. The concept of 'hybrid organic inorganic' materials emerged only very recently, when the interest shifted to more sophisticated materials with a higher added value. The blending of organic and inorganic components and the synergism of their properties in one material is particularly useful and allows the development of materials with totally new properties. Recently, the study of organic inorganic nanocomposite networks and gels became an expanding field of investigation. These new materials promise new applications in many fields such as optics, electronics, ionics, mechanics and biology. At first glance, these materials can be considered biphasic, where the organic and inorganic phases are mixed at the nm to sub-\(\mu\)m scales. But the properties of these materials are not just the sum of the individual contributions; the role of the inner interfaces is predominant. The nature of the interface has been used recently to divide these materials into two distinct classes.\textsuperscript{72} In class I, organic and inorganic compounds are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure. In class II materials, the two phases are linked together through strong chemical bonds (covalent or ionic-covalent bonds). Obviously, within class II hybrid materials, organic and inorganic components can also interact via the same kind of weak bonds that define the class I hybrids.\textsuperscript{73}

Thermal stability of organics are limited to around 250 °C, and the sol-gel process offers the most viable synthesis methodology for processing the hybrids. Hybrid materials are made by mixing organic and inorganic components. Control of the properties of the final material is achieved by controlling the chemical nature of the organic and inorganic phases, the size and morphology of these domains (nm to sub-\(\mu\)m scale) and the nature of the interphase interaction.
Small organic molecules entrapped in an inorganic network is the most simple representation of a hybrid material. It corresponds to the doping of sol-gel matrices by organic dyes, inorganic ions or molecules, resulting in fluorescence, photochromic or non-linear optical (NLO) properties. Organic molecules such as rhodamines, pyranines, coumarins, porphyrins, phthalocyanines and spiropyrans, as NLO dyes have been entrapped in inorganic networks such as silica, aluminosilicate or transition metal oxide based gels (ZrO$_2$, TiO$_2$).$^{74-76}$ Transparent monoliths of large size with a tunable refractive index can be obtained for optical applications by filling the pores of sol-gel derived matrices by a monomer (methylmethacrylate, butadiene and derivatives, etc.) and polymerizing it inside the pores. The properties can be tuned depending on the size and geometry of the holes, the difference in the refractive index between the two phases and the organic:inorganic ratios.$^{77,78}$ Inorganic clusters have also been prepared inside a polymer structure by starting from the polymer and metal alkoxide.$^{79}$ In extension to this method is the use of organically modified metal alkoxide precursors. Here there is no preformed network and both organic and inorganic networks are prepared from the monomers. This leads to interpenetrating organic inorganic networks which may be linked together by covalent bonds.$^{80,81}$ Organically modified silane precursors are the most extensively investigated group of alkoxides and are now available commercially with organic groups with variety of functional groups and chain lengths.

Sol-gel processing of organically modified silanes can be done sequentially. First, the inorganic network is created by the polycondensation of the silicon alkoxide, which leads to the formation of the inorganic network surrounded by organic groups. In the second step, the organic polymerization is achieved. Organic polymerization of methylmethacryl, vinyl, ally and epoxy R’ groups have been extensively studied and described. The polymer brings new properties to the inorganic network like flexibility, hydrophobicity, refractive index modification, etc.$^{82}$ Organic groups which are no longer reactive have also been investigated. These network modifiers (e.g. Si-CH$_3$) are studied extensively for surface modification of films or particles in the fields of corrosion protection, surface treatment, membranes and chromatography.
The concept of organic inorganic hybrids in aerogels widens the spectrum of properties of aerogels without influencing the existing positive properties, such as good heat insulation, transparency, and high surface area. Most frequently encountered examples are the improved hydrophobicity and the elastic properties of SiO₂ aerogels by the incorporation of organic groups.⁸³,⁸⁴

Modification of aerogel network after drying imposes serious difficulties due to the need to expose the filigrane network to liquids which usually results in the shattering of the network. Gas phase reaction is an alternative but of limited use due to the ease in modifying the network prior to drying.⁸⁵-⁸⁷ A more useful route is the integration of organic molecules or groups already during sol-gel processing. Embedding molecules into gels without chemical bonding is achieved by dissolving the molecules in the precursor solution. The gel matrix is formed around them and traps them. The network is then dried to obtain the modified aerogel. Doping the aerogels with fluorescent dyes has been successfully attempted for applications ranging from fluorescent probes to sensitized solar cells.⁸⁸-⁹¹ Fullerene doping has also been attempted to achieve luminescence.⁹²-⁹⁵ Similar efforts have been reported for incorporating polypyrrole in carbon aerogels for photovoltaic applications.⁹⁶

One of the earliest attempts in the direction of organic inorganic hybrid aerogels is the hydrophobisation of aerogel surface using alkyl modified groups. The need for hydrophobic aerogels for long term applications have led to investigations using several alkyl groups with reactive ends that can react to surface silanols. Alkyl modified silanes can be co-condensed with tetraalkoxysilanes to induce hydrophobicity in the final aerogel. Triethoxysilane, ethyltrimethoxysilane, methyltrimethoxysilane, phenyltrimethoxysilane, polyethoxydisiloxane, trifluoropropyltrimethoxysilane, hexamethyldisilazane etc. has all been used to modify the hydrophobicity of aerogels.⁹⁷-¹⁰⁵ Rao et al. has compared the effect of six co-precursors on the hydrophobic properties of the final aerogels.¹⁰⁶ On the other hand Tris(hydroxymethyl)aminomethane has been incorporated in to the gel during condensation to impart hydrophobicity.¹⁰⁷ Surface modification with
trimethylchlorosilane is a standard procedure for the modification of aerogel surface, but involves the evolution of toxic HCl during the process.\textsuperscript{108}

The use of methyltrimethoxysilane precursor for the preparation of aerogels has also given rise to one of the most fascinating developments in the fields, flexible aerogels. The aerogels prepared from methyltrimethoxysilane alone could endure up to \(~ 80\%\) linear compression and then spring back to more than 95\% of their original size. The bulk modulus of these flexible aerogels was found to be comparable to values for conventional silica aerogels. But the Poisson’s ratio was 0.12 compared to 0.2 of silica aerogels indicating that the relatively soft and continuous skeletons undergo a substantial deformation, by folding inward towards the pores.\textsuperscript{109,110} These aerogels had contact angles as high as 160°.\textsuperscript{111,112}

Kim et al. attempted the preparation of aerogel-PVB composites by hot pressing in order to overcome the mechanical limitations of aerogels. Starting from a waterglass precursor and using a surface modification treatment using trimethylchlorosilane technique they prepared aerogels at ambient pressure. Aerogels were crushed and mixed with PVB. They found that a mixing technique involving wet mixing of aerogels with PVB and mixing this composite with aerogel powder prior to hot pressing gave homogeneous composites with aerogel properties.\textsuperscript{113}

Novak investigated the development of interpenetrating organic inorganic network in sol-gel materials and their effect on mechanical properties.\textsuperscript{114} In aerogels, their first approach involved addition of preformed polymers poly(2-vinylpyridine), poly [methylmethacrylate-co-(3-trimethoxysilyl)propylmethacrylate]], and silanol-terminated poly(dimethylsiloxane) (PDMS) to the sol-gel precursor solutions. In another approach they formed the organic polymer cross-linked poly(N,N-dimethylacrylamide) in situ.\textsuperscript{115} In both cases they found that the bonding of the organic phase to the SiO\textsubscript{2} structure is important and crosslinking of the organic polymer further improved the properties. Schaefer studied the structure of arylene-bridged polysilsesquioxane derived aerogels and xerogels and found domains in the nanometer range with distinct fractal character. They associate these domains with porosity rather than microphase separation of organic and
inorganic moieties. The higher the organic content, the smaller the domain size.\textsuperscript{116} Mackenzie observed that in polydimethylsiloxane modified hybrid systems, from a macroscopic mechanical point of view, the behaviour ranges from brittle solids to rubbery elastomers according to the polymer content.\textsuperscript{117} de la Rosa-Fox investigated these hybrid aerogels for their mechanical properties and found that the clustered elementary particles of inorganic porous silica aerogel of 1–2 nm average size are surrounded by the organic polymer forming blobs of 6–8 nm average size, which are mass fractal with dimension of 2.5. These units were clustered into larger aggregates maintained in equilibrium by the “frozen-in” elastic constraints between such units.\textsuperscript{118}

Leventis added a new dimension to the organic inorganic hybrid aerogels when he started nano engineering aerogels to increase mechanical strength.\textsuperscript{119} In order to strengthen monolithic aerogels the interparticle necks need to be widened. To accomplish this with minimum addition of new material, the contour surface of silica was used as a template for the deposition and growth of the interparticle cross-linker. Initially he chose the reaction between the surface silanol groups and a diisocyanate to introduce a polyurethane like network to reinforce the aerogel structure. The procedure involved the immersion of the hydrogel in a propylene carbonate/diisocyanate solution for the crosslinking. The gels were then dried supercritically to form the crosslinked aerogel. These composite aerogels were less hygroscopic and more robust than pure silica aerogels. There was a dramatic improvement in the strength of the new material as tested with a three point flexural bending method and took more than 100 times higher load to break a monolith with density 0.447 gcm\textsuperscript{-3} (~15 kg) than to break a native silica aerogel monolith (~120 g).\textsuperscript{119} His group further extended the work to tri-isocyanates and also changed the isocyanate delivering solvent to acetone, which reduced the processing time considerably. Even though the density of the crosslinked aerogels increased compared to pure silica aerogels, large part of the porosity was retained and low dielectric constant, close to that of native aerogel was obtained. The increased shrinkage was then attributed to the compression of the inorganic network due to the organic networking. The method reinforced the aerogel structure by a factor of ~300 times.\textsuperscript{120} The isocyanates reacted not
only with surface silanols, but also with surface adsorbed water to form amines which further reacted with isocyanate to give polyurea networks. In order to control the network formation and to convert the crosslinking network to polyurea network, the same group modified the inner lying silica surface with amine functionality. This was achieved by co-condensing amine modified silane precursor along with TEOS. This eliminated the formation of polyurethane network formed from the reaction between surface silanols and isocyanate. They also observed that the all compressive specimens failed due to lateral strain. The observed properties were found to depend quadratically on the silane concentration, isocyanate concentration, water concentration, number of washings performed after gelation and temperature of synthesis. The diisocyanate was replaced with epoxy functionalities to develop an epoxy crosslinked network. It was found that while elastic modulus follows a similar trend with density, maximum strength is attained neither at the maximum density nor at the highest concentration of amine groups, suggesting surface saturation effects. Aerogels cross-linked with the trifunctional epoxide always show improved strength compared with aerogels cross-linked with tetra or di epoxides under identical conditions. On reacting the surface amine groups with p-chloromethylstyrene free-radical polymerization process could be initiated using AIBN and styrene to develop a polystyrene network. These mechanically strong aerogels had very high hydrophobicity (>120 °).  

**Drying methods**

Drying is the most important step in the preparation of aerogels. This is the stage where the property of an aerogel is decided against that of the xerogel. If the drying happens without the shrinkage of the gel network then aerogel results, considerable shrinkage leads to xerogels. According to earlier definition, only supercritically dried gels were called aerogels. But ambient pressure drying techniques has developed considerably in recent years and aerogel like properties have been achieved by drying at ambient pressure.

Evaporation of the liquid from a wet gel is very complex, and occurs in different stages. At the first stage, the gel shrinks by the volume that was previously occupied by
the liquid followed by the liquid flowing from the interior of the gel body to its surface. If the network is compliant, as for gels derived from alkoxides, the gel deforms. Upon shrinkage, hydroxyl groups at the inner surface approach and condense with each other. As drying proceeds the network becomes increasingly stiffer and the surface tension in the liquid rises correspondingly, because the pore radii become smaller. In the second stage of the drying process the gel body is too stiff for further shrinkage and the surface tension is no longer capable of deforming the network. At this critical point the tension in the gel becomes so large that the gel cracks. During the second stage of drying, the liquid/gas interface retreats into the gel body. Nevertheless, a continuous funicular liquid film remains at the pore walls; that is, most of the liquid still evaporates from the exterior surface of the gel body. In the next stage of drying this film is ruptured. Eventually only isolated pockets contain liquid, which can leave the network only by diffusion into the gas phase. Collapse of the network can happen due to two reasons: First, the slower shrinkage of the network in the interior of the gel body results in a pressure gradient which causes cracks. Second, larger pores empty faster than smaller ones during drying; that is, the meniscus of the liquid drops faster in larger pores and the walls between pores of different sizes are therefore subjected to uneven stress and crack.  

Supercritical drying eliminates the capillary stress by eliminating the gas liquid interface. Practically, supercritical drying consists of heating the wet gel in a closed container, so that the pressure and temperature exceeds the critical temperature, Tc, and critical pressure, Pc, of the liquid entrapped in the pores inside the gel. Supercritical drying is performed either hot (organic solvents) or cold (CO2) depending on Tc. Commonly used organic solvents are acetone and alcohol and the conditions required are about 250 °C and 5 - 8 MPa. Problems arise from the combination of high temperatures and high pressures as well as the flammability of these solvents. In addition to the risks connected with supercritical drying in organic fluids, rearrangement reactions in the gel network are highly probable because of the high temperatures. Organically modified aerogels are particularly sensitive to the high temperatures, and functional organic groups may be destroyed during drying. An alternative to drying in organic solvents is the use
of liquid carbon dioxide.\textsuperscript{128,129} The advantage of the process is the low critical
temperature (31 °C) and moderate critical pressure (7.3 Mpa) required. Exchanging the
original pore liquid for liquid CO\textsubscript{2} is required and is determined by the diffusion of
carbon dioxide into the gel, and is therefore dependent on the dimensions of the gel body.
Hence the solvent exchange process is time consuming.\textsuperscript{33} Deliberate structural changes
can be induced in SiO\textsubscript{2}/TiO\textsubscript{2}, ZrO\textsubscript{2}, and Nb\textsubscript{2}O\textsubscript{5} aerogels by varying the temperature above
T\textsubscript{c} during supercritical drying with CO\textsubscript{2}, for example, the ratio between crystalline and
amorphous regions.\textsuperscript{130}

Another possibility for avoiding phase boundaries between the liquid and gas
phases during drying is freeze-drying. The pore liquid is frozen and then sublimed under
vacuum. Several attempts were made to use this method for producing aerogels.\textsuperscript{131}
However, aging periods have to be extended to stabilize the gel network, the solvent must
be exchanged for another with a low expansion coefficient and a high pressure of
sublimation, and low freezing temperatures should be achieved by addition of salts.
Another disadvantage is that the network may be destroyed by crystallization of the
solvent in the pores. Cryogels are therefore only obtained as powders.

Even though the low temperature supercritical drying brought down the risks
involved in supercritical drying large scale application still prefers an ambient pressure
process that will give aerogel properties.\textsuperscript{35} Efforts in this direction have always been part
of the growing aerogel technology. Kirkbir studied the drying of silica gels using
different solvents at various pressures ranging from supercritical pressures to atmospheric
pressure. Aerogels could be thus obtained at pressures much lower than the supercritical
pressure depending on the solvent.\textsuperscript{132} Techniques for ambient pressure drying mainly
centre on increasing the strength and stiffness of the gel network and hydrophobisation of
the gel surface.

Increasing the strength and stiffness of the gel network help the gel to cope with
the stress developed during drying. Aging of the wet gel in a precursor solution mostly
tetraethylorthosilicate is a general method to increase the stiffness of the gel. Haereid et
al. studied the effect of aging of alkoxide derived gels in silane solution. New monomers
add to the already formed network and hydrolysis, condensation and specific precipitation of these monomers favourably increase the strength and stiffness of the alcogel.\textsuperscript{133} In tetramethoxysilane (TMOS)-based gels, the shear modulus, $G$, was increased by 15 times and the corresponding shrinkage was reduced by about 30% giving xerogels with a considerably lower density compared with unaged samples. Density as low as 0.24 gcm\textsuperscript{-3} could be achieved by changing aging parameters such as time and temperature. Monomers precipitate on to necks between the primary particles, where the silica solubility is lowest and then in the smallest pores. The shear modulus increased by 23 times and the modulus of rupture by five times, reducing the corresponding shrinkage during drying to \~ 0.5%. They also identified that the removal of water from the pores of the gel prior to drying and the use of a low surface tension liquid as the drying solvent improved the drying technique.\textsuperscript{134-137} They later extended the technique to water glass based aerogels. Colloidal silica based gels had an added advantage that their pore radius was larger and hence the capillary stress developed was low.\textsuperscript{138} Fidalgo observed that the chemical control, particularly pH of the hydrolysis condensation reactions could give aerogel like properties when dried at ambient pressure.\textsuperscript{139} Einarsrud has reviewed the aging of the wet gel in the precursor solution and subsequent silylation to improve the gel strength for drying at ambient pressure.\textsuperscript{140,141} This formed the basis of the ambient pressure process developed by Rajesh et al. which was successfully extended to mixed oxide aerogels by Aravind.\textsuperscript{46,142} They optimised the aging concentration, aging time and temperature to obtain high surface area aerogels.\textsuperscript{143,144}

Hydrophobisation of the gel network prior to drying introduces a large concentration of alkyl groups on the inner surface of the gel. During ambient pressure drying the shrinkage of the gel network cannot produce irreversible pore collapse due to the elimination of condensation reactions between the silanol groups on the pore walls. Further more on close approach the bulky alkyl groups start to repel and the repulsion push back the gel network to the original shape. This spring back effect is exploited for the ambient pressure drying of aerogels. The method was demonstrated by Brinker for the preparation of aerogel films at ambient pressure.\textsuperscript{145} Later Schwertfeger used the process
to dry water glass derived gels to obtain aerogels. Rao et al. further compared the effects of precursors, alkoxide and water glass, different solvents and surface modifying agents to obtain transparent aerogel monoliths through modified ambient pressure drying. They found that the while alkoxide precursors with the modifying agent, hexamethyldisilazane and alkane solvents gave the best transparency, water glass based aerogels had the best monolithicity based on the strength and larger pore sizes. Investigations on the effect of preparation conditions were also performed. Recently the research team from Korea successfully demonstrated the spring back phenomenon on water glass derived silica gels on drying at ambient pressure. Ideal ratios could be identified which gave gels that could recover fully from drying shrinkage.

**Applications of aerogels**

Applications of aerogels are limitless and almost every feature of aerogel gives rise to a potential application. The table points to the versatility of the material.

Apart from these other very interesting applications has also been reported. Some of the interesting reported commercial applications include: wastewater treatment, moulds for casting aluminium metal, aerocapacitors, and heat storage device for automobiles, cosmic dust capture, muonium atom studies, and helium phase transition studies.

Aerogels were used for particle detection using the Cherenkov Effect even in the early 1980s. High energy physics studies relied on aerogels having specific refractive indexes for threshold detectors. Preparation of large aerogel plates were attempted for application in Cherenkov counters. Another important early application of aerogel material was as fuel capsules for direct-drive, inertial confinement fusion experiments.

The supercapacitor is a high power density, high energy density, electrochemical double layer capacitor that uses carbon aerogels as electrodes. The electrodes possess very high surface per unit volume and are electrically continuous in both the carbon and electrolyte phases.
### Table 1.1. Property and corresponding possible application of aerogels

Aerogel materials exhibit the lowest thermal conductivities of any of the solid or porous materials. This key property of the material leads to many applications including insulation for architectural purposes, piping, heat and cold storage appliances and devices, automotive exhaust pipes, transport vehicles and vessels.\(^\text{158}\)

Catalytic applications of aerogels are obvious. Almost all catalytic oxides can be prepared in the form of aerogels. Compounded by these facts there are numerous reactions that can be thought of which can be catalyzed by aerogels. Some are nitrooxidation of hydrocarbons to nitriles (NiO/Al\(_2\)O\(_3\) with SiO\(_2\) and MgO, PbO/ZrO\(_2\)), hydrogenation of nitrobenzene to aniline and of toluene to methylcyclohexane (Ni/SiO\(_2\), Pd/Al\(_2\)O\(_3\)), hydrogenation and hydrogenolysis after hydrogen spillover activation (ZrO\(_2\),

<table>
<thead>
<tr>
<th>Property</th>
<th>Features</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity</td>
<td>Best insulating solid</td>
<td>Architectural and appliance insulation, portable coolers, transport vehicles, pipes, cryogenic, skylights</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Spae vehicles and probes, casting molds</td>
</tr>
<tr>
<td></td>
<td>High temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lightweight</td>
<td></td>
</tr>
<tr>
<td>Density / porosity</td>
<td>Lightest synthetic solid</td>
<td>Catalysts, sorbers, sensors, fuel storage, ion exchange</td>
</tr>
<tr>
<td></td>
<td>Homogenous</td>
<td>Targets for ICF, X-ray lasers</td>
</tr>
<tr>
<td></td>
<td>High surface area</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Multiple composition</td>
<td></td>
</tr>
<tr>
<td>Optical</td>
<td>Low refractive index solid</td>
<td>Cherenkov detectors, lightweight optics, lightguides, special effect optics</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Multiple composition</td>
<td></td>
</tr>
<tr>
<td>Acoustic</td>
<td>Lowest sound speed</td>
<td>Impedance matchers for transducers, range finders, speakers</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Elastic lightweight</td>
<td>Energy absorber, hypervelocity particle trap</td>
</tr>
<tr>
<td>Electrical</td>
<td>Lowest dielectric constant</td>
<td>Dielectrics for ICs, spacers for vacuum electrodes, vacuum display spacers, capacitors</td>
</tr>
<tr>
<td></td>
<td>High dielectric strength</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High surface area</td>
<td></td>
</tr>
</tbody>
</table>
SiO₂, MgO, Al₂O₃), isomerizations (Nb₂O₅, Nb₂O₅/SiO₂), Fischer-Tropsch syntheses (Fe₂O₃/Al₂O₃, Fe₂O₃/SiO₂), polymerization of ethene or propene (TiCl₄/Al₂O₃), deNOₓ reactions (Fe₂O₃/Cr₂O₃/Al₂O₃, Pt/C), catalysis for combustion of car exhaust (Pd/Al₂O₃, Pt/Al₂O₃, Pd/Al₂O₃/SiO₂), and fluorinations (Cr₂O₃).³⁵,¹⁵⁹-¹⁶¹

Aerogels can be sintered at low temperatures and can therefore be processed to extremely pure and totally homogeneous glasses.¹⁶²-¹⁶⁵ Partially sintered aerogels can be used for the storage, thickening, or transport of liquids, like rocket fuels.¹⁶⁶

SiO₂ aerogels are suitable as ecologically sound insecticides against pests in grain and seeds or on the ground, such as mites, ticks, cockroaches, or silver fish.¹⁶⁷-¹⁷⁰

SiO₂ aerogels are currently one of the standard media for collecting cosmic dust, and they are fixed outside a spacecraft.¹⁴⁹ Silica aerogels were also engaged in the PATHFINDER MARS mission to insulate the Sojourner Mars Rover, which had an inside temperature of 21 °C, even when the outside temperature of Mars dropped to -67 °C at night. The space exploration applications of aerogels have been well reviewed by Jones.¹⁷¹

Power et al. described a solid biosensor prepared and tested under the form of an aerosol of aerogel containing Escherichia coli and the green fluorescent protein (GFP). When a virus, like the bacteriophage T7 polymerase promoter also in the form of an aerosol, contacts the bacteria, green fluorescence is emitted. Silica aerogels offer the advantage to immobilise the sensor part of the detector, which can then give an easily detectable and even quantified response to a biological organism existing as an aerosol in the environment.¹⁷²

In the search of new biomaterials for clinical applications that require low density bioactive monoliths with high pore volume, like small bone prosthesis, organic-inorganic hybrid aerogels have been tested for their bioactivity.¹⁷³

Silica aerogels has also been investigated for nuclear waste confinement. Since aerogels can be easily converted to glass, the approach will give waste, immobilised in glass matrix at pretty low temperatures.¹⁷⁴
A novel concept of using aerogels as an architectural model for the creation of functional 3-D linked quantum dots has been reported. According to this methodology metal chalcogenide nanoparticles are assembled into nanostructures by controlled oxidative removal of surface thiolate ligands, followed by supercritical drying to retain the structure of the wet gel. The technique represents an effective way to organize metal chalcogenide nanoparticles into 3D architectures without the presence of intervening ligands that can potentially limit the electron transport properties and thermal stability.\textsuperscript{175}

The research and application of photoactive molecules confined or covalently bound in an inorganic network has been increased over the last few years, since they excite much interest in the fluorescent sensors fields. Fluorescent benzazole dyes have been covalently bound to the aerogel silica matrix with an eye on potential applications like UV-light polymer stabilizers, solid-state laser dyes, fluorescent probes for labelling proteins and scintillation detectors.\textsuperscript{176}

Solid state dye lasers are new application prospect investigated for aerogels. Open porous network of the aerogel was saturated with laser dyes dissolved in appropriate organic monomers, and polymerized inside the silica structure. Highly photostable laser emission with good lasing efficiency was observed.\textsuperscript{177}

Aerogels present a vivid landscape of potential applications and the recent advances in the field have proved that the possibilities are really endless.
Definition of the Present Problem

As observed in the introduction aerogels present a seemingly endless possibility of applications in a vivid landscape of areas and are limited only by the brittleness and the supercritical drying required for the preparation. As pointed out, the need to explore ambient pressure drying for aerogel like materials is inevitable for the wide scale and commercial applications for these materials. Even though many attempts are made for using ambient pressure drying techniques with varying degree of success, there is need for further investigation to incorporate new developments in the fields. For example, organically modified aerogels have escorted the aerogel technology to the new functional materials era, but the attempts to incorporate these advances in to the ambient pressure drying techniques is largely missing from the state of the art in aerogel technology.

Leventis has demonstrated the advantage of developing organic networks coexisting with the inorganic network in preparing mechanically strong aerogels. Simultaneously Warrier’s group had optimised the conditions for an ambient pressure drying technique for the synthesis of high surface area silica aerogels. This thesis envisages combining the concept of organic inorganic hybrid networks and ambient pressure drying for aerogel like hybrid networks. The organic functionalisation and ambient pressure process for its preparation is expected to double the potential impact of these materials in the field.

Optimisation of the ambient pressure process for organic inorganic hybrid aerogels is primarily required. Chemical control of the sol-gel reactions by varying the parameters like precursor ratio, water for hydrolysis ratio and the effect of an organic crosslinker also needs to be addressed. Moreover, the actual performance of the network needs to be compared with that of supercritically dried aerogels. Demonstration of a potential application is also necessary.

So the effect of organically modified precursors on the properties of ambient pressure dried aerogels will be investigated first. Crosslinking of the organic groups will be attempted next. This requires the identification of a polymerisable organic group which will be compatible with sol-gel processing. 3-glycidoxypropyl group is an epoxy
group which can link by the polymerization of the epoxy group. The epoxy polymerization is far more facile than other reported cross linking mechanisms. The presence of an added organic crosslinker will also be considered. This will help to increase the organic network density independent of the inorganic network. The cross linked systems will be characterized for the dielectric response to identify the ideal composition to achieve exact aerogel properties. Finally from an application perspective photoactive aerogel coatings for possible application as cleaning of noxious gases will be undertaken. Titania is an eco friendly and widely accepted photocatalyst prevalent in development of self cleaning surfaces. Titania supported on the aerogel represents a symbiotic hybrid material where the titania will act as the degrading agent and the porous nature of the aerogel support will ensure the presence of large volume of the contaminant on the titania surface. The applicability of these surfaces will be finally checked.

Summing up in brief the work undertaken in this thesis can be divided as follows.
1) Studying the effect of an organically modified precursors on the ambient pressure process for aerogels.
2) Developing a synthesis methodology for the preparation of crosslinked organic inorganic networked gel structure and the ambient pressure drying of these networks.
3) Measurement of dielectric properties of these ambient pressure dried networks.
4) Potential application of these networks as support for photoactive surfaces in the form of films on glass substrates.
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