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An Overview of Silica Aerogels

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Abstract: In recent years, silica aerogels have attracted more and more attention due to their surprising properties and their existing and potential applications in wide variety technological areas. Silica aerogel is a nanostructured material with high specific surface area, high porosity, low dielectric constant, low density and outstanding heat insulation properties. Release of some active ingredients from the aerogel-drug formulation is faster than that of the crystalline drugs and commonly used formulations, can be explained by both the increase in the specific surface area of the drug adsorbed on the aerogel and its non-crystalline structure. Aerogel-drug formulations may be effectively used as drug delivery systems for drugs whose immediate release is desirable. It can also be used as a carrier for drug delivery, propellant replacement, to improve flow properties and molecular imprinting. This review address synthesis, properties, and characterization of silica aerogels, application in field of pharmaceuticals and its future prospects.
Key words: Silica aerogels; Carrier; Synthesis; Characterization

1. Introduction

Aerogels are advanced materials almost like solid smoke, an aerogel resembles a hologram, appearing to be a projection rather than a solid object. They consist of more than 96 percent air. The remaining four percent is a wispy matrix of silicon dioxide[1].Aerogels, consequently, are one of the lightest weight solids ever conceived.

An aerogel is made by the so called "sol-gel process". During this process, organic compounds containing silica undergo a chemical reaction producing silicon oxide (SiO_2) [2]. This mixture is a liquid at the creation of the reaction, and becomes more and more viscous as the reaction proceeds. When the reaction is completed, the solution looses its fluidity and the whole reacting mixture turns into a gel. This gel consists of a three-dimensional network of silicon oxide filled with the solvent[3]. During the special drying procedure, the solvent is extracted from the gel body leaving the silicon oxide network filled with air. This product is called aerogel[3,4]

Silica aerogels (SiO2) are highly porous, optically transparent solid materials. It is composed of individual particles only a few nanometers in size, which are linked in a three - dimensional structure[5]. Aerogels can be synthesized not only from silicon oxide (silica aerogels), but also from different organic and inorganic substances, for example titanium oxide, aluminum oxide, carbon etc.

This novel material has many unusual properties, such as a low thermal conductivity, refractive index, sound speed, along with a high surface area and thermal stability. An aerogel can be made with a density only three times larger than that of air. Being environmentally friendly and non-toxic, silica aerogels can be used in the pharmaceutical industry[6]. Aerogels also have many applications in different fields of science and industry. Their large surface area and open pore structure make them to an ideal potential carrier material. Reports also suggested that the use of hydrophilic silica aerogels as a carrier material for pharmaceuticals[16].

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2. Synthesis of silica aerogels

The synthesis of silica aerogels can be divided into 3 general steps:

a) Preparation of the gel

The gel phase is normally obtained by the so-called sol-gel process. Here, the terms "sol" and "gel" are used as defined.

i) Sol: A sol is a colloidal system of liquid character in which the dispersed particles are either solid or large molecules whose dimensions are in the colloidal range (1-1000 nm).

ii) Gel: A gel is a colloidal system of solid character in which the dispersed substance forms a continuous, coherent framework that is interpenetrated by a system (usually liquid) consisting of kinetic units smaller than colloidal entities. A gel can be easily imagined as a three-dimensional network filled with a solvent. Gels frequently contain only a small amount of the dispersed phase (1-3%) and exhibit some measure of rigidity and elasticity[7]. The gels are usually classified according to the dispersion medium used, e.g., hydrogel or aquagel, alcogel and aerogel (for water, alcohol, and air respectively). The most common Example of a gel is gelatin. A large variety of chemical reactions can be used to obtain a Gel phase. The choice of reaction depends on the desired properties of the final aerogel Product.

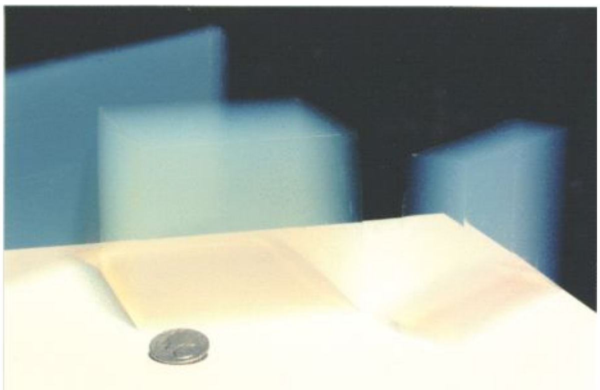

Figure 1: Samples of silica aerogels

b) Aging of the gel

The gel prepared in the first step is aged in its mother solution[8]. This aging process strengthens the gel, so that shrinkage during the drying step is kept to a minimum.

c) Drying of the gel

Drying of the gel is a critical step. Drying is governed by capillary pressure. Shrinkage of the gels during drying is driven by the capillary pressure, Pc, which can be represented by (1).

$$Pc = -\gamma lv / (\gamma p - \delta) \quad (1)$$

Where γlv is the surface tension of the pore liquid, γp is the pore radius, δ is the thickness of a surface adsorbed layer[2].

$$\gamma p = 2Vp / Sp \quad (2)$$

where Vp and Sp are pore volume and surface area, respectively.

Drying can be done by several ways:

(a) In supercritical drying (SCD) method the pore liquid is removed above the critical temperature (Tcr) and critical pressure (Pcr) of the concerned liquid. At this point there is no liquid–vapour interface and, thus, no capillary pressure[2].

(b) By drying at ambient pressure, the surface tension between liquid and vapor cannot be avoided. Stress within the gel is proportional to the viscosity of the pore liquid, the drying rate and inversely proportional to the permeability of the wet gel.

(c) Another drying method where the phase boundary between the liquid and gas phase does not exist and thus the capillary pressure does not play an important role, is freeze-drying. Here, the solvent must be exchanged with a low expansion coefficient and a high sublimation pressure. The pore liquid is frozen and sublimed under vacuum[3] .

3. Properties of silica aerogels

The widespread interest in silica aerogels, is due to their unusual solid material properties. Table 1 provides an overview of the important physical properties of silica aerogels.

Table 1: Physical properties of silica aerogels[9]

Property	Value	Comments
Apparent density	0.003-0.35 g/cm^3	Most common density is 0.1g/cm^3
Internal surface area	600-1000 m^2/g	As determined by nitrogen adsorption/desorption
% Solids	0.13-15 %	Typically 5% (95% free space)
Mean pore diameter	20 nm	As determined by nitrogen adsorption/desorption (varies with density)
Primary particle diameter	2-5nm	Determined by electron microscopy
Refractive index	1.0-1.05	Very low values for a solid material
Thermal tolerance	> 500 ºc	Shrinkage begins slowly at 500°C, increasing with increasing temperature. Melting point is >1200°C
Coefficient of thermal expansion	2.0-4.0*10^{-6}	Determined using ultrasonic methods
Dielectric Constant	1.1	For a density of 0.1 g/cm^3. Very low for a solid material
Sound Velocity	100 ms	For a density of 0.07 g/cm^3. One of the lowest velocity values for a solid material

3.1 Pore structure

Aerogels have an unusual combination of high porosity and small pore size, making porosity characterization by conventional techniques such as mercury intrusion (MIP), thermoporometry (TPM), and nitrogen adsorption/desorption (NAD), difficult[9]. All these techniques are based on the application of capillary pressures on the aerogel network, which may cause large volumetric compressions, leading to incorrect values for pore size and volume.

3.2 Density of silica aerogels

Volume shrinkage of the aerogels is calculated from the volumes of the hydrogel and aerogel. Two different terms are used to characterize silica aerogels: bulk density and skeletal density. This value can be as low as 0.003 g/cm^3 (the density of the air is 0.001 g/cm^3). This makes aerogels the lightest solid material known at present.

Bulk density (ρb) is defined as the ratio of the aerogel's mass to its volume. The skeletal density of these particles is supposed to be very close to that of the bulk solid. These values were obtained by using helium picnometry[10] .

The percent of volume shrinkage, pore volume and porosity of the aerogels are determined as follows:

$$\%Vs = (1 – Va/Vg) \times 100 \quad (3)$$
$$\text{Pore volume (cm3/g)} = (1 /\rho b - 1 / \rho s) \quad (4)$$
$$\text{Porosity} = (1 – \rho b/ \rho s) \times 100 \quad (5)$$

Where *V*a and *V*g are the volume of aerogel and alcogel respectively. ρs is the skeletal and, ρb is the bulk density of the silica aerogel.

3.3 Optical properties

The optical properties of silica aerogels are best described by the phrase "silica aerogels are transparent". This may seem obvious, for silica aerogels are made of the same material as glass. While distant objects can be viewed through several centimeters of silica aerogel, an illuminated material displays a slightly bluish haze when viewed against a dark background and the transmitted light is slightly reddened. The scattering in the aerogel can be divided into two different types: bulk scattering and exterior surface scattering. In silica aerogels, a network of pores can act themselves as scattering centers.

3.4 Thermal conductivity

Thermal conductivity is one of the widely studied properties of silica aerogels[17]. Kistler demonstrated that the thermal conductivity of an aerogel is on the order of 0.02 W/mK at ambient pressure in air and on the order of 0.01 W/mK when evacuated. The passage of thermal energy through an insulating material occurs through three mechanisms: solid conductivity, gaseous conductivity and radioactive (infrared) transmission. The sum of these three components gives the total thermal conductivity of a material.

3.4.1 Velocity of sound and mechanical properties

The sound velocities in SiO_2 aerogels with values between 100-300 ms^{-1} are among the lowest for inorganic solids. The sound is carried solely by the delicate SiO_2-structure, and not by the air within the porous body. The elastic properties of an aerogel powder have been studied by Stark using atomic force microscopy (AFM). This method allows for the direct measurement of local elastic sample properties.

3.4.2 Hydrophobicity

Silica aerogels can either be hydrophilic or hydrophobic, depending on the conditions during synthesis. Generally, aerogels synthesized by unmodified hydrolysis and condensation of alkylorthosilicates and dried by high temperature SCD are hydrophobic, and those dried by CO_2 are hydrophilic[9]. This difference is due to the different surface groups formed during the supercritical drying process. LTSCD (Low temperature supercritical drying) results in hydroxyl groups (-OH) on the surface of the aerogel and, thus, in hydrophilic aerogels. Adsorption and capillary condensation of the water in the aerogel takes place, eventually resulting in cracking of the gel body. HTSCD (High temperature supercritical drying) allows for the reaction of the surface hydroxyl groups with the solvent to form methoxy groups ($-OCH_3$) v and thus results in hydrophobic aerogels (Figure 2).

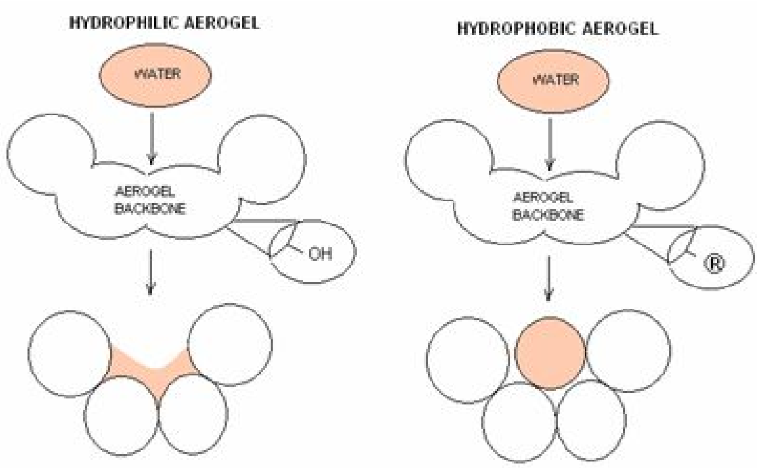

Figure 2: Hydrophilic and hydrophobic aerogels

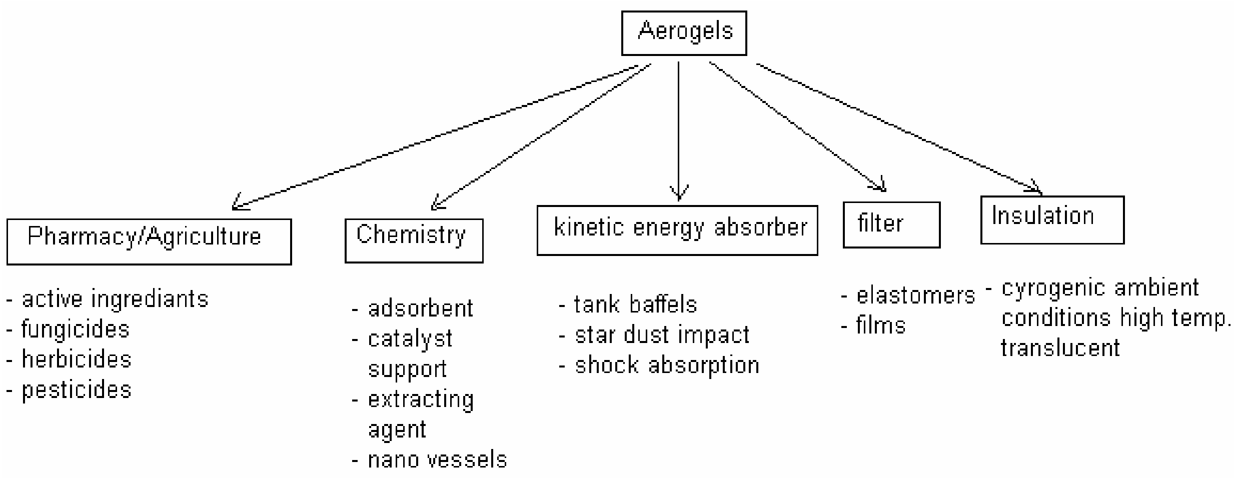

Figure 3: Aerogel applications

4. Aerogel applications

Being chemically inert and non-harmful to the human body, silica aerogels may easily find an application in the pharmaceutical industry and agriculture. There are vast amounts of literature describing already existing and potential applications of an aerogels. Some of these areas are presented in Figure 3.

a) As a carrier material for drug delivery

Use of silica aerogels as potential carrier materials in medicine and agriculture[11]. Here both hydrophobic and hydrophilic aerogels were loaded with pharmaceuticals by means of adsorption from corresponding liquid solutions. By choosing a suitable hydrophilic or hydrophobic aerogel, the substance with which the aerogel is loaded can be released in an accelerated or a delayed form. Ambient dried aerogels, having a relatively high density (ρ >0.1 g/cm^3) were used for this purpose. In recently reported that the dispersed the aerogels in a solution of the target substance. The loading with the target compound took place and then the resulting mixture was filtered in order to yield the loaded aerogel. The resulting powder was dried and could be used as a drug delivery system (DDS).

b) Molecular imprinting

Silica based materials are extremely rigid due to the high degree of cross-linking found in the (SiO2)n network. This property is very important in the design and synthesis of imprinted materials since both the size and shape of the cavities created by the template must be retained after the removal of the template. High thermal stability of sol–gel derived material provides an easy way to remove imprint molecule using high temperature such as in calcinations method. In addition, sol–gel glasses are structurally porous and can be engineered to have extremely high surface area (200–2000 m2/g). These properties make silica sol–gel matrix as an imprinting host[12].

c) In agricultural industry

Having a small particle size and very large surface area, aerogel powders can absorb the protective lipid layer of insects causing the organisms to lose body fluid and, consequently, die. The chemical composition of silica aerogels is identical with that of fumed silicon oxide, produced by combustion of silicon chloride.

d) As a replacement material to Aerosil

It has been shown that orally administrated Aerosil passes through the gastrointestinal tract without being resorbed in detectable quantities. It is expected that silica aerogels having the same chemical composition and amorphous structure as Aerosil would have similar clinical characteristics.

Aerosil has an average surface area around 200 m^2/g. Aerogels have much larger internal surface (500-1000 m^2/g), enabling them to exhibit superior properties to Aerosil, in particular applications.

e) Improved flow properties of powder

The flow characteristics of powder are especially important in the pharmaceutical industry for pellet production. It has been shown that the addition of 0.5 % aerogel powder to lactose powder improves the flow properties of the resulting powder, compared to the addition of the same amount of the conventional products used for this purpose (Aerosil and Sipernat).

f) As a replacements of chlorofluorocarbon-propelled refrigerant foams

They have another critical advantage over foam. Foams are blown into refrigerator walls by chlorofluorocarbon (CFC) propellants, the chemical that is the chief cause of the depletion of the earth's stratospheric ozone layer[13]. The ozone layer shields life on Earth from ultraviolet light, a cause of human skin cancer. Use of aerogels could replace chlorofluorocarbon-propelled refrigerant foams.

g) Radiation detection

Currently, they are components of Cerenkov radiation detectors used in high- energy physics research at CERN near Geneva, Switzerland. Another scientific application currently under consideration involves utilizing aerogels in space like a soft, spongy net to capture fast-moving micrometeroids without damaging them[14] .

h) Improving dissolution profiles of drugs

Specific surface area is one of the very important parameters controlling both the dissolution rate of drug and its absorption in the body. A large specific surface area allows for a fast dissolution and thus, an effective absorption in the body[15] . The specific surface area of the active component may be increased either by particle micronization, or by increasing the surface area adsorption of the drug on the carrier. Since aerogels have an extremely large surface area, we could expect that its use as a carrier can improve the dissolution and adsorption of drugs.

5. Future prospects

Aerogels were cloudy rather than totally transparent. Before they could be used in double-pane windows or skylights, clarity had to be improved. Aerogels are fine insulators but in order for them to become a cost-effective alternative to existing products, they have to be made even more thermally resistant. From the standpoint of fabrication, several obstacles emerged. The extant chemistry and processing technology was too expensive and it was potentially explosive. Finally, processing required toxic compounds which presented yet another obstruction. Taken together, a formidable phalanx of technological barriers prevented aerogels from making the leap from the laboratory to the consumer. Molecular imprinting technology still needs to overcome few limitations such as template leakage, poor accessibility of the binding sites, low binding capacity and non-specific binding

6. Conclusions

This paper provides a complete review of the synthesis, structure, properties, characterization, and pharmaceutical applications of silica aerogels. Aerogel-drug formulations may be effectively used as drug delivery systems for drugs whose immediate release is desirable, release of such compounds can be significantly improved by adsorption on silica aerogels. This method can be used as an alternative to the micronization procedure, used for these purposes at present time. Aerogels show great promise for use in variety of technological areas where special structure and physical properties are required. Substantial progress have has been made in the development, processing and characterization of aerogel materials over the recent years. Special consideration has been paid to the use of inexpensive precursors such as sodium silica (waterglass) and the drying technology to make the production commercial.

7. Refereces

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