LOW COST SILICA AEROGEL PRODUCTION

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ABSTRACT

Buildings form a major part of the energy demand in Switzerland. Silica aerogels as high performance insulation materials have the potential to reduce the energy demand for heating and cooling. Silica aerogel insulation materials, can achieve the same thermal insulation performance with only half of the thickness of conventional insulation materials. Translucent, superinsulating silica aerogels exhibit the lowest thermal conductivity of any solid known, typically of the order of 0.015 $W\cdot m^{-1}\cdot K^{-1}$ at ambient temperature, pressure, and relative humidity. The interest in silica aerogels as insulation materials is illustrated by the rapid growth of the aerogel market: in 2004, only about 25 million US$ of aerogel insulation materials were sold, but this had increased to about 500 million US$ by 2013. Still the major drawback for a large scale usage of silica aerogels as standard insulating material in the building sector is their production cost. As a result, most of the current aerogel production is used for industrial applications such as pipeline insulation, rather than building insulation.

Silicon alkoxides such as tetramethoxysilane (TMOS), and tetraethoxysilane (TEOS) are the most common precursors for the production of silica aerogel. Although the chemistry of silicon alkoxide gelation is straightforward from a chemical perspective, alkoxides have their drawbacks, for example their high production cost due to a multi-step synthesis procedure. Although less reactive, TEOS is often preferred over TMOS because its price is about four times lower and because it is less hazardous. Still the minimum material cost of the raw materials for silica aerogel production is 700-800 CHF/m^3 of aerogel.

Our group developed an alternative route for the silica aerogel production using low cost silica precursors and ambient pressure drying technique. This potentially lowers the material cost by a factor of two or more. With the development of more cost-efficient large-scale production technologies, silica aerogel materials have the potential to gain a significant share of the building insulation market by 2020, particularly for retrofit applications.

Keywords: insulation, silica aerogel, raw materials

INTRODUCTION

Energy saving and lowering CO_2 emissions are hot topics in many areas of science and economics worldwide. Still, it is a surprise to many people that HVAC (heating, ventilation and air conditioning) of buildings account for approximately 40 % of the global energy consumption. HVAC systems of buildings can be improved with minimal effort by installing a proper thermal insulation and thus reduce CO_2 emission cost-effectively.

The most economical approach to decrease thermal losses of buildings is to install thicker layers of conventional insulation materials. There is naturally an aesthetic disadvantage linked to such façade construction: the insulated object occupies more space and the usable living space decreases. Silica aerogel insulation materials, can achieve the same thermal insulation performance with only half of the thickness of the conventional insulation materials (Figure 1). Thermal conductivity is a material property which defines the potential of a material as a thermal insulator. Transparent silica aerogels exhibit the lowest thermal conductivity of any solid known, typically of the order of 0.015 $W \cdot m^{-1} \cdot K^{-1}$ at ambient temperature, pressure, and relative humidity. This extremely low thermal conductivity is due to the combination of low density and small pores [1]. With such thermal conductivity value they belong to the group of so called “super-insulation” or ‘‘high-performance insulation’’ materials [2,3].

In the building industry, space saving is the most important reason for the use of superinsulation. Typical cases are interior insulation solutions for building retrofit as well as thin facade insulation for the renovation of old historically important buildings, side balcony and roof balcony constructions. For practical reasons in the construction industry the thermal conductivity is expressed through U-value. The U-value shows heat loss through a given thickness of a specific material, taking account the three major ways in which heat loss occurs – conduction, convection and radiation. In Figure 1 you can see comparison of U and cost values for the most standard insulating materials including silica aerogels.

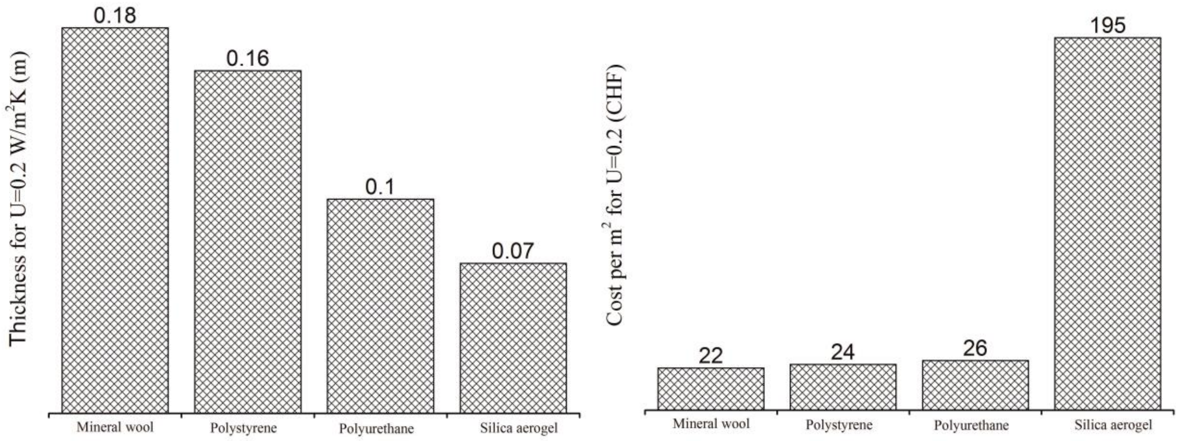

Figure 1. Comparison of thermal properties (U-value) and cost per m^2 of most common thermal insulation materials

Despite their clearly superior thermal properties, silica aerogels are still not used in the large extent in the construction industry due to very high production costs. The main reasons for the high production costs are expensive raw materials and complicated/expensive processing technology. Lately, a lot of work has been done in simplifying processing technology by using ambient drying instead of super critical drying, the details about could be found elsewhere [4,5]. Our group also worked on optimization of process of production of silica aerogels, the current state of art will be presented by Lukas Huber at CISBAT 15 [6].

Sodium silicate is relatively inexpensive and was the first material used for silica aerogel production, but the aerogel manufacturing process is expensive, time and solvent consuming because it requires multiple solvent exchange processes [7]. Silicon alkoxides such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) allow for easier processing and are the most commonly used raw materials for the production of silica aerogels today. TEOS is often preferred over TMOS because its price is about four times lower and because it is less hazardous. Still, even TEOS based raw materials are expensive and they dominate the cost of the final product. Our group have been intensively working on strategies to find the cheaper raw materials and optimise the process with them. In Table 1 the prices of TEOS and possible other raw materials which can be used as precursors to silica aerogels are shown. From table it is clear that alternative raw materials such as silicon tetrachloride would cut the cost by at least half of the price.

Raw material	Cost (CHF/kg)	SiO_2/kg (kg)	Cost/kg SiO_2(CHF)
Metallurgical Si	2.2	2.14	1.03
Silicon tetrachloride	0.3	0.35	0.85
TEOS	1.6	0.29	5.51
Sodium silicate	0.4	0.28	0.70

Table 1: Prices and silica yield of raw materials which can be used as silica precursors

PREPARATION OF TEOS

In order to decrease the costs of raw materials we developed an alternative processing cycle for the production of silica aerogels (Figure 2). Instead of buying TEOS from a manufacturer, the idea is to start with metallurgical silicon, make silicon tetrachloride and from there make TEOS as a precursor to silica aerogel. The advantage of this process is that during TEOS synthesis from silicon tetrachloride, hydrochloric acid is produced as side product and this can be later easily decomposed to chlorine and hydrogen. The chlorine gas can then be used for a production of silicon tetrachloride from metallurgical silicon. Furthermore, most of the ethanol can be also recycled from final product and reused for a production of TEOS from silicon tetrachloride.

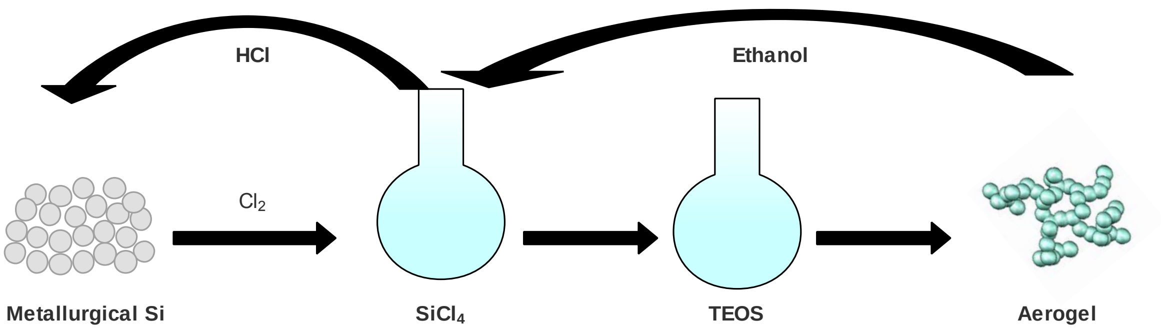

Figure 2: Schematically illustrated process of circular raw material/aerogel production

In order to start producing silica aerogels in such circular system, we first optimise the synthesis of TEOS from silicon tetrachloride. When anhydrous ethanol is treated with silicon tetrachloride the product is TEOS, as shown in chemical reaction below:

$$SiCl_4 + 4EtOH \rightarrow Si(OEt)_4 + 4HCl \tag{1}$$

If ethanol contains some water, as it typically does, pre-hydrolysed TEOS can be synthesized and the amount of water in the reaction determines hydrolysis degree of TEOS [8,9].

Anhydrous ethanol (99.9%) was added to silicon tetrachloride (99%, Sigma Aldrich) in pre-determined rates by syringe pump at 50°C. The reaction is performed in 3 necks round bottom flasks, and the tube for introducing ethanol was in the close proximity of magnetic stirrer to ensure immediate mixing with silicon tetrachloride. The final solution was left for two hours at 50°C and after that remaining HCl in the solution is removed by sparging the solution with compressed air for four hours: the bubbling time and stirring speed pH are optimized to reach the desired pH value. Small aliquots are taken for pH measurements. After achieving the desired pH (2-3), the solution is stored in fridge at 5°C.

The TEOS solutions prepared from silicon tetrachloride are stable for more than three months when they are sealed and stored in the fridge. The ^{1}H-^{29}Si HMBC NMR spectra of commercially available TEOS (Evonik Degusa, Germany) and TEOS synthesized in our group are shown in Figure 3. The sample prepared in our laboratory shows that the solution consists of ca. 70% of monomers (Q^0 at -80 ppm in the Si dimension, $Si(OEt)_4$) and 30% of dimers (Q^1 at -88 ppm in the Si dimension, $(EtO)_3Si$-O-$Si(OEt)_3$). The commercially available TEOS consist only of the monomer. The presence of the dimer indicates that the reaction conditions were not completely free of water.

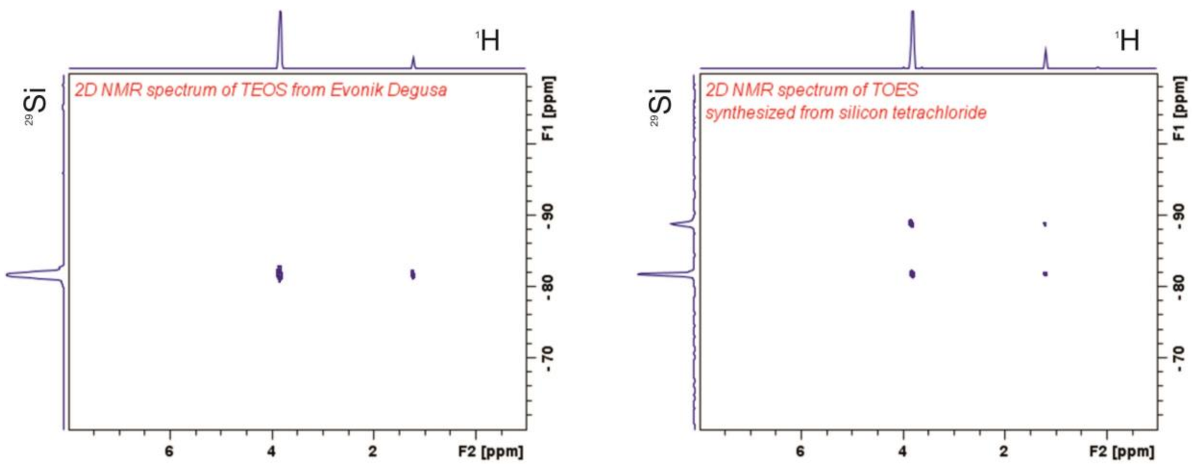

Figure 3: ^{1}H-^{29}Si HMBC NMR spectra of commercially available TEOS (left) and TEOS synthesized in our laboratory (right).

A mixture of monomers and dimers is not a disadvantage to further sol-gel process since dimers, trimers and higher molecular clusters are all formed during the condensation step in sol-gel process anyway. Freshly synthesized TEOS was used for the synthesis of aerogels according to the procedure described below.

AEROGELS SYNTHESIS

The TEOS solution prepared at EMPA was used to prepare polyethoxydisiloxane (PEDS), a pre-polymerized form of TEOS and common intermediate in aerogel production containing. The PEDS was prepared from water/TEOS in a molar ratio of 1.5 and a SiO_2 content of w/w 20%, according to the recipe found in literature [9]. Freshly prepared PEDS was mixed with ethanol, water and 5.5 M ammonia under constant stirring to form a gelation-initiated sol. This was then poured into polystyrene boxes and allowed to gel and age at 65°C for 24 hours. The aged gels were then transferred to glass beakers and and additional amount of ethanol, HMDSO and HCl was added to graft hydrophobic organic groups onto the silica surfaces and prevent shrinkage. The hydrophobization occurred at 65°C for an additional 24 hours. Finally, the aerogels were dried at 150°C for three hours.

The appearance (Figure 3b) and density of silica aerogels are the same regardless whether TEOS prepared at EMPA or commercial TEOS is used. The density of the synthesized silica aerogels measured by the powder displacement method (GeoPyc 1360, Micromeritics, US) is 0.15 g/cm^3. The mesoporous structure with pore size between 20 and 50 nm, which give rise to the low thermal conductivity of aerogels, can clearly be observed in the Scanning Electron Microscopy image (SEM) (Figure 4a).

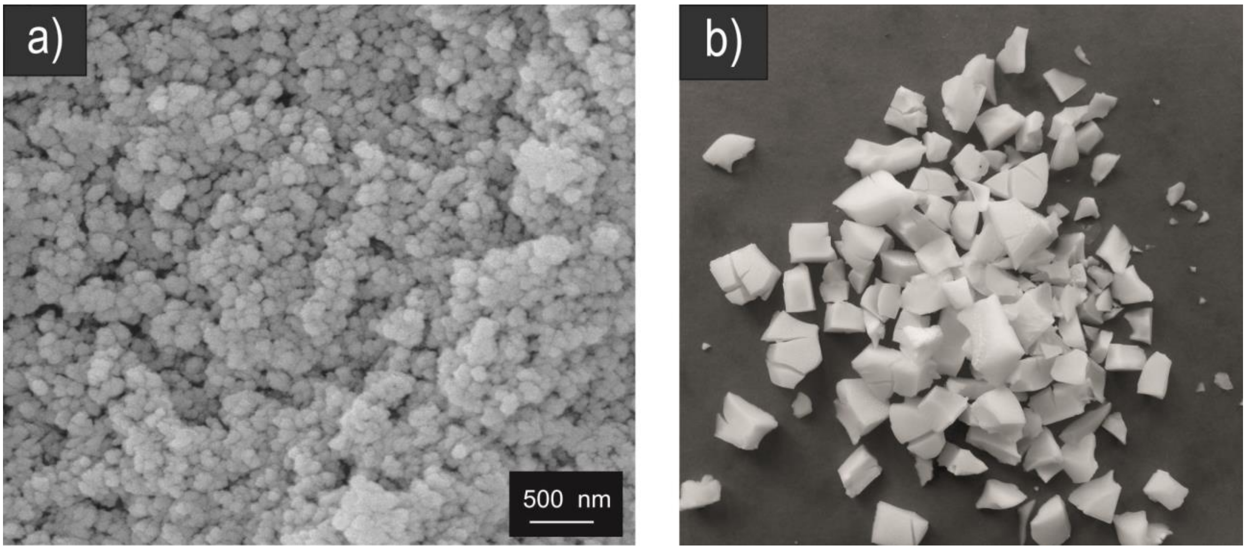

Figure 4: a) SEM image and b) photo of silica aerogels prepared from TEOS synthesized from silicon tetrachloride in our laboratory

CONCLUSIONS

Building insulation requires much larger volumes compared to industrial insulation (e.g. pipes). Thus, aerogels can only take a significant share of the building insulation market if we can capitalize on their thermal superinsulation properties at a lower price than is currently available [10]. Thus, traditional ways of preparing aerogels, which includes expensive raw materials and supercritical drying processes, are suppressing further commercialization and usage on the large scale and the development of new, cheaper raw materials is an absolute pre-requisite for the further expansion silica aerogel in the building insulation market. The optimization of the synthesis of TEOS from silicon tetra chloride presented here is the first step in optimization of the entire production chain. A plant where most of the compounds will be re-cycled on site is the most ecologically and economically viable way for further scale up of silica aerogel production.

ACKNOWLEDGMENTS

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