Cost-effective pilot-scale demonstration of ambient-dried silica aerogel production by a novel one-pot process

Lukas Huber, Shanyu Zhao, Matthias M. Koebel

Laboratory for Building Energy Materials and Components, EMPA, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

ABSTRACT

Over the past decade, aerogel based insulation products have established their place in various niche markets, such as thermal insulation for aerospace, apparel, petrochemical pipelines and pumping fluid media in industry applications. In the building industry, aerogel superinsulation enables superior insulation performance compared to conventional insulation materials. This allows putting in place a slimmer insulation layer (and thus space saving) or improving the insulation performance (U-value) of the building envelope. The widespread application of silica aerogels is currently hindered by their poor mechanical properties [1] and high materials cost. Aerogel insulation products have a tremendous growth potential in excess of 20 % by volume per annum [2]. For comparison conventional insulation products grow at an annual rate on the order of 5 %.

One of the cost limiting key challenges in aerogel production is the cumbersome multistep synthesis methodology. Today's aerogel production requires several solvent exchange steps which is not only very time and labor intensive but also costly. Supercritical drying from CO_2 is another major obstacle in the mass production of silica aerogels due to the fact that it is done in high pressure autoclaves. Not only does this process require an additional solvent exchange step into CO_2 but it is also accompanied by a significant energy cost.

Two years ago, a novel one-pot production process for silica aerogels was invented and patented at our laboratory which allows the production of silica aerogel granulate by ambient pressure drying within only 5 hours from start to finish. This simplified chemical synthesis consists of only three steps: gelation, modification and ambient pressure drying. Currently we are able to produce up to 70 liters at a time, following a first successful scale-up study. Our in-house aerogel has a thermal conductivity of 17.9 mW/(m K), which is identical to that of commercially available granulate (e.g. Cabot P300).

In summary, this new process gives access to a new generation of low-cost high-quality aerogel granulate and is expected to substitute today's conventional processes. A significant price reduction of silica aerogel materials is expected to reshuffle the insulation market. In the future we should look forward to seeing new aerogel insulation products and companies appear on the world markets.

Keywords: Aerogel, Thermal insulation, Sol-gel

INTRODUCTION

Silica aerogel was first produced in the early 1930's by Steven Kistler [3,4] from silica gels by replacing the pore fluid with a gas. Due to their extremely low density and outstanding physical properties, especially for thermal and acoustic insulation, they were commercialized a few years later by Mosanto Chemicals in the form of powder. However, the time-consuming and labor-intensive solvent-exchange steps led to a slowdown of their development for the following three decades. In the late 1960's Teichner [5] achieved a major technological breakthrough by the replacement of Kistler's sodium silicate precursors by alkoxysilanes. This eliminated the formation of inorganic salt byproducts from the gels and the need for a water-to-alcohol exchange step. In the late 1990's, Schwertfeger *et al.* [6] described the synthesis of "ambigel" type aerogels, by ambient pressure drying without any use of a supercritical drying equipment. Ambient pressure drying was applied with great success to the synthesis of silica aerogels from alkoxides, as well as from sodium silicate, and today can be viewed as the most promising manufacturing technique for silica aerogels [7].

Figure 1 compares the production flow path of silica aerogels from sodium silicate (which involves many solvent exchange steps) to that from alkoxide precursors using our novel one-pot process. The process starting from sodium silicate precursors requires 7 times more solvent than the volume of the final aerogel whereas our novel one-pot process necessitates only 1.1 times the volume of the final aerogel.

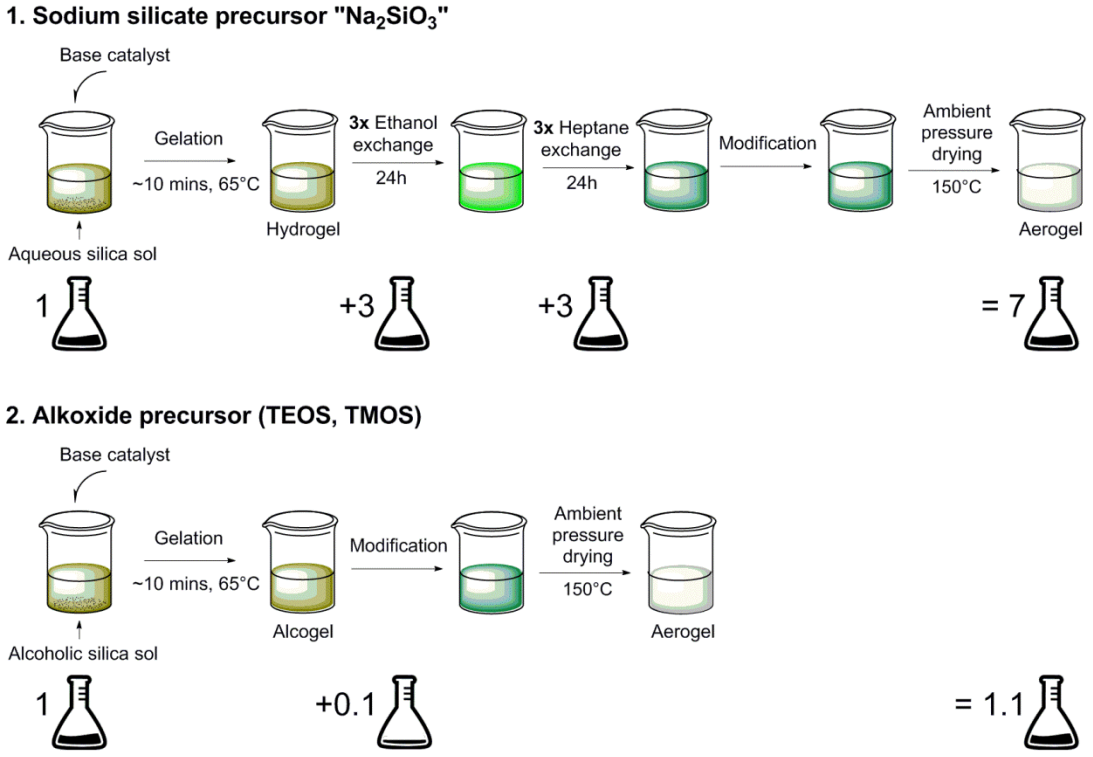

Figure 1: Schematic overview of the two main synthesis paths of silica aerogels from sodium silicate and silicon alkoxides using our novel one-pot process

METHOD

Preparation of the silica aerogel

Scale-up tests of the simplified one-pot production route [8] were carried out in a custom built pilot reactor. Prior to gelation, a silica sol mixture was prepared as follows: A silica sol (prepolymerized tetraethoxysilane, TEOS), water and ethanol were mixed in a drum. To this homogeneous solution, a hydrophobization agent (hexamethyldisiloxane, HMDSO) and 2 M Ammonia solution were added and the mixture homogenized again. This silica sol was poured into a 75 liter reactor (Figure 2) and slowly heated up to 65°C. The gelation onset was about 10 minutes from the point of ammonia addition. After gel aging, the syneresis liquid was removed before a dilute HCl solution was added to catalyze the hydrophobization. After this modification step at 65°C, the gel was removed from the reactor and dried for 3 hours at 150°C.

Figure 2: Reactor used for upscaling experiments

Characterization

The envelope density of the aerogels was measured with a GeoPyc 1360 form Micromeritics with 10 measurement cycles using a consolidation force of 4 N. The measured envelope density was used for the nitrogen sorption/desorption measurements which were carried out at 77 K on a gas sorption analyzer Micromeritics 3flex. Prior to the measurement, approximately 200 mg aerogel granulate was degassed at 250°C for 4.5 hours at a pressure of

1.3×10^{-2} mbar. The Brunauer-Emmet-Teller (BET) method [9] was used to calculate the specific surface area of the materials.

The thermal conductivity of aerogel granulate was determined (in packed bed configuration) using a guarded hot plate device according to the methods described in SN.EN 12667 and ISO 8302 in agreement with the Swiss SIA 279 standard “Thermal insulation material". Prior to the measurements, two frames (490 mm x 490 mm x 50 mm) were filled with approximately 1900 g of aerogel granulate. A square, flat heating element is sandwiched symmetrically between the two test objects, the outer surfaces of which are maintained at a constant temperature by cooling elements (Figure 3). This guarantees maintaining a stationary temperature difference. For highest possible measurement accuracy the hotplate is divided into a central measurement zone which is thermally isolated from the surrounding edge zone, with both zones being maintained at the same temperature. In the measurement zone, the electrical heating power under stationary conditions is measured and the heat flux with respect to the two surfaces is determined. The thermal resistance is given by the quotient of the measured temperature difference and the heat flux. The layout of the test setup is shown schematically in the drawing. The two filled frames with aerogel granulate lie horizontally sandwiched between the hotplate and the two cooling plates, and are surrounded by a thick layer of thermal insulation. Measurements are made automatically using an electronic control and data acquisition system. In order to maintain stable operating conditions deviations from set temperatures, the temperature difference between the core and edge zones, the temperatures within the heating and cooling plates and the input power are all regulated so as to lie within narrow limits. The instrument was calibrated with known standard materials prior to the test measurements.

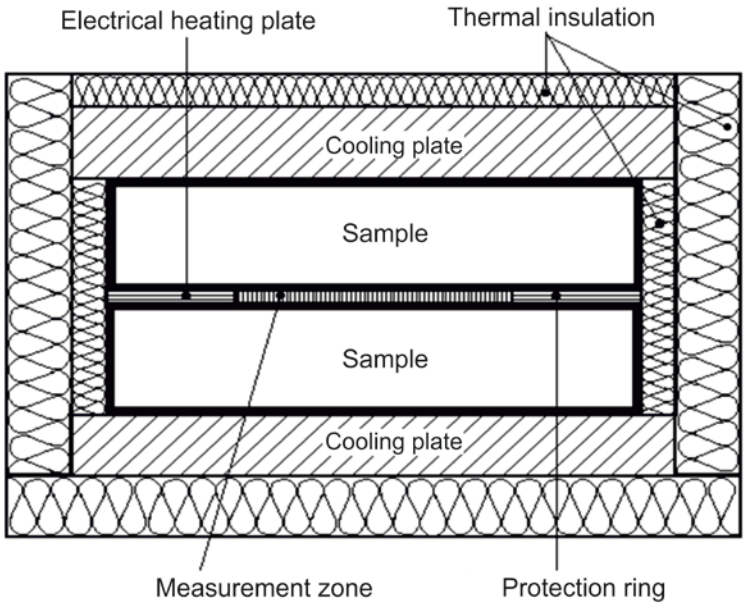

Figure 3: Measurement setup for the thermal conductivity

RESULTS AND DISCUSSION

Figure 4a shows a photograph of silica aerogel granulate produced in-house by the new one-pot method. The scanning electron micrograph of the one-pot aerogel granulate clearly reveals a colloidal particle network structure (Figure 4b). Table 1 summarizes the apparent density, thermal conductivity and BET surface area of commercial and one-pot silica aerogel granulate for comparison. The commercial silica aerogel granulate has a thermal conductivity of 17.9 mW/(m K) at an apparent density of 76 kg/m^3. The one-pot aerogel granulate which was not sieved after drying has a density of 83 kg/m^3 and a thermal conductivity of 17.4 mW/(m K). After sieving, the one-pot aerogel granulate (meshsize: 2 mm) the thermal conductivity increases to 18.7 mW/(m K), due to differences in particle size and packing density [10].

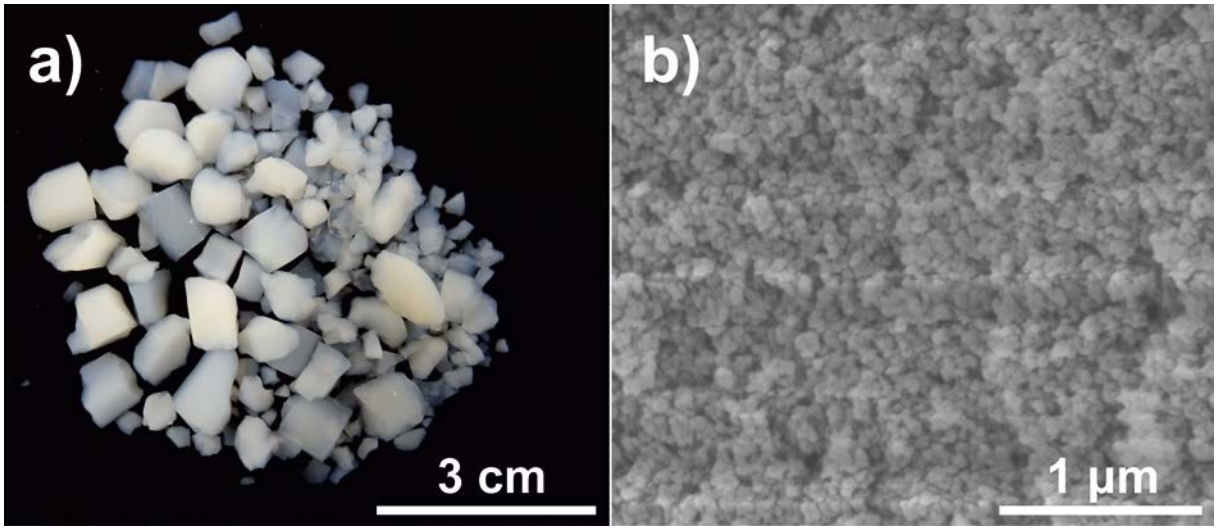

Figure 4: (a) Aerogel granulate after drying at 150°C for 3h and (b) scanning electron micrograph of silica aerogel granulate

Table 1: Apparent density, thermal conductivity and BET surface area of commercial and one-pot aerogel granulate

	Apparent density [kg/m^3]	λ_{10} [mW/(m K)]	S_{Bet} [m^2/g]
Commercial silica aerogel granulate (Cabot P300)	76	17.9	702
One-pot aerogel	83	17.4	-
One-pot aerogel (sieved)	78	18.7	797

CONCLUSIONS

We demonstrated the successful scale-up of silica aerogel granulate production by means of a novel synthesis route [8] to the 75 liter scale. The resulting, superinsulating, aerogel granulate has identical properties to commercially available materials. The novel one-pot process does not require any solvent exchanges and this enables fast production times, lower infrastructure investment cost (CAPEX) and lower operation cost (OPEX). This method is a promising technique for the inexpensive large-scale manufacture of silica aerogel granulates.

REFERENCES

1. Wong, J. C. H., Kaymak, H., Brunner, S. & Koebel, M. M. Mechanical properties of monolithic silica aerogels made from polyethoxydisiloxanes. *Microporous Mesoporous Mater.* **183**, 23–29 (2014).

2. Koebel, M., Rigacci, A. & Achard, P. Aerogel-based thermal superinsulation: an overview. *J. Sol-Gel Sci. Technol.* **63**, 315–339 (2012).

3. Kistler, S. S. Coherent Expanded-Aerogels. *J. Phys. Chem.* **36**, 52–64 (1931).

4. Kistler, S. S. Coherent Expanded Aerogels and Jellies. *Nature* **127**, (1931).

5. Nicolaon, G. A. & Teichner, S. J. Preparation of silica aerogels from methyl orthosilicate in alcoholic medium, and their properties. *Bull Soc Chim Fr 1906–1911* (1968).

6. Schwertfeger, F., Frank, D. & Schmidt, M. Hydrophobic waterglass based aerogels without solvent exchange or supercritical drying. *J. Non. Cryst. Solids* **225**, 24–29 (1998).

7. Aegerter, M. A., Prassas, M. & Koebel, M. M. *Advances in Sol-Gel Derived Materials and Technologies*. (Springer publishing, 2011).

8. Koebel, M., Zhao, S., Brunner, S. & Simmen, C. Process for the production of an aerogel material. (2015) WO2015014813A1

9. Brunauer, S., Emmett, P. H. & Teller, E. Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **60**, 309–319 (1938).

10. Neugebauer, A. *et al.* Thermal conductivity and characterization of compacted, granular silica aerogel. *Energy Build.* **79**, 47–57 (2014).