

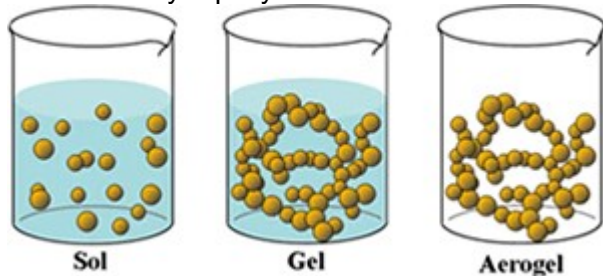


What is an Aerogel?

To give you an idea of what makes aerogel special materials for so many uses, it is instructive to provide some structural and functional definitions.

What is a gel?

Many chemical reactions that involve polymerization of molecules form dispersed nanoparticles in solution, particularly those that occur in three dimensions via cross-linking between growing solid chains. A gel precursor is a chemical or mixture of chemicals that can be activated toward molecular nucleation into small colloidal particles. A gel forms when a solution of these dispersed nanoparticle colloids (also called “sols”) are induced to form a semi-solid form via interparticle condensation. Sols can be stable for very long periods of time if the solution conditions are not conducive to interparticle condensation. When a catalyst is added to create the appropriate conditions for interparticle condensation, the viscosity of the solution can increase very rapidly as the semi-solid state is reached.



At the gel point, the liquid phase within a gel structure is not able to diffuse freely and will not flow or change shape if the volume is tilted on an axis. When the chemistry approach is designed correctly, the solid in the wet gel phase can define a high surface area network of pores that confine the liquid within the structure. Aerogels processes various materials to contain liquid filled pores that average about ten nanometers (a nanometer is 1/100,000th the diameter of a human hair), with a distribution of pore sizes typically between 1 and 100 nanometers. The general approach to generating nanoparticle sols and their subsequent gel phase is called the sol-gel process. The sol gel process has been commonly applied to metal oxide precursors where the metal is silicon, aluminum, or titanium. However, there are many examples of organic aerogels and mixed inorganic/organic aerogel structures.

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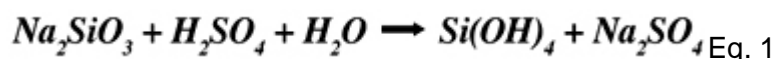
An aerogel is directly derived from a wet gel in a process that replaces the entrained liquid phase with air. If the gel is formed from a water phase, the resulting semi-solid is called a hydrogel, and the water must be exchanged with organic solvent prior to drying. If the gel is formed within an alcohol phase, the resulting semi-solid is called an alcogel, and can be dried directly. This is accomplished by increasing the temperature and pressure of the solvent phase inside of the gel structure beyond its critical point. This “supercritical” extraction condition lowers the surface tension between the liquid and the solid pore surfaces so that depressurization of the system at temperatures above the critical temperature leaves the pore structure filled with gas.

A supercritical drying process avoids the tremendous pressures exerted when liquids evaporate from tiny pores. The crushing forces during evaporation are inversely proportional to the pore radii; thus a nanoporous material is easily crushed during ambient pressure drying. Some well-known chemical processing approaches chemically modify a gel surface structure to mitigate much of the damage caused

by ambient pressure drying. Drying a gel at near ambient pressures is called a “xerogel” process, and produces aerogel materials that are typically denser than supercritically dried aerogel materials.

What are Aerogels made of?

Aerogel materials derived from silicate materials. Aerogels represent a structural morphology (amorphous, open-celled nanofoams) rather than a particular chemical constituency. However, a great deal of study has been devoted to silica aerogels and their properties over the past 70 years. Silica aerogels were first discovered in 1931 by Kistler[1]. His process used polymerization of silicic acid (Si(OH)₄), which in turn was generated by acidic neutralization of sodium silicate in water (Equation 1).



Using Kistler’s method, the aqueous silica hydrogels were repeatedly rinsed with volumes of fresh anhydrous methanol to remove all but trace amounts of water. Kistler brought the contents of the gel past the critical point of methanol (240°C and 1600 psi; making the solvent system “supercritical”) in a high-temperature autoclave and slowly depressurized the system at a temperature that prevented recondensation of methanol within the porous silica gel structure. This method has numerous disadvantages, particularly in the toxicity of methanol, and in the handling of a flammable solvent at very high temperatures and pressures.

In the seven decades since Kistler’s seminal work, there have been significant advances made in both the use of new precursor materials, and in the removal of solvent from them. For instance, Teichner and others established in the 1960’s that silicon alkoxides (e.g. tetraethylorthosilicate or TEOS) are the preferred soluble silica source for formation of silica gels because the need for water/alcohol solvent exchange could be avoided.[2,3] Ethanol based processing using silicon ethoxide derivatives such as TEOS and polydiethylsilicate (PDEOS) have become the preferred precursors to silica aerogels over the last few decades. With these materials, water is added to liberate alcohol and silicic acid. The silicic acid is very sensitive to condensing with itself, and rapidly building sol particles. As the process continues, a three dimensional gel network is formed, filling the mold volume and entraining all of the liquid solvent. The gels can then be further strengthened and treated in an alcohol solution, avoiding the need for solvent exchange if desired.

In the past 20 years, the use of supercritical carbon dioxide as a solvent for drying of gels containing organic solvent has made the process safer and more economical. Hunt pioneered the use of supercritical carbon dioxide as the solvent medium for aerogel processing [4], further reducing hazards associated with venting of superheated methanol vapor.

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