

Aerogels – new materials with promising applications

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This work focuses on the dependence preparation conditions – structure – physical properties of hydrophobic silica aerogel granules and micro powders, all of them prepared under subcritical drying conditions with potential application as insulation materials. The so prepared nanoporous hydrophobic silica aerogel granules and powders are analyzed with scanning electron microscope, infrared spectroscopy, differential scanning calorimetry and thermal conductivity measurements. The physico-chemical properties of the aerogels are compared with that of commercial aerogel granules. It has been proved that a long solvent exchange times and surface hydrophobization lead to aerogel micro powders with a specific surface of about 850 m²/g and a bulk density of about 0.1 g/cm³.

Keywords: aerogels, silica, sol-gel, thermal insulation.

INTRODUCTION

Sol-gel technology is a powerful method for the preparation of oxide matrixes at low temperatures. Most important advantages of sol-gel technology are the use of liquid chemicals, the possibility for preparation of complicated chemical compositions and the low temperature preparation. Sol-gel chemistry offers a possibility for the ambient preparation of optical materials like xerogels or layers doped with rare earth ions. In the same way a wide range of useful ceramic materials based on Al₂O₃, ZrO₂, SnO₂, SiO₂ can be easily prepared. Gels are solids confining a solvent in a three-dimensional network. The solvent may be enclosed as quasi-liquid in a pore system. At this state, the gels are called hydrogels (water as solvent) or alcogels (alcohol as solvent), etc. If the network has nano-dimensions or is index-matched, the gel looks transparent. Sol gel-chemistry is based on three basic chemical reactions: water hydrolysis of liquid alkoxides (the most important reagents in sol-gel chemistry) followed by condensation. Condensation (better known as gelation), could be performed as a water condensation or alcohol condensation [1]. The results of sol-gel process strongly depend on the reaction conditions: it is possible to obtain micro or nanopowders,

transparent xerogels, transparent thin films or even aerogels – porous solids with extremely low thermal conductivity and density.

One of the most important advantages of sol-gel chemistry is the preparation of aerogels. Aerogels are a class of porous, solid materials with extreme and valuable materials properties. Most notable aerogels are known for their extreme low densities (which range from 0.001 to 0.5 g/cm³). In fact, the lowest density solid materials that have ever been produced are all aerogels, including silica aerogels. The advantages of silica aerogels are: low density, theoretically down to (0.001 g/cm³), optical refraction index (1.002), thermal conductivity (0.02 W/m·K), speed of sound through a material (70 m/s) and a relative dielectric constant 1.008 at 3–40 GHz [2].

There are two main technological strategies for preparation of aerogels: supercritical drying and subcritical drying techniques, leading to bulk aerogels, aerogel powders or granules depending on preparation conditions. The supercritical preparation is combined with liquid carbon dioxide drying of gels at supercritical conditions, following the pioneer investigations of Kistler, 1931[3]. The expensive supercritical drying can be replaced by subcritical drying at low temperature and pressure. This method include several basic steps: preparation of wet gel, solvent exchange of the solvent in the pores of the wet gel, surface hydrophobization and vacuum drying of the materials. In this way powders or bulk materials with the same physical

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properties as in the case of supercritical drying can be obtained [4, 5].

Despite of the large number of investigations of hydrophobic silica granules and micro powders, there are open questions concerning the physico-chemical nature of solvent exchange taking place in the pore system of aerogels, variation of subcritical drying conditions and microstructure of the aerogel micro powders and granules. Recently we demonstrated for the first time that silica aerogels are suitable matrixes in the production of light emitting composites containing hybrid molecules, $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ [6].

The aim of the present contributions is to compare the physico-chemical properties of subcritical produced amorphous silica aerogels in order to achieve a better understanding of preparation – structure – properties relationship of aerogel powders and granules.

EXPERIMENTAL

Millimeter scaled aerogel granules (sample notation SAA). Millimeter scaled aerogel granules were prepared using standard tetraethylortosilicate (TEOS), 99% ethanol (EtOH), 0.23 M hydrochloric acid, 0.14 M ammonia solution, trimethylchlorosilane (TMCS), n-hexane, acetone and distilled water. First, a mixture of TEOS and EtOH was prepared. After 5 minutes stirring distilled water was added followed by the hydrolyzing agent, the 0.23 M HCl. The hydrolysis reaction took about one hour, after that a 0.14 M ammonium solution was used to catalyze the condensation reaction. The gelation time, t_{gel} , was 10–15 minutes, after that EtOH was added to start the solvent exchange reaction at room temperature. The solvent exchange continued for 48 hours followed by hydrophobization in a mixture of TMCS and n-hexane. The hydrophobization continued for 24 hours at room temperature. Drying of the aerogel SAA was performed for 24 hours in a vacuum dryer at 0.5 atm and 70 °C. The bulk density of aerogel granules SAA was 0.1 g/cm³, combined with a very low thermal conductivity, $\lambda = 0.033$ W/m·K and a specific heat $C_p = 1440$ J/kg·K at 30 °C. Details about the thermal insulation properties of aerogel granules depending on preparation conditions are discussed in [4].

During the preparation we used a vacuum drying camera NÜVE EV 018 with a volume $V = 1240$ cm³ equipped with a LABOR port diaphragm pump (delivery 30 l/min and power 300 W) working at 0.15–0.2 atm.

Subcritical drying at room temperature and 0.150 atm, sample notation S1. Samples obtained at room temperature drying, using the above given

sol-gel preparation conditions (S1) were prepared. The scheme led to granules with bulk density of 0.12 g/cm³. The physical properties expected are close to that of the samples described above because of the dependence between density and thermal properties of aerogels [2, 4]. This confirms that the drying temperature is not a determining factor for the physical properties of aerogel granules.

Aerogel micro powders (sample notations D1 and D2). We developed a new preparation scheme for the preparation of micro powders based on long solvent exchange at room temperature or 40 °C at stirring, followed by drying of the aerogel at subcritical conditions. The preparation of aerogel micro powders was accomplished through four steps, given in Figure 1. The gel preparation and hydrophobi-

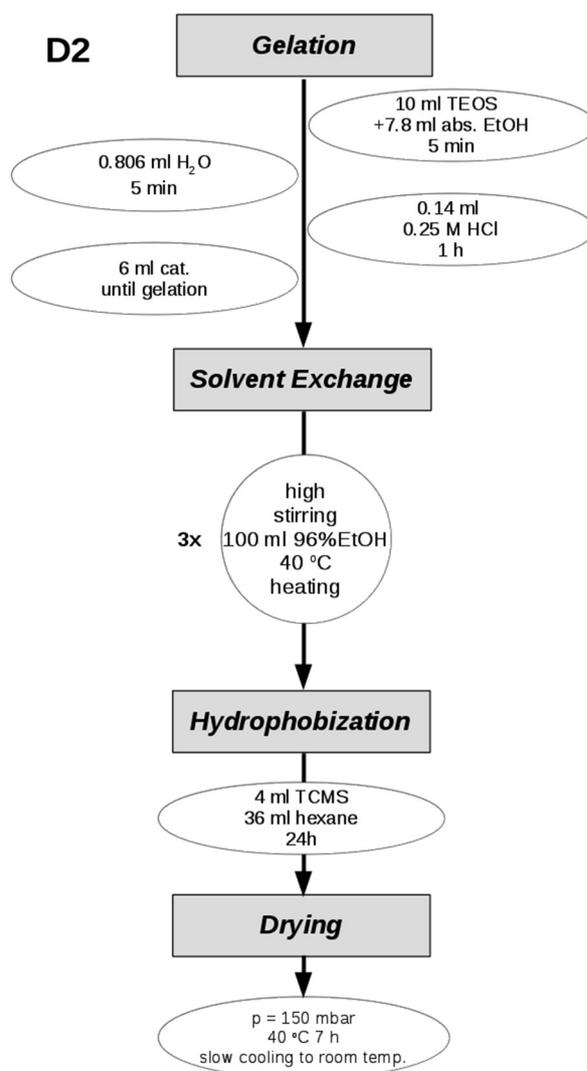


Fig. 1. Sol-gel scheme for preparation of aerogel micro powders at long solvent exchange and 40 °C (sample D2).

zation conditions were close to that of samples SAA and S1, discussed above.

The solvent exchange conditions, however, were changed significantly in order to obtain powders. The solution used here was 100 ml 96% ethanol, the solvent exchange was conducted at stirring. The solvent exchange conditions used were: room temperature and total time of exchange 21 days (*sample D1*) and 40 °C and total time of exchange 11 days (*sample notation D2*). For both samples the solvent was changed two more times.

The last preparation step was the drying of the aerogel micro powders. It was conducted at subcritical conditions – pressure of 0.150 atm and 70 °C temperature for 7 h. The bulk density of these micro powders was about 0.08 g/cm³ [4].

The amorphous silica micro powders D1 and D2 prepared in this paper possess a typical aerogel morphology, visualized in Figure 2, where a representative SEM picture of aerogel micro powders is given. Here, a wide network of closed and open micropores and mesopores leads to the low density of the pow-

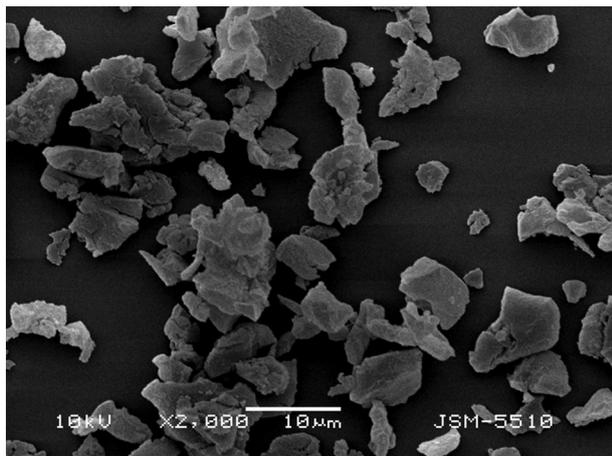


Fig. 2. SEM investigations of aerogel micro powders, sample D2. A typical “cloud – like” morphology of the particles is visible at higher magnifications. The mean particle diameter of powder is in the range of about 5–10 μm.

ders. It is well known, that thermal insulation properties of aerogels depend significantly on the occurrence of nanopores in the range of 10–30 nm [7, 8].

The so prepared, millimeter scaled nanoporous hydrophobic silica aerogel granules and micro powders were analyzed with thermal conductivity measurements and chemical analysis. The thermal conductivity of aerogel granules was measured using a C-THERM TCI–thermal conductivity analyzer using a powder/liquid cell. Scanning electron

microscopic (SEM) investigations were performed using a standard electron microscope JEOL 5510 working on SE regime. Particles were Au – covered. The texture characteristics of the so prepared micro powders and granules were determined by low-temperature (77 K) nitrogen adsorption in a Quantachrome Instrument NOVA 1200e instrument. The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following parameters: specific surface area (S_{BET}), total pore volume (V_{t}) and associated average pore diameter (D_{av}) [9]. All samples were outgassed for 16 h in vacuum at 150 °C before the texture measurements.

Measurements of pH combined with a temperature control were performed using a computer driven pH-meter Hach H270. Infrared (IR) spectra were measured on a standard Thermoscientific 6700 IR spectrophotometer using the KBr preparation technique. Absorption peaks were mathematically treated as overlapping Gaussian curves, peak maxima were determined from second derivative spectra.

RESULTS AND DISCUSSION

The pH dependence vs. time of the solvent exchange process is investigated in order to describe the physico-chemical nature of solvent exchange. Figure 3 displays the experimental data obtained together with temperature measurements; here pH of the solvent exchange solution is measured for a long time continuously together with temperature measurements. The curve obtained can be distinguished into two parts, a fast decrease of pH and an increase of pH. From general chemical point of view the decrease of pH seems to be related to the deprotonation of R-Si-OH groups of the prepared gel. Increasing of pH is due to leaving ammonium cations from the inner pores of the aerogel granules toward the solvent exchange solution of ethanol because ammonium hydroxide is used as a gelation catalyst. The second step is limited by diffusion of the ammonium ions from the pores of the aerogel granules through the ethanol solution.

Using the pH dependence a rate of the solvent exchange (from point 2 to 3) of $2.5 \cdot 10^{-4}$ mol/l·s can be extracted. The deprotonation step (from point 1 to 2) is faster. Further investigation are necessary to develop a kinetic model of solvent exchange describing quantitatively the deprotonation and diffusion limited steps. It is visible that pH measurements could be successfully used to describe microscopically the complicated processes of solvent exchange accompanying the subcritical production of aerogels.

The physicochemical properties of aerogel granules and micro powders discussed here are summa-

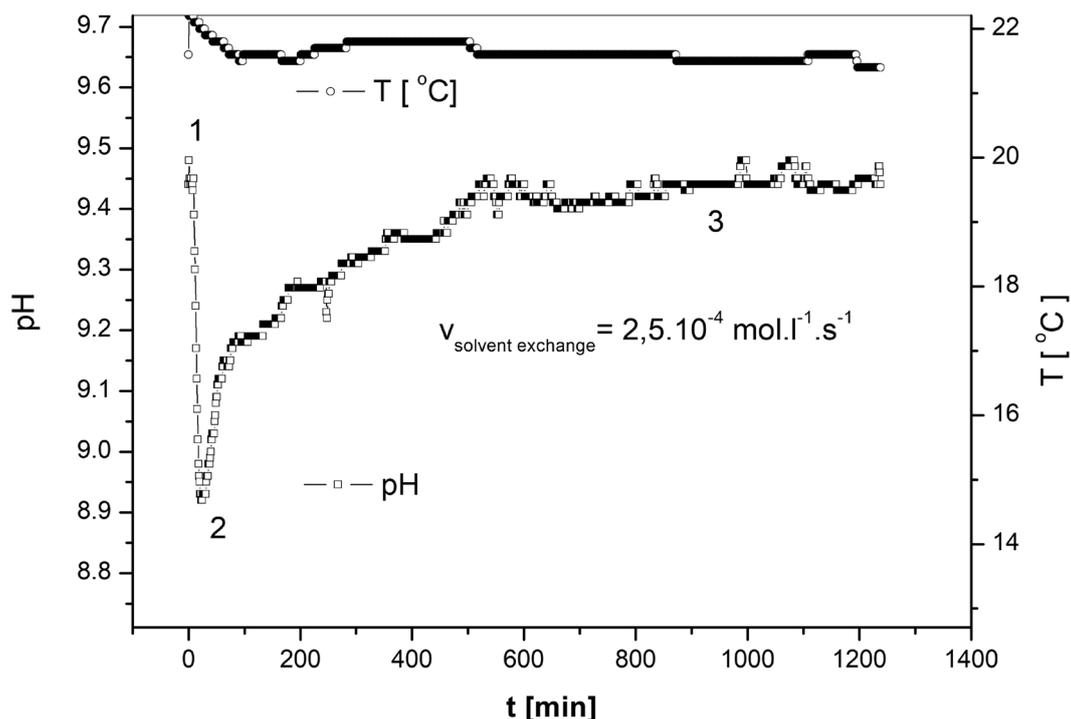


Fig. 3. Representative pH and temperature vs. time investigations during solvent exchange.

ized in Table 1, where results from nitrogen adsorption–desorption isotherms are summarized. It is visible that the developed sol-gel scheme leads to the production of high-class aerogel materials, possessing a very high specific surface area. Insulation properties of the produced gels depend strongly on the nanopores, formed in the gels. It is visible, that temperature of drying do not play an important role in aerogel granules production, drying pressure, hydrophobization and solvent-exchange are crucial for the texture properties of aerogel granules and micropowders. The process of powderization of aerogel granules depends strongly on the solvent exchange conditions. The physico-chemical properties of commercial millimeter scaled Cabot Lumira aerogel granules with bulk density of 0.08 g/cm³ (sample Cabot) are given for comparison.

In Figure 4 IR spectra of Cabot Lumira aerogel granules (sample Cabot) and aerogel granules produced in this contribution are compared.

Figure 4 shows that IR spectra of the investigated samples are identical and demonstrate the reproducibility of the sol-gel technology approach discussed here. Based on [10–12] the intensive peak at wavenumbers near 1090 cm⁻¹ or 1220 cm⁻¹ correspond to the stretching vibration of Si–O–Si bonds and the peaks at about 840 cm⁻¹ and 460 cm⁻¹ are assigned to the antisymmetric and symmetric stretching vibration of Si–O–Si, respectively. The bands at

Table 1. Physico-chemical properties of aerogel granules and micropowders. Specific surface area (S_{BET}), the total pore volume (V_t) and associated average pore diameter D_{av} are given. Samples Cabot, SAA and S1 are millimeter scaled granules, while D1 and D2 are micro powders

Sample	S_{BET} , m ² /g	V_t , cm ³ /g	D_{av} , nm
S1	796	3.40	17
D1	840	2.25	11
D2	950	2.67	11
SAA	785	3.12	16
Cabot	699	3.8	21

3440 cm⁻¹ and 1632 cm⁻¹ represent the stretching and bending vibrations of Si–OH bond and the vibrations of physically adsorbed water. In the spectra a sharp peak coming from Si–CH₃ vibrations at about 1260 cm⁻¹ is visible, confirming the successful performed hydrophobization.

Using the discussed preparation conditions we produced about 1500 ml hydrophobic granules (sample SAA) and incorporated it as fillers in a glass textulite case-insulation of a Stirling engine cylinder operating at low temperatures. More about the Stirling engine and its components can be found in [13].

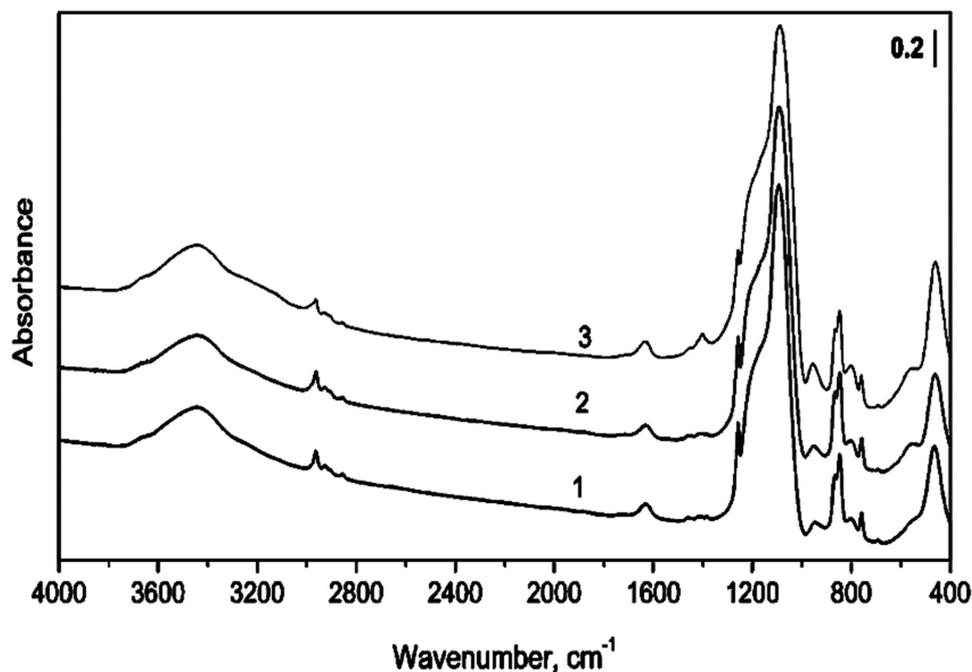


Fig. 4. IR spectra of aerogel millimeter scaled granules: Cabot (1), SAA (2) and (3). Curve 2 and 3 represents spectra of aerogel granule fractions with a density of 0.1 g/cm³ and 0.2 g/cm³, respectively.

CONCLUSIONS

A reproducible sol-gel preparation scheme for the production of hydrophobic aerogel granules and micro powders with a specific surface area S_{BET} of about 800 m²/g and total pore volume of about 3.2 cm³/g is demonstrated. The insulation properties of aerogel granule and powders in this contribution depend strongly on the nanopores (10–20 nm) formed in the material. The process of powderization of aerogel granules depends on the solvent exchange conditions and drying pressure. The solvent exchange process of aerogels can be separated in two steps, a fast deprotonation reaction and a diffusion limited step. IR spectra are an important tool for controlling the efficiency of aerogel powder production.

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АЕРОГЕЛОВЕ – НОВИ МАТЕРИАЛИ С ПЕРСПЕКТИВНИ ПРИЛОЖЕНИЯ

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(Резюме)

Настоящото изследване е насочено към изследване на зависимостта препаративни условия – структура – физикохимични свойства на хидрофобни аерогелни гранули и микропрахове от силициев диоксид, получени при субкритични условия. Продуктите са с потенциално приложение като изолационни материали. Получените нанопорьозни гранули и микропрахове са анализирани със сканираща електронна микроскопия, диференциална сканираща калориметрия и термични изследвания. Физикохимичните свойства на получените материали са сравнени с тези на комерсиални аерогелни гранули. Показано е, че продължителният процес на обмен на разтворител води до получаването на аерогелни микропрахове със специфична повърхност около $800 \text{ m}^2/\text{g}$ и плътност около $0.1 \text{ g}/\text{cm}^3$.