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Synthesis of Silica Aerogel by Supercritical Drying Method

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Abstract

The purpose of this paper was to prepare the silica aerogel using the sol-gel and supercritical drying processes. The supercritical drying was chosen as the most effective process, ensuring the best properties of product. For this reason the authors designed and built the supercritical dryer stand that allowed drying samples in high pressure and elevated temperature. The obtained silica aerogels exhibited good transparency, homogeneity, and comparable density. The specific surface measured by means of BET analysis equaled 870.5 g/cm³.

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Keywords: nano-composites, silica aerogel, sol-gel polymerization, supercritical drying, BET analysis.

1. Introduction

Fast growth of technique increases energy demands in everyday life, forcing the scientific world to look for modern and more efficient solutions which can help save the energy. Residential and commercial retrofit insulation has been found as one of the most cost effective actions for greenhouse gas abatement. Therefore, traditional insulation materials were and are being used in thicker or multiple layers which result in more complex building details, an adverse net-to gross floor area and heavier load bearing constructions [1]. One of the most interesting science of the material engineering which has been recently indicated rapid development is nanotechnology. Nanotechnology is a science concerning nanomaterial – a polycrystalline substances composed of grains smaller than 100 nanometres, at least in one direction [2].

The purpose of this paper was to prepare the silica aerogel – nanomaterial which was firstly discovered about 1930 by Dr Samuel Stephen Kistler. This fascinating nanomaterial is made of more than 90% of air, what guarantee an excellent thermal conductivity, extremely low weight, and moreover, the transparency of aerogel. All those properties make aerogel an ideal material for thermal insulation of walls as well as windows, causing the decrease of heat and energy consumption [3], [4].

The aerogel can be prepared in different ways including supercritical drying process. This particular process was chosen as the most effective one, ensuring the best product properties. For this reason the authors designed and built the supercritical dryer stand that allows drying samples in high pressure and elevated temperature.

2. Chemistry of aerogel synthesis

Nanomaterials and/or nanoparticles are used in a broad spectrum of applications. Today they are contained in many products and used in various technologies. Most nanoproducts produced on an industrial scale are nanoparticles, although they also arise as byproducts in the manufacture of other materials.

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Most applications require a precisely defined, narrow range of particle sizes. Specific synthesis processes have to be applied to produce the various nanoparticles, coatings, dispersions or composites. Defined production and reaction conditions are crucial in obtaining such size-dependent particle features. Particle size, chemical composition, crystallinity and shape of nanomaterials can be controlled by temperature, pH-value, concentration, chemical composition, surface modifications and process control.

The selection of the respective process depends on the chemical composition and the desired features specified for the nanoparticles. Two basic strategies are used to produce nanoparticles [5]:

- top-down strategy – refers to the mechanical crushing of source material using a milling process. In this process the pristine material is broken down into more basic building blocks,
- bottom-up strategy – building complex systems by combining simple atomic-level components. Structures are built up by chemical processes.

Bottom-up methods are based on physicochemical principles of molecular or atomic self-organization. This approach produces selected, more complex structures from atoms or molecules, better controlling sizes, shapes and size ranges. Bottom-up methods include aerosol processes, precipitation reactions and sol-gel processes. As mentioned before, a large majority of aerogels are derived from gels made through the sol-gel process. The term sol-gel refers to a process in which solid nanoparticles dispersed in a liquid phase (sol) agglomerate together to form a continuous three-dimensional network extending throughout the liquid phase (gel). The aerogel production can be characterized by a series of distinct steps as follows [Fig. 1] [6], [7]:

Step 1: Formation of different stable solutions of the alkoxide or solvated metal precursor (sol).

Step 2: Gelation resulting from the formation of an oxide- or alcohol- bridged network (gel) by a polycondensation or polyesterification reactions that result in a dramatic increase in the viscosity of the solution.

Step 3: Aging of gel (syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels is critical to the prevention of cracks in gels that have been cast.

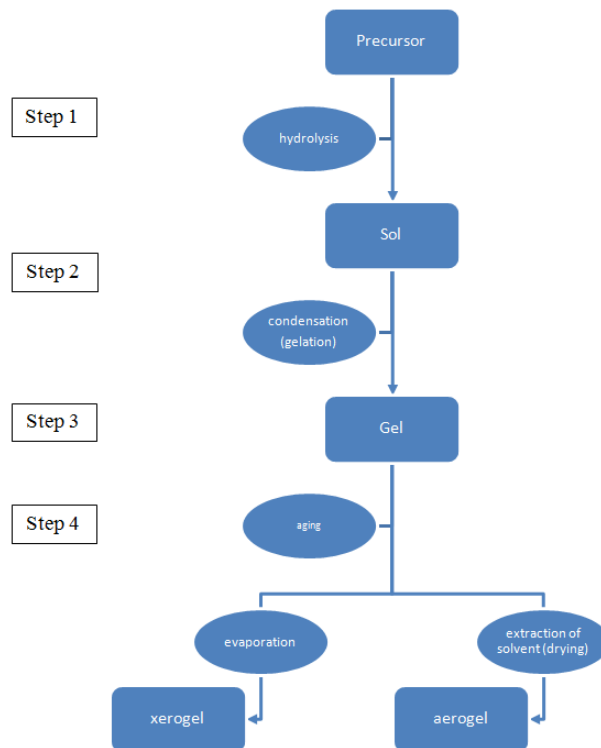


Fig. 1. Distinct steps of aerogel production

Step 4: Shaping of gel into the desired form or shape followed by drying. In this step solvent is removed. The manner in which the liquid phase is removed from wet gel determines whether the dried material is a highly porous aerogel or a denser xerogel. A xerogel is formed by the solvent evaporation from the wet gel, resulting in collapse of the wet-gel structure. If the network is compliant, the gel deforms because of capillary forces generated by the liquid. Supercritical drying or ambient pressure drying of the wet gels result in aerogels. Aerogels are actually nanoscale mesoporous materials of low density and high surface area.

Depending on the method used to extract the pore fluid from a wet gel, dry solid with variable porosity is obtained. Strong capillary forces create a xerogel, weak capillary forces create an ambigel, and zero capillary forces create an aerogel that nominally retains the low-density framework for the wet gel.

Sol-gel chemistry is particularly sensitive to the following parameters:

- pH – the pH is connected with the hydrolysis step which is important in producing nanoparticles and eventually the gel network [8].
- Solvent – the solvent keep the nanoparticles dissolved and enables the joining of nanoparticles together [9].
- Temperature – the temperature plays a significant role in the formation of nanoparticles and it facilitates the nanoparticles undergo into a gel network [10].
- Time – in general, if a gel is formed slowly, it usually has a much more uniform structure and produced aerogel exhibits better mechanical properties [4].
- Catalysts (both acids and bases) – accelerate a chemical reaction and have a substantial impact on the time of gelation. In many cases catalysts can reduce gel time from hours, days, or weeks to minutes.
- Agitation – mixing a sol during gelation process is important to controlling the uniform progress of chemical reactions in the solution.

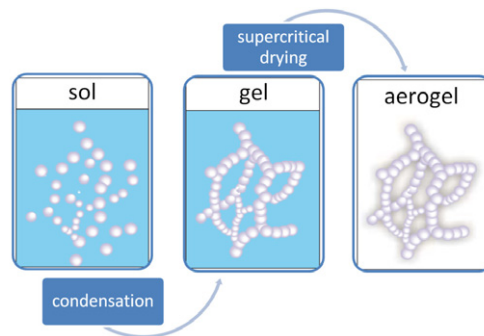


Fig. 2. Representation of nanoparticles agglomeration during aerogel production process

Supercritical drying is a process in which the liquid is removed in a precisely controlled way. As the substance in a liquid body crosses the boundary from liquid to the gas phase, the liquid changes into gas, while the liquid body's volume decreases. When it happens the surface tensions in the liquid body pull against any solid and delicate structures of silica gel, and the tiny machinery of microelectromechanical devices, tend to be broken. To avoid this point, the sample must be brought from the liquid phase to the gas phase without crossing the liquid–gas boundary. This is possible via two alternate paths [11]:

- In freeze drying process going around the liquid-gas boundary, accompanied by low temperature and low pressure. However, some structures are disrupted even by the solid–gas boundary.
- In supercritical drying process going around the liquid-gas boundary, accompanied by high temperature and high pressure. This route from liquid to gas does not cross any phase boundary, instead passing through the supercritical region, where the distinction between gas and liquid ceases to apply. Densities of the liquid phase and vapour phase become equal at critical point of drying. One of the fluids suitable for supercritical drying is carbon dioxide of critical point in 31.1 °C at 73.9 bar. Nitrous oxide has similar physical behavior to carbon dioxide, but is a powerful oxidizer in its supercritical state.

In supercritical drying process, alcohol is first used to wash away all water, exploiting the complete miscibility of these two fluids. The alcohol is then washed away with high pressure liquid carbon dioxide. The liquid carbon dioxide is then heated until its temperature goes beyond the critical point, and subsequently the pressure is gradually released, allowing the gas escape and leaving a dried product.

3. Sol-gel process

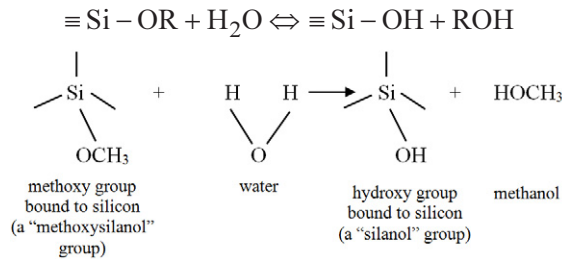
The most common technique used for producing silica gels is the alkoxide gelation. This technique involves the reaction of a silicon alkoxide with water in a solvent such as ethanol or acetone, usually in the presence of basic catalyst. In this technique every ingredient has its own function [5]:

- silicon alkoxide (usually tetramethoxysilane TMOS or tetraethoxysilane TEOS) serves as the source for the silica, water acts as a reactant to help join the alkoxide molecules together,
- catalyst (such as ammonium hydroxide or ammonium fluoride) helps the underlying chemical reactions go fast enough to be practically useful,
- solvent (such as methanol, ethanol or acetone) which is miscible with both silicon alkoxides and water initiate the chemical reactions in one phase.

When a silicon alkoxide reacts with water to form a silica gel, the following reactions at the molecular level occurs [12]:

- Hydrolysis

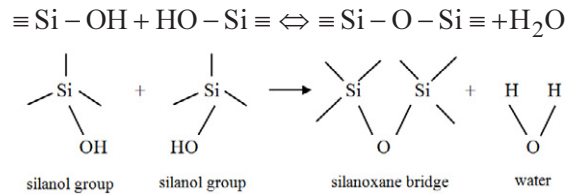
Silicon alkoxide reacts with water to form silanol (Si-OH) groups:



where: R – alkyl group

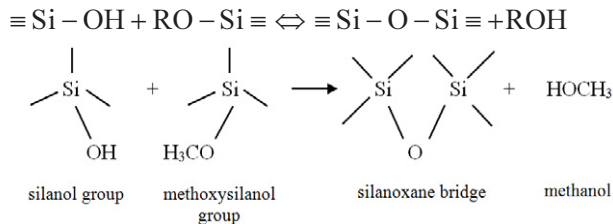
- Water condensation

Silanol groups react with each other:



Alcohol condensation

Silanol groups react with an alkoxide groups (Si-OR) to form a siloxane bridge (Si-O-Si), resulting in the joining of two molecules into one larger molecule:



where: R – alkyl group

Each silicon atom can form the four siloxane bridges resulting in connection of small molecules into the giant molecules which contain thousands of silicon-oxygen bridges. These large assemblies of silicon and oxygen bridges are called silica nanoparticles, and have diameters of a few nanometers. As consequence, the agglomeration of nanoparticles leads to the formation of continuous network through the liquid solution, and the gel is formed.

4. Experimental procedure

In presented research, the silica aerogel was derived by mixing tetramethoxysilane (TMOS, supplied by Sigma-Aldrich) with ammonium hydroxide 28.0–30.0% (supplied by Sigma-Aldrich) diluted in water and methanol (supplied by CHEMPUR).

Silica gel samples were prepared by sol-gel process described precisely earlier. Firstly, in order to initiate the gelation process two separate solutions were prepared: TMOS in methanol (solution A) and ammonium hydroxide in methanol (solution B). Then, the solution B was slowly poured into the solution A and simultaneously stirred. In the next step, obtained mixture was poured into three separate containers made of plastic syringes. The transparent gels were formed via the next 15 min and afterward the gel samples were extruded to 250 ml glass jar filled with 100 ml of methanol. In the next stage the silica gel samples were aged for 3, 6 and 9 days. Then, the samples was subjected to supercritical conditions (31.1 °C at 73.7 bar) for minimum 2 hours and 30 minutes. For purpose of this research the building of stand for supercritical drying was an essential step. Supercritical dryer is a kind of autoclave, where pressure and temperature are determinate manually. Device was design and build by authors to dry the gel samples in strictly defined conditions, what is an important step in preparing fine silica aerogel.

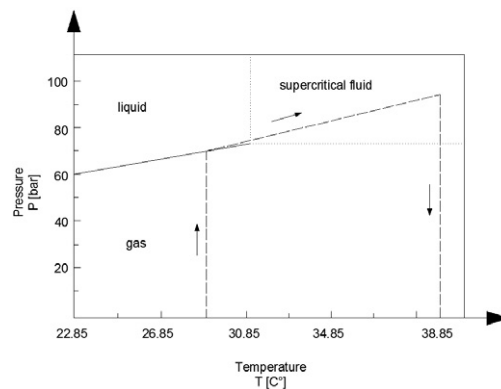


Fig. 3. The operating path involved in the supercritical CO₂ drying process

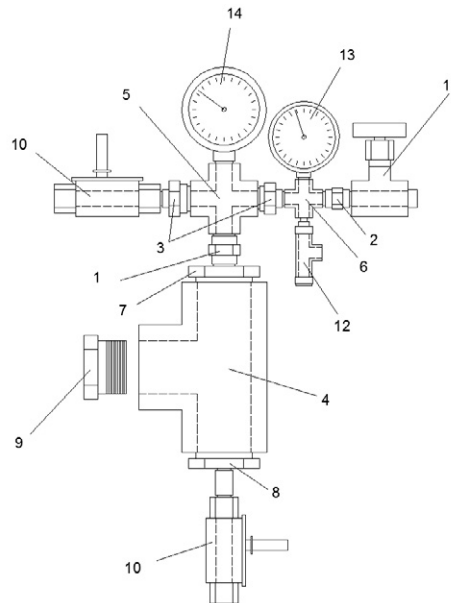


Fig. 4. Scheme of supercritical dryer, 1, 2 – hex nipple male, 3 – hex reducing nipple male, 4 – female tee, 5, 6 – female cross, 7, 8 – reducing bushing, 9 – pipe plug, 10 – ball valve, 11 – needle valve, 12 – relief valve, 13 – manometer, 14 – thermometer

As mentioned before, the Haunt Process used by authors to dry gel samples, bases on the knowledge that the critical point of carbon dioxide [Fig. 3] can be achieved only if the temperature is maintain over the value of 31.1 °C, and the pressure is maintain over the value of 73.9 bar. Authors decided to use elements with National Pipe Thread (NPT thread), which seemed to be the best available thread type for such high pressure systems and exhibited satisfied technical conditions. All elements are matched in Fig. 4.

The example of pressure and temperature in time diagram is placed in Fig. 5.

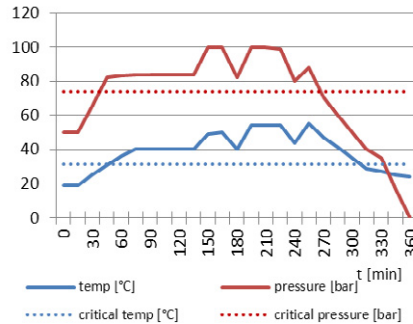


Fig. 5. Example of pressure – temperature relationship in time for supercritical drying of gel samples

5. Results and discussion

The basic parameters of synthesis of silica aerogels and their density were presented in Table 1.

Table 1. Basic parameters of silica aerogel synthesis

No	Time of aging, days	Time of drying, min	Density, g/cm ³
Sample 1	3	170	0.128
Sample 2	6	280	0.128
Sample 3	9	150	0,127

As can be seen in Fig. 6, the structures of silica aerogels derived from gel samples no. 1, 2 and 3 are very similar. All of them were derived from the gels of identical chemical composition and exhibited good transparency and homogeneity. The specific surface area for obtained silica aerogels determined by means of BET analysis equaled 870.5 g/cm³. They only differed in the quantity of cracks, the structure of aerogel no. 2 was less cracked than the other ones. This may be caused by slower and longer aging and supercritical drying processes, as well. However, the comparable densities of prepared silica aerogels proved the satisfying repeatability of conducted experiment.

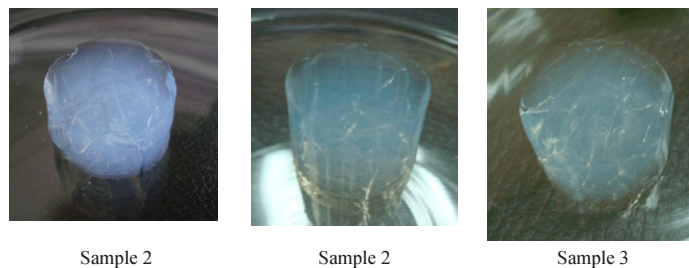


Fig. 6. The structures of silica aerogels

6. Conclusions

The silica aerogel was prepared by the sol-gel method using the supercritical drying. It was shown that obtained silica aerogels exhibited good transparency and homogeneity. The comparable values of density for all samples proved the satisfying repeatability of conducted experiment.

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