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Accelerated aerogel development *via* Soxhlet extraction and freeze-drying

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The tedious and time-consuming solvent exchange during aerogel production was sped up using a standard Soxhlet extractor. Optimizing the setup with a vent and molecular sieve allowed to save up to 80% of the production time compared to batchwise extractions while maintaining state-of-the-art samples of silica and polyurethane aerogels, *i.e.* MTMS aerogels with a thermal conductivity of 15 mW m^{-1} K^{-1} and PU aerogels with 17 mW m^{-1} K^{-1} and good mechanical properties even after freeze-drying, which is generally more stressful than supercritical drying. The syntheses had to be carried out in high-boiling solvents, but adaptation and optimisation were made possible rapidly due to the method developed.

1. Introduction

Aerogels first appeared over 90 years ago and have been researched and optimised ever since.[1] Typically they are sol–gel products, which are characterized by a homogeneous open-pored structure, a density of less than 0.2 g cm^{-3} and low thermal conductivity.[2,3] Aerogels are primarily used as a high-performance insulation material, whereby some materials are also suitable for windows due to their translucent appearance.[4,5] The properties are based on the structure and chemical composition of the solid phase, which can be organic (*e.g.* polyurethane- or polyimide-based), inorganic (*e.g.* silica- or metal oxide-based) or a hybrid system.[6] The networks usually have a particulate, fibre-like or non-particulate structure.[7,8] Due to their fine structure and high porosity, aerogels are usually mechanically fragile and often exhibit brittle and fragile behaviour, especially purely inorganic aerogels like SiO_2. A great effort has been made to synthesise robust materials while at the same time maintaining their insulating properties.[9] We would like to emphasise two materials in particular. Firstly the non-transparent polyurethane aerogels (Slentite (BASF)) are characterised by particularly high mechanical stability due to the formation of polyisocyanurate while maintaining low thermal conductivity, which is why they are well suited for wall insulation.[10–13] Secondly, the impressive hybrid aerogels from Nakanishi and Kanamori, which, depending on their composition, are characterised by unusually good flexibility, transparency, insulation behaviour and the possibility of ambient pressure drying, but are significantly more fragile than PU materials.[14–16] Odling *et al.* describe an interesting approach for the large-scale production of recyclable methyltrimethoxysilane (MTMS) aerogels.[17] Even though the materials are fundamentally different, there are similarities in their synthesis. A suitable solvent (mixture) is extremely important for creating a homogeneous fine structure.[18,19] Furthermore, the synthesis solvent usually has to be exchanged for a suitable drying solvent in several steps. A large excess is often used to ensure the fastest and most complete exchange possible, but the process often takes several days. Together with gel production, ageing and drying, production times of 2 weeks are not uncommon.

Improvements for solvent exchange have received little attention to date and is hardly mentioned in a recent critical review that highlights all other challenges in aerogels.[20] In life cycle analyses, solvent exchange and consumption was identified as the major problem in aerogel sustainability.[21] In 2021, Schwan *et al.* described the use of a peristaltic pump and zeolites in comparison to classic static exchange on RF aerogels.[22] Typically, the solvent exchange in the laboratory is accelerated *via* artificially generated convection (shaker), increased temperature and a large excess of the target solvent.

Frequent changing of the solution increases the concentration gradient and also helps with rapid exchange. All these parameters are part of a classic Soxhlet extraction (SE). The Soxhlet extractor was invented by Franz von Soxhlet in 1879 and was originally used to extract fats from solids.[23–25] Soxhlet extraction was used in connection with aerogels to wash out intentionally adsorbed substances.[26,27] In 2021, we described a solvent exchange with simultaneous extraction of gelators for polyolfine aerogels, but without scientifically investigating this

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aspect.[28] In this paper we describe the use of Soxhlet extractors for solvent exchange in aerogel synthesis, the necessary conditions and advantages using the example of silica systems and PU materials. We describe these two different systems to illustrate the flexibility of the method. The materials were selected based on their properties and their scientific relevance in the field of aerogels. The aim is to show that high quality aerogels for research purposes can be produced and analysed in a shorter period of time.

2. Experimental

2.1 Materials and methods

The following materials were used in this work:

2-Octanone, 2-nonanone, cyclohexanone, propylene carbonate, potassium sorbate, ethylene glycol, triethylene glycol, cyclohexane, acetic acid (1 M), ammonia water 25% (for analysis), benzene and methanol were purchased from VWR Chemicals (Radnor, Pennsylvania, USA). 3,3′,5,5′-Tetraethyl-4,4′-diaminodiphenylmethane and benzyl alcohol (BzOH) are supplied by Sigma Aldrich (St. Louis, Missouri, USA). M20 and Lu3300 were provided by BASF (Ludwigshafen, NRW, Germany). Methyltrimethoxysilane (97%) was purchased from ABCR (Karlsruhe, Germany) and *tert*-butanol (*t*BuOH) (99%) from S3 Chemicals (Bad Oeynhausen, Germany).

2.2 Synthesis

2.2.1 MTMS-aerogels. For the production of MTMS-based aerogels, comparable formulations were analysed and a synthesis in benzyl alcohol was developed (see SI Fig. S2 for reaction scheme).[29–31]

To prepare the MTMS aerogel, 3.34 mL MTMS was mixed with 0.166 mL acetic acid and hydrolysed for 1 hour with stirring. 5.27 mL BzOH was added and stirred for a further hour. The stirrer was then removed and a defined amount (1.0; 1.5; 1.75 mL) of 25% ammonia water was added, the reaction vessel was closed and shaken for 5–10 seconds to ensure homogeneous distribution before gel formation took place. To simplify handling, the solutions can be pre-cooled to reduce the reaction speed and thus allow more time for homogeneous distribution. After 3 hours, the resulting gel is aged at 60 °C for 6 days, as ammonia is slow catalyst.[32] It is recommended to have only a small gas space above the sample or to use shielding gas. The aged gel must now undergo a solvent exchange and then be dried.

2.2.2 PU-aerogels. BASF precommericalized a robust PU-based aerogel[13] that we adapted to a Soxhlet extraction and freeze-drying. A catalyst solution (SorbTEG) was first prepared to produce the PU aerogels. For this, 1 g of potassium sorbate was dissolved in 2 g of ethylene glycol (EG) and 1 g of triethylene glycol (TEG) and then topped up with 2.5 g of TEG. Alternatively, a 20 w% of potassium sorbate in EG is also suitable. An isocyanate solution (A) and an amine solution (B) are prepared for the synthesis. A mixture of 60 w% 2-octanone or 2-nonanone and 40 w% cyclohexanone is used as the solvent. Alternative solvent combinations are listed in the SI (Table S1). For solution A, 1.2 g M20 is dissolved in 4 g solvent and 0.02 g Lupranol 3300 is added. For solution B, dissolve 0.3 g of 3,3′,5,5′-tetraethyl-4,4′-diaminodiphenylmethane (MDEA) in 7 g of solvent and add 0.04 g of SorbTEG while stirring. Once both solutions are homogeneous, they can be poured into each other, mixed briefly but thoroughly and then poured into the mould. Gel formation occurs within approx. 1 min at RT. After gel formation, a few drops of solvent are applied to the surface and the gel is aged for 24 hours in a sealed container.

2.2.3 Soxhlet. For solvent exchange *via* Soxhlet extraction, a classic Soxhlet set-up is used. The sample is placed in the Soxhlet chamber, and a small amount of solvent is added. This is to prevent the monoliths from being damaged by evaporating solvent until the extraction starts. The target solvent is placed in the still pot. Ideally, the volume used is 3–4 times the volume of the chamber. During distillation, the solvent is vaporised, condenses on the cooler, drips to the sample, mixes with the synthesis solvent and is fed back into the still pod *via* the siphon. The distillation runs (depending on the sample geometry and volume) for about 8 hours. The sample can then be removed and dried. For better exchange results and/or improved handling, various modifications have been made to the Soxhlet chamber. Fig. 1 shows a sketch of the optimised Soxhlet setup.

In order to be able to extract several samples at the same time without them lying directly on top of each other, it is recommended to build a sample holder with grids so that the solvent can flow around the individual samples. Depending on the design, this also makes it easier to insert and remove the

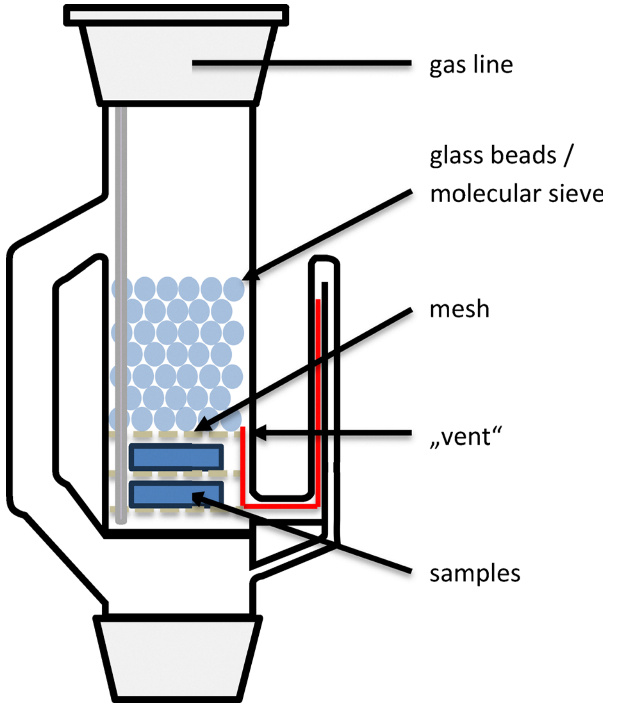

Fig. 1 Sketch of a Soxhlet chamber with two samples, a gas line, packing material and a vent.

solvogels from the chamber. Glass beads can be used to reduce the dead volume in order to realise a faster exchange. The sample should be shielded by a grid to avoid external stress. For the use of hydrophilic solvents, the glass beads can also be replaced by 3 Å molecular sieves to keep the sample free of water. This is particularly useful when working with *t*BuOH. For better mixing in the chamber, a tube can be inserted *via* the reflux condenser to inject dry air or N_2 gas close to the sample. The flow accelerates the exchange, but also cools the liquid, which is why the gas flow should be set only as high as necessary to have some bubbles per minutes to ''agitate'' the solvent. Moreover, a small tube can be introduced in the siphon of the Soxhlet as a ''vent'': when the solvent level in the chamber falls below the vent, gas enters the siphon and the drain of solvent is stopped. This is not absolutely necessary, as there is always a saturated solvent atmosphere above the sample during the distillation process, but it improves the exchange. In the event of interruptions, it also provides effective protection against superficial drying of the sample.

2.2.4 Classical solvent exchange. For the classical solvent exchange, the solvogels were placed in airtight containers and covered with 10 times the amount of target solvent. The containers were sealed and placed on a shaker for 24 hours. After this time, the solvent is removed, collected for recycling and replaced with new solvent. This process is repeated at least 4 times. In the case of *t*BuOH, pre-dried solvent is used for the last two replacement steps and 3 Å molecular sieve is added. To avoid crystallisation at room temperature, the exchange is carried out at 30 °C.

2.2.5 Supercritical drying. For supercritical drying, the samples are placed in a high-pressure reactor, which is flooded with liquid CO_2 (see illustrations in the SI (Fig. S3)). The CO_2 is replaced every 12 hours. The washed out solvent is collected and its volume determined during draining and expansion. The exchange is considered complete if no more solvent escapes from the samples within one day. For drying, the reactor is heated in a water bath until approximately 90 bar is reached. The temperature is maintained and the pressure is slowly reduced *via* a needle valve until room pressure is reached.

2.2.6 Freeze drying. For freeze-drying, the samples are removed from the excess solvent in which they are stored and rapidly frozen on a pre-cooled grid over liquid nitrogen. If the samples are cooled too quickly, they break; too slowly and crystallisation can cause damage. The grid is placed in a freeze dryer (Christ Alpha 1–4 LSC) at −55 °C on a metal block and a high vacuum pump is used to generate a pressure of 60 µbar. Depending on the sample volume and geometry, drying can take up to 18 hours. Individual small samples (thickness < 5 mm) can be dried within 2 hours under ideal conditions. The resulting aerogels can be removed and the solvent recycled.

2.3 Characterization

All analyses were carried out in at least two repetitions, contact angle and Shore hardness in at least 5 measurements. The reaction success of the MTMS gels was determined using IR spectroscopy. The density was measured with a buoyancy balance (Mettler-Toledo XP 2005) in water at 20 °C. Durometers of type A and A0 were used to determine the Shore hardness. The thermal conductivity was measured with a Thermtest HFM25 in a plate-plate setup with an average temperature of 30 °C. To determine the extraction behaviour, 100 µL samples were taken every 30 min from batch and Soxhlet samples and measured *via* GC-MS. The samples were diluted with acetone, benzene was used as internal standard. The surface of the aerogels was measured using nitrogen adsorption (Quantachrome Quantasorb – BET). The contact angle of water on the aerogel surface was recorded using the sessile drop method with a DigiMicro Scale Digital Microscope from dnt, a 100 µL microliter syringe from VWR (approx. 11 mg drops) and digitally evaluated using a Zissmann plot. SEM images of the aerogels were taken with a Zeiss Sigma 300 VP scanning electron microscope using a secondary electron detector. The thermal properties were measured by dynamic differential scanning calorimetry (DSC) using a DSC 214 (NETZSCH) and the degradation was determined by thermogravimetric analysis (TGA) using a TG 209 F1 Libra (NETZSCH).

3. Results and discussion

The results and discussion are divided into two parts. In the first part we look at the actual core of the work; solvent exchange *via* Soxhlet extraction, its conditions and advantages. In the second part, the samples produced are described based on their material properties to show that the method is also suitable for state-of-the-art materials.

3.1 Solvent exchange

For solvent exchange *via* the Soxhlet extractor, a relevant difference between the vapor pressure of the original solvent from the synthesis and the target solvent is necessary. A boiling point difference of at least 60 K should be aimed for so that a complete exchange (residual amount $\ll$ 1%) is possible. This means that the solvogels must either be produced in high-boiling solvents or exchanged for liquefied gases under pressure (results will be published in a separate work). As boiling points of *t*BuOH and cyclohexane are 82.2 °C and 80.7 °C, they can be replace benzyl alcohol with a boiling point of 205 °C, the Antoine equation predicts a vapor pressure of approximately 10 mbar at 85 °C. In contrast, the low-boiling butanone (Methyl ethyl ketone, MEK) (b.p. 79.6 °C) for the PU system needed to be replaced. similar Hansen parameters allowed to adapt the existing formulation to high-boiling solvents, cyclohexanone (b.p. 155 °C) and 2-octanone (b.p. 172 °C). By using solvent (mixtures) with similar solubility parameters, it is usually possible to create and optimize a new formulation with just a few laboratory tests.

The purpose of solvent exchange *via* Soxhlet extraction is to save a significant amount of time compared to batch exchange. This applies not only to the production of individual samples, but also to the manual work involved in the laboratory. Basically, the exchange rate with a suitable solvent depends on several factors, with the sample geometry having by far the greatest influence. If we consider a typical cylindrical sample body where the diameter is greater than the height, the diffusion distance over half the sample height is the speed-limiting factor. If the diameter is smaller than the height, the radius of the sample determines the exchange speed. This problem occurs in every diffusion-driven exchange, but must be considered more intensively in Soxhlet due to the desired time reduction. The exchange rate in the gel body of the sample depends mainly on concentration gradients and the temperature (Fick's first law).[33] The concentration gradient to the exchange solvent is kept as high as possible in the chamber by regularly draining and overlaying with fresh solvent. This behaviour follows Nernst's distribution law, which is why exchange with more frequent small Soxhlet cycles is more suitable than large chambers that are renewed less frequently.[34] For this reason, the use of filling bodies to reduce the dead volume is recommended. The solubility of the solvents in each other and the diffusion rate are both directly dependent on temperature. This not only enables faster exchange, but also allows the exchange of liquids that are not or hardly soluble in each other under normal conditions. An example of this is the exchange of trichlorobenzene for *t*BuOH. Since the solvent in the chamber cools slowly at high residence times, a short cycle time is also preferred here. Fig. 2 shows a false-color image of a Soxhlet setup during extraction.

As can be seen in the figure, a temperature gradient forms in the chamber. In the case of low boiling speed (a), the resulting temperature in the sample area is 14 K lower than in normal operation (b). The temperatures displayed refer to the surfaces and do not indicate the actual values in the Soxhlet, but they do provide a good indication. The use of a diffuse gas stream for mixing can be both advantageous and disadvantageous. Although mixing ensures a better concentration gradient around the sample and improves temperature distribution, if the gas flow is too high, it can also act as active cooling, which is counterproductive. Although it is possible in principle to introduce preheated gas, this is very costly, especially in our setup, where the gas hose is fed through the cooler. The use of a sufficiently low flow rate (some bubbles per minutes) seems to be a good compromise. Another option would be a magnetic stirrer under the sample, but this is not possible in a standard Soxhlet with filling bodies.

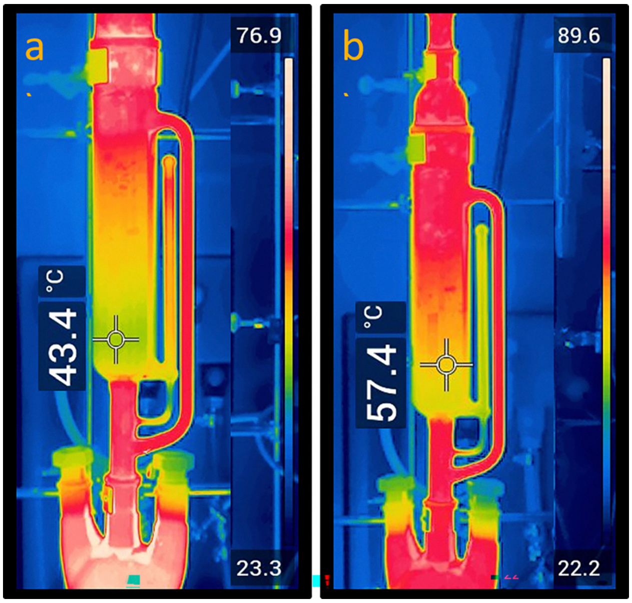

Fig. 2 False-colour image of a Soxhlet extraction with *t*BuOH (without mixing using gas, filled shortly before drainage) (a) very low heating rate (b) normal heating rate.

As described above, a high number of cycles is advantageous, which is why a small chamber volume is preferable. This conflicts with the simultaneous exchange of as many samples as possible. For this reason, the use of packing material and a bypass/valve in a larger Soxhlet setup makes sense. In the optimized setup shown earlier (Fig. 1), the samples are spatially separated from each other and surrounded by liquid on grids. Direct stacking results in non-flushed areas, which behave analogously to a single large sample body and are therefore subject to the diffusion limitations described above. The upper sample is also protected by a grid in front of the packing. If several samples are stacked in this way, the installation of a vent is preferable. When the liquid overflows, only enough solvent is drained off to ensure that the top sample is always covered with solvent. For a single sample, the volume from the siphon's backflow and the trailing solvent is usually sufficient for this purpose. Since the vent only occupies part of the siphon, the solvent also flows downwards, thus evenly washing all samples.

In this work, solvent exchange experiments were mainly carried out with cyclohexane and *t*BuOH, as both are well suited for the gels used and for freeze drying. Like many other silica formulations, the MTMS gels used contain water, which forms an azeotropic mixture with *t*BuOH and must be removed. The mixture boils at 79.91 °C, 101.3 kPa and contains 88.24 w% *t*BuOH.[35] Heterogeneous azeotropic batch distillation with cyclohexane could be integrated into the Soxhlet, but is very difficult to implement. For this reason, an attempt was made to add 3 Å molecular sieve to the chamber. While the balls in the still pot are quickly destroyed by the boiling solvent and stirring, they simultaneously act as water absorbers and fillers in the chamber above the sample. The minimum amount of molecular sieve required can be calculated based on the water content of the samples and the solvent used. TGA measurements of used molecular sieve have shown that it was able to adsorb about 11.2 w% water in its nanopores. The macroporous portion (6.8 w%) is occupied by the azeotrope and therefore does not contribute to the drying process. Since recovering these small quantities from the molecular sieve does not make sense, this solvent is lost in the process. An analysis of all substances introduced into the process showed that 96% of the material used could be recovered with manageable effort.

In order to compare the solvent exchange in a Soxhlet extractor with an agitated batch exchange, various samples were prepared and the progress of the exchange was checked

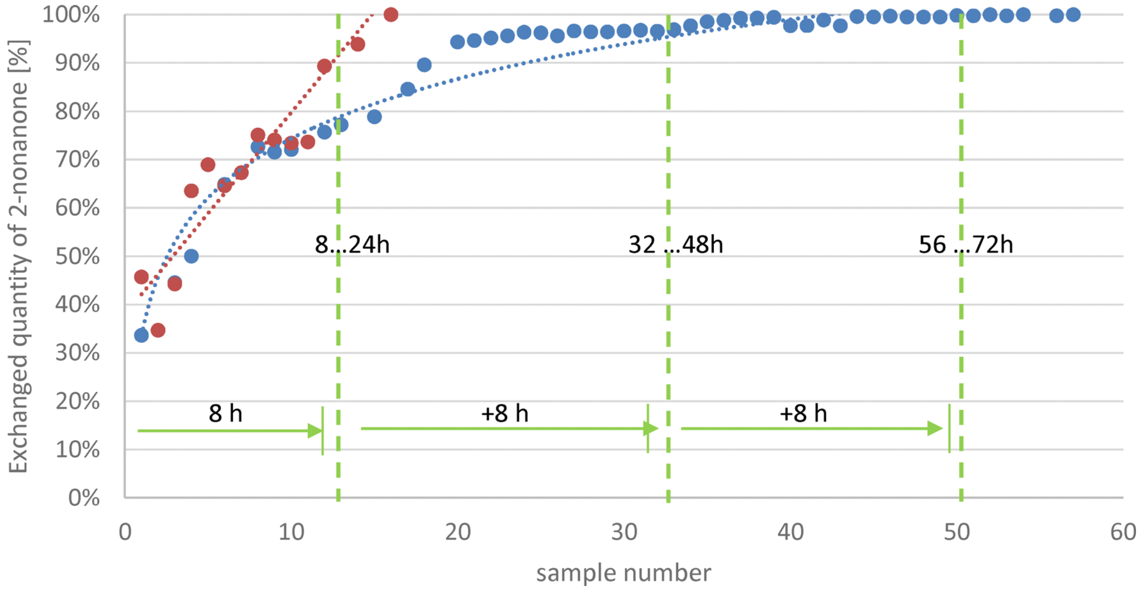

Fig. 3 Solvent exchange of PU aerogels, viewed over the extracted amount of 2-nonanone; red = Soxhlet, blue = batch; green dotted lines = new solvent in batch. (The dotted lines are intended as a visual aid and do not reflect actual trends.)

every 30 minutes *via* GC-MS. PU solvogels with a height of 1 cm and a diameter of 2.8 cm were exchanged against *t*BuOH (with 0.1% benzene as internal standard). In the batch, 10 times the amount of solvent was added, samples were taken in the first 8 hours, and after a total time of 24 hours, the solvent was replaced with new solvent. The exchange was completed after 4 days. The Soxhlet exchange was used for 8 hours with a still pot containing 150 mL of solvent. Fig. 3 shows the exchange process of the solvogels based on the accumulated amount of extracted synthesis solvent.

The measurements of the Soxhlet extraction are subject to strong fluctuations, but show a clear trend towards complete replacement. The problem with Soxhlet sampling is that a sample can only be taken after a cycle has been completed, as otherwise the light distillate is depleted by boiling and the concentration is measured incorrectly. Although the aim was to achieve sampling that was as uniform as possible, some fluctuations cannot be prevented. Sampling in batch experiments is less critical. Here, only residual solvent from the previous exchange can be identified as a relevant source of error. In batch exchange, a gradual progression can be observed, which slowly approaches the theoretical distribution equilibrium, *i.e.* about 10% of the initial concentration. In the closely monitored 8-hour segments, this equilibrium is not reached in the samples, but after one day the equilibrium is almost attained. In the third exchange step, the exchange is 99% complete. Depending on the gel, drying is already possible at this point, but in most cases a residual amount of $\ll 1\%$ synthesis solvent is required, which is only achieved after the fourth exchange. PU aerogels containing propylene carbonate (PC) were also produced using solvent mixtures. During extraction with *t*BuOH, PC is less easily washed out than 2-nonanone, which means that four exchange steps are always necessary (figure in SI (Fig. S4)).

To test the minimum time for Soxhlet exchange and taking into account that theoretically the diffusion time should increase quadratically with the diffusion distance, MTMS aerogels with a thickness of 5.5 mm and a diameter of 48 mm were produced and extracted for different lengths of time. Fig. 4 shows the course of the thermal conductivities which are very sensitive to residual solvent after SE with cyclohexane and *t*BuOH for different extraction times. Since an exchange time of 8 hours is sufficient for a sample height of 10 mm (5 mm diffusion path), it should theoretically be possible to exchange a sample with a height of 5 mm in 2 hours which was the case for *t*BuOH. Since cyclohexane is the poorer solvent for the reactants used, a longer extraction time is generally required for complete exchange. Here, an exchange time of at least

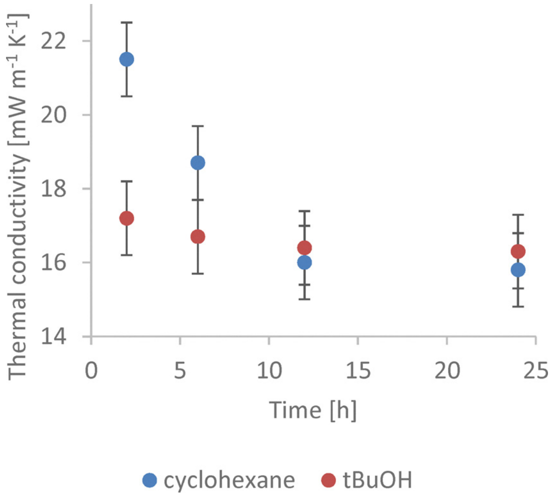

Fig. 4 Thermal conductivity of MTMS aerogels after SE with cyclohexane and *t*BuOH for different times after freeze drying.

12 hours is necessary for reproducible good results. In the case of *t*BuOH, an exchange time of more than 5 hours does not lead to any significant improvements. In principle, freeze drying from cyclohexane should be gentler due to its less polar structure, but the removal of water with molecular sieves in *t*BuOH produces comparably good results. The slightly better measured values after complete exchange with cyclohexane are within the margin of measurement accuracy.

The time savings are particularly evident when comparing a conventional solvent exchange followed by supercritical drying with SE followed by freeze drying. Fig. 5 shows the production time for PU and MTMS aerogels from synthesis to the finished aerogel. Most importantly solvent exchange is shortened from more than 4 days to less than 1 day (red bar). Also, in freeze drying the solvent exchange to liquid CO_2 can be omitted, saving another 5 days in our setup which is not optimized and may be faster in other setups. Similarly, the time required for gel ageing was not minimized, with MTMS 6 days and PU 1 day. In all cases, the method described greatly saves up to 80% of the time for solvent exchange and thereby accelerates research progress, especially for the development and optimisation of formulations.

3.1.1 MTMS aerogels. The gels produced were compared with materials from batch exchange followed by freeze drying, as well as with methanol-exchanged supercritically dried samples. Apart from the time saved, no difference between the exchange methods could be found, although water removal by molecular sieve in *t*BuOH is also necessary in batch processing. Fig. 6 shows the thermal conductivity of MTMS aerogels as a function of their density and the drying method used.

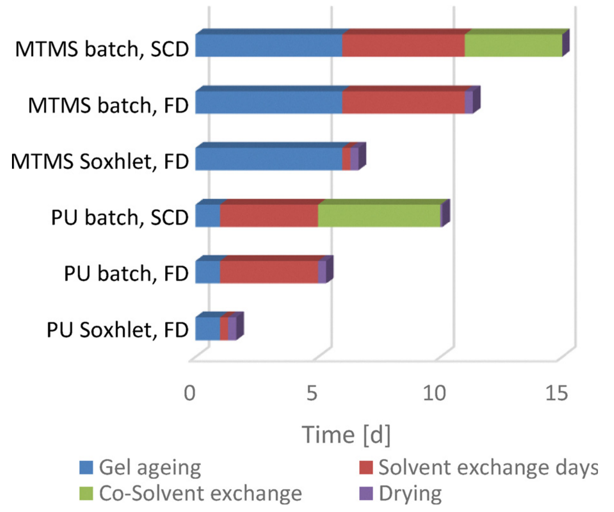

Fig. 5 Aerogel production times in batch *vs.* Soxhlet exchange – SCD supercritical drying, FD: freeze drying.

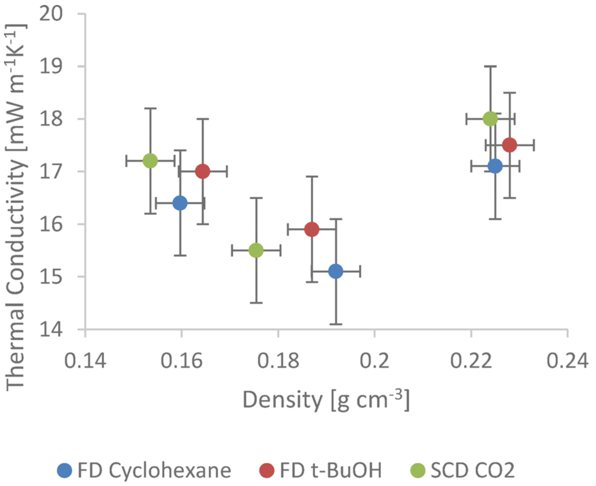

Fig. 6 Thermal conductivity of MTMS aerogels over the density of differently dried samples.

The densities of the samples were adjusted using the amount of aqueous ammonia used. Supercritical drying results in the lowest shrinkage (<1%), which is why the densities of the aerogels are slightly lower. With freeze drying, the volume decreases slightly more depending on the solvent used. For cyclohexane and *t*BuOH a shrinkage of 2 ± 2% was observed. Regardless of this, comparable thermal conductivities can be achieved regardless of the drying method. The minimum thermal conductivity is achieved in samples with a density of 175–200 mg cm^{-3}. In this range, the stronger Knudsen effect outweighs the increase in solid-state thermal conductivity in the aerogel. Shore A_0 measurements were performed on the aerogels to classify their mechanical properties. Fig. 7 shows the measured Shore hardness as a function of density depending on the drying method.

Table 1 shows the specific surface areas of the MTMS aerogels measured using nitrogen sorption from SI Fig. S10.

The mechanical stability of the samples shows a linear correlation to density, which is to be expected. Freeze drying from *t*BuOH and supercritical drying from MeOH yield similarly good results. Although cyclohexane should be well suited for drying, the samples obtained are significantly less stable

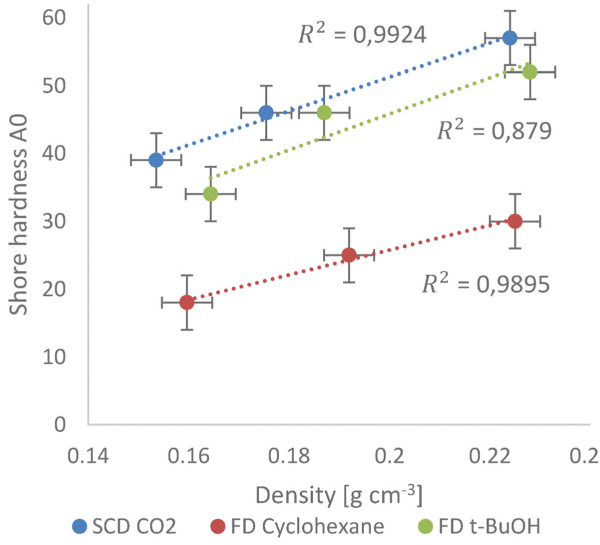

Fig. 7 Shore hardness A0 of MTMS aerogels over the density of samples dried from different solvents.

Table 1 BET specific surface area of MTMS aerogels

	SCD (CO_2)	FD (cyclo-hexane)	FD (*t*-BuOH)
Surface area [m^2 g^{-1}]	728	718	707
Density [g cm^{-3}]	0.176	0.192	0.187

than aerogels with similar densities that were dried using other methods. To better understand this phenomenon, SEM images of the bulk structure of the gels were taken. Fig. 8 shows selected SEM images of the prevailing aerogel structures.

All samples show a uniform microstructure in the nanometre range.

The macroscopic image of the cyclohexane sample shows the greatest difference in the structures examined. In contrast to the others, these lines show a preferred direction at the fracture edges. When the sample is broken, needle-like splinters form along these edges, which run vertically through the sample.

Reference tests with batch-exchanged samples show the same behaviour. Considering that cyclohexane is a poor solvent for the reactants of the synthesis, we suspect that they are not completely washed out and accumulate locally within the exchange and freezing process, thereby reducing bulk stability.

This hypothesis is supported by the fact that the samples also show a horizontal line at half height, exactly where the diffusion fronts meet during exchange. Furthermore, the preferred direction shifts to an almost radial behaviour at the outer edges of the sample. Aerogels that have previously been exchanged with their synthesis solvent or another solvent suitable for the reactants do not exhibit this behaviour.

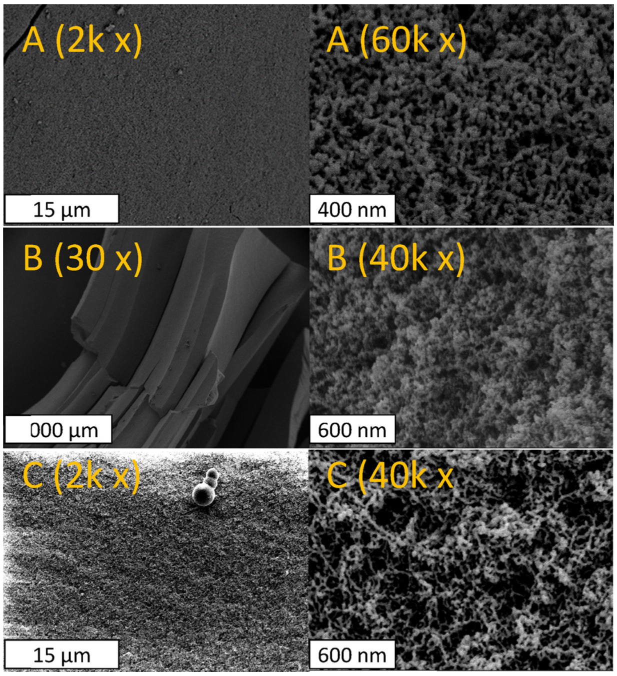

Fig. 8 SEM images of MTMS aerogels at different magnifications (A = *t*BuOH FD; B = cyclohexane FD; C = MeOH SCD).

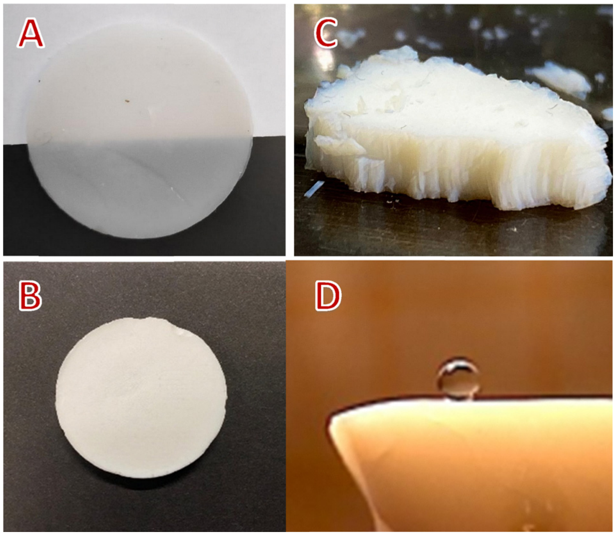

Fig. 9 Images of MTMS aerogels (A = MeOH SCD; B = *t*BuOH FD; C = cyclohexane FD; D = water contact angle of B.

Fig. 9 shows images of various samples and fracture edges. As can be seen in image C, the fracture edges with preferred orientation can also be seen with the naked eye. The orientation changes at the right edge of the sample. The supercritically and thereby most gently dried sample in image A shows higher translucency than the freeze-dried samples where the microstructure apparently coarsened and lower surface area was obtained in BET analysis. The contact angle of water is between 150° and 162° for all samples (example image D).

The solvogels and aerogels were also subjected to thermal analysis. Aerogels are thermally stable up to 300 °C and the organic part begins to decompose at higher temperatures (TGA under nitrogen atmosphere (see SI Fig. S5)). DSC measurements on solvogels have shown that the solvents used for freeze-drying are subject to a freezing point depression due to the capillary effects of the pores.[36] The freezing point of *t*BuOH drops from 26 °C to 4.5 °C, and that of cyclohexane from 7 °C to −9 °C (example see SI (Fig. S6 and S7)). Freeze drying was carried out at −55 °C to ensure that the samples were completely frozen.

3.1.2 PU aerogels. PU aerogels behave similarly to MTMS systems in terms of solvent exchange. However, due to their higher strength, these samples are less sensitive, but the use of molecular sieves in Soxhlet is still advantageous here (see SI Fig. S8 for images).

The samples that were exchanged for cyclohexane in the Soxhlet show greater shrinkage than comparable materials that were dried using *t*BuOH or supercritical drying. While drying with cyclohexane results in a volume loss of 10 ± 2%, the other samples show shrinkage of $<5\%$. For this reason, comparably produced samples show different densities after drying. As can be seen from the density range of *t*BuOH-replaced samples, the hardness of PU aerogels also correlates linearly with density (SI Fig. S9). For supercritically dried samples and freeze-dried samples from *t*-BuOH, the Shore A hardness can be adjusted

Table 2 Thermal conductivity of PU aerogels and their densities

Sample	Thermal conductivity [mW m^{-1} K^{-1}]	Density [mg cm^{-3}]
SE *t*BuOH FD	17.4 ± 1	141 ± 5
SE cyclohexane FD	19.0 ± 1	183 ± 5
SCD	16.8 ± 1	145 ± 5

linearly from 50 to 70 at densities of 140 to 170 g cm^{-3}. Due to the shrinkage of the samples dried with cyclohexane, the density shifts upwards without any improvement in hardness.

During the production of PU aerogels, reactive groups may remain, which can make the structure more polar. The use of *t*BuOH as an exchange agent has the advantage that these react and ensure that a hydrophobic surface is present. In a few cyclohexane-exchanged samples that were not saturated with a primary alcohol, slightly hydrophilic behaviour was observed. The subsequent water absorption led to local collapse of the bulk structure and, in the long term, to xerogel formation. In general, the samples show a contact angle of 140°–150° and cannot be visually distinguished from the purchased reference material, nor between supercritical and freeze drying. The specific surface area 50–80 m^2 g^{-1}.

Regarding thermal conductivity, the best results were achieved with a density of approximately 145 mg cm^{-3}. Table 2 shows the thermal conductivity of selected samples.

Within the limits of measurement accuracy, supercritical drying delivers results equivalent to those obtained by freeze drying from *t*BuOH. The insulating performance of the samples produced corresponds to that of the reference material (BASF's SLENTITE (18 mW m^{-1} K^{-1})).[10]

4. Conclusion

As demonstrated by the example of MTMS and PU gels, the use of a Soxhlet extractor for solvent exchange is a time-efficient alternative to the conventional method. The use of a molecular sieve and a vent ensures a robust process that quickly delivers equally good results as batchwise solvent exchange. A manual exchange procedure that would normally take at least four days (and often longer) can be completed in eight hours without any manual work. The dimensions of the test specimens are decisive for the replacement time, but specimen thicknesses of 10 mm are usually sufficient for laboratory tests, analysis and practical applications. For thicker samples a Soxhlet extraction could be performed overnight and a custom-built Soxhlet could provide additional features (*e.g.* reduce solvent and energy consumption, temperature and pressure control, as well as online-analysis and larger samples), but here we wanted to demonstrate the learnings and the merits of a basic setup.

For example, choosing the right system is crucial for solvent exchange. Cyclohexane could be used for solvent exchange of benzyl alcohol, but it is not a suitable solvent for the reactants and any by-products and oligomers that may be present, leading to instable domains in the aerogel and thus poor mechanical properties, therefore *t*BuOH is the better choice. Similarly, during solvent exchange in PU gels *t*BuOH ensures a hydrophobic surface simultaneously. In principle, there are few necessary rules that must be followed for Soxhlet extraction. The solvents must simply be separable by distillation (difference in boiling points should be at least 50 K), miscible at the temperature in the chamber, suitable for the reactants, and the target solvent must be suitable for subsequent drying. Based on this, the method should be adaptable to many aerogel systems and speed up their development.

From an ecological and economic point of view, the use of Soxhlet exchange is debatable. On the one hand, it is possible to work with small amounts of solvent, which can be recycled relatively easily and saves a lot of time. On the other hand, the method presented here is relatively energy-intensive compared to batch exchange with subsequent reprocessing. Including solvent recovery, the Soxhlet exchange is almost twice as energy-demanding as the batch method (see SI for example calculation).

In terms of the samples produced, it was demonstrated that it is possible to adapt recipes to high-boiling solvents for gel formation and exchange into low-boiling solvents for (freeze) drying without any problems. The obtained materials are comparable in quality to the state of the art: MTMS aerogels with thermal conductivities of down to 15 mW m^{-1} K^{-1} and PU aerogels down to 17 mW m^{-1} K^{-1} were produced in various sizes.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI), *i.e.* schematics and details of exchange and drying process, details of synthesis, DSC and TGA, Shore hardness measurements and nitrogen sorption data. Further data and samples can be obtained from the author upon request. Supplementary information is available. See DOI: https://doi.org/10.1039/d5ma01307k.

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Notes and references

1 S. S. Kistler, *J. Phys. Chem.*, 1932, **36**, 52–64.

2 N. Hüsing and U. Schubert, *Angew. Chem., Int. Ed.*, 1998, **37**, 22–45.
3 A. C. Pierre and G. M. Pajonk, *Chem. Rev.*, 2002, **102**, 4243–4266.
4 I. Smirnova and P. Gurikov, *J. Supercrit. Fluids*, 2018, **134**, 228–233.
5 M. Ganobjak, W. J. Malfait, J. Just, M. Käppeli, F. Mancebo, S. Brunner and J. Wernery, *J. Build. Eng.*, 2023, **64**, 105600.
6 A. Du, B. Zhou, Z. Zhang and J. Shen, *Materials*, 2013, **6**, 941–968.
7 S. Rezaei, A. Jalali, A. M. Zolali, M. Alshrah, S. Karamikamkar and C. B. Park, *J. Colloid Interface Sci.*, 2019, **548**, 206–216.
8 S. G. Mosanenzadeh, Z. Saadatnia, F. Shi, C. B. Park and H. E. Naguib, *Polymer*, 2019, **176**, 213–226.
9 S. Karamikamkar, H. E. Naguib and C. B. Park, *Adv. Colloid Interface Sci.*, 2020, **276**, 102101.
10 E. Günther, S. Bichlmair, S. Latz and M. Fricke, *E3S Web Conf.*, 2020, **172**, 01006.
11 M. M. Koebel, L. Huber, S. Zhao and W. J. Malfait, *J. Sol-Gel Sci. Technol.*, 2016, **79**, 308–318.
12 S. Latz, F. Scholzen, A. Thewes and S. Maas, *Bauphysik*, 2022, **44**, 9–20.
13 M. Fricke, D. Weinrich and M. Nobis, *US Pat.*, US20170204242A1, 2017.
14 K. Kanamori, A. Stojanovic, G. M. Pajonk, D. Y. Nadargi, A. V. Rao, K. Nakanishi and M. M. Koebel, in *Springer Handbook of Aerogels*, ed. M. A. Aegerter, N. Leventis, M. Koebel and S. A. Steiner III, Springer International Publishing, Cham, 2023, pp. 367–391.
15 R. Ueoka, Y. Hara, A. Maeno, H. Kaji, K. Nakanishi and K. Kanamori, *Nat. Commun.*, 2024, **15**, 461.
16 G. Zu, T. Shimizu, K. Kanamori, Y. Zhu, A. Maeno, H. Kaji, J. Shen and K. Nakanishi, *ACS Nano*, 2018, **12**, 521–532.
17 G. Odling, H. Logan, A. Chan, A. J. Bissel, C. R. Pulham and D. E. Oliver, *Mater. Adv.*, 2023, **4**, 3724–3732.
18 K. Kanamori, K. Nakanishi, K. Hirao and H. Jinnai, *Langmuir*, 2003, **19**, 5581–5585.
19 Z. Zhu, G. M. B. F. Snellings, M. M. Koebel and W. J. Malfait, *ACS Appl. Mater. Interfaces*, 2017, **9**, 18222–18230.
20 S. Takeshita, S. Mine and T. Ono, *Angew. Chem., Int. Ed.*, 2025, **64**, e202504250.
21 I. Turhan Kara, B. Kiyak, N. Colak Gunes and S. Yucel, *J. Sol-Gel Sci. Technol.*, 2024, **111**, 618–649.
22 M. Schwan, S. Nefzger, B. Zoghi, C. Oligschleger and B. Milow, *Front. Mater.*, 2021, **8**, 662487.
23 J. G. Reynolds, P. R. Coronado and L. W. Hrubesh, *J. Non-Cryst. Solids*, 2001, **292**, 127–137.
24 C. F. Poole, *Liquid-Phase Extraction*, Elsevier, 2019.
25 M. A. López-Bascón and M. D. Luque de Castro, in *Liquid-Phase Extraction*, ed. C. F. Poole, Elsevier, 2020, pp. 327–354.
26 M. D. Luque de Castro and F. Priego-Capote, *J. Chromatogr. A*, 2010, **1217**, 2383–2389.
27 R. T. Buratto, E. G. Hoyos, M. J. Cocero and Á. Martín, *J. Supercrit. Fluids*, 2019, **146**, 120–127.
28 F. Leven, M. Ulbricht, J. Limberg and R. Ostermann, *J. Mater. Chem. A*, 2021, **9**, 20695–20702.
29 K. Kanamori, *J. Ceram. Soc. Jpn.*, 2024, **132**, 69–78.
30 K. Kanamori, K. Nakanishi and T. Hanada, *MRS Online Proc. Libr.*, 2009, **1134**, 706.
31 B. Nowak, E. Radomska, M. Klimek and K. Pielichowska, *J. Energy Storage*, 2025, **110**, 115280.
32 K. Kanamori, R. Ueoka, T. Kakegawa, T. Shimizu and K. Nakanishi, *J. Sol-Gel Sci. Technol.*, 2019, **89**, 166–175.
33 A. Fick, *Ann. Phys.*, 1855, **170**, 59–86.
34 H. Elias, S. Lorenz and G. Winnen, *Chem. Unserer Zeit*, 1992, **26**, 70–75.
35 W. Huiyuan and X. Songlin, *Chem. Eng. Technol.*, 2006, **29**, 113–118.
36 G. W. Scherer, *J. Non-Cryst. Solids*, 1993, **155**, 1–25.