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Shortened Aerogel Fabrication Times using an Ethanol-Water Azeotrope as a Gelation and Drying Solvent.

L. S. White[1], M. F. Bertino[1,*], G. Kitchen[2], J. Young[2], C. Newton[2], R. Al-Soubaihi[3], S. Saeed[3] and K. Saoud[3,*]

[1] Department of Physics, Virginia Commonwealth University, Richmond, VA 23060
[2] Department of Sculpture, Virginia Commonwealth University, Richmond, VA 23060
[3] Department of Liberal Arts and Sciences, Virginia Commonwealth University, Doha, Qatar

[*] Corresponding Authors. Email: mfbertino@vcu.edu, s2kmsaou@vcu.edu

Native and cross-linked aerogel monoliths were fabricated in a few hours using a technique that does not require solvent exchange prior to supercritical drying. Native oxide alcogels were synthesized by alkoxide hydrolysis-condensation using an ethanol-water azeotrope mixture as the gelation solvent. Cross-linked alcogels were synthesized by replacing part of the gelation solvent with a monomer, followed by visible light photopolymerization for which Eosin Y was used as an initiator and a tertiary amine used as a coinitiator. After aging for 2 hours, the alcogels were removed from the molds, placed in a pressure vessel, and dried using a supercritical ethanol/water azeotrope mixture. Starting from the sol, dried aerogels could be fabricated in about 6 hours. Most importantly, since solvent exchange was not required, native oxide and polymer cross-linked aerogels could be fabricated at the same . A systematic study was carried out to confirm that monoliths produced with our technique had density, surface area and modulus comparable to those of aerogels produced following more conventional pathways, such as supercritical CO_2 drying. We synthesized samples using base- and acid-catalyzed chemistries, varied alkoxide concentration and, for cross-linked aerogels, monomer concentration. Depending on alkoxide concentration, native oxide aerogels had densities between about 0.06 and 0.17 $g \cdot cm^{-3}$ and surface areas between about 300 and 500 $m^2 \cdot g^{-1}$. Depending on monomer type and concentration, cross-linked monoliths had a modulus between about 10 and 400 MPa, a density between 0.25 and 0.5 $g \cdot cm^{-3}$ and a surface area between 150 $m^2 \cdot g^{-1}$ and 350 $m^2 \cdot g^{-1}$. Shrinkage was about 5% for base-catalyzed synthesis, about 20% for acid-catalyzed synthesis and about 10% for cross-linked monoliths. Infrared and Raman spectroscopies, solid state NMR and thermogravimetric analysis confirmed that drying in a supercritical ethanol-water azeotrope did not significantly affect the cross-linking polymer used to produce mechanically strong aerogels.

1.   Introduction

The unique physical properties of aerogels make them attractive for applications ranging from environmental remediation to space dust collection;[1-4] however, aerogel production is slow and tedious. Wet gels, termed aquogels or alcogels depending on the solvent, can be rapidly synthesized following well-established procedures, [5,6] but drying is time-consuming. Because of capillary forces, in fact, the solvent cannot be evaporated without cracking and shrinking the monolith. Several methods have been developed to circumvent capillarity issues, the most

popular being supercritical CO_2- and ambient pressure- drying. The principle of supercritical CO_2 drying is simple. The gelation solvent is exchanged with liquid CO_2 in an autoclave which is then heated and vented once the supercritical point of CO_2 is reached. In practice, the water used to catalyze gelation is poorly miscible in liquid CO_2, requiring the gelation solution to be exchanged with water-free solvents prior to drying[7]. In ambient pressure drying, a silane such as trimethylchlorosilane is diffused through aquogels. The silane attaches to the pore walls and derivatizes them with an hydrophobic moiety which reduces surface energy and capillary stresses.[8-11] In systems with ordered, hierarchically organized porous structures, the hydrophobic moiety can even expel water from the pores.[12] Thus, the most common drying routes require at least one solvent exchange step. This solvent exchange step represents the processing bottleneck because it is controlled by diffusion time of the solvent through the gel. The apparent diffusion coefficient of water and most solvents in silica gels is on the order of 10^{-6} $cm^2 \cdot s^{-1}$ and the effective diffusion coefficient is about one order of magnitude lower.[13-15] Because of the comparatively small diffusion coefficient, solvent exchange is slow[15] and it requires about 25 hours for a monolith with a smallest dimension of 10 mm. Since diffusion times depend on the square of the size of wet gels and multiple solvent exchanges are often necessary,[15] aerogels are usually fabricated with a smallest dimension that does not exceed a few millimeters.[8,10,16] Besides being time-consuming, solvent exchange is also expensive. Smith *et al.*[15] determined that each exchange step requires a volume of fresh solvent about 10 times larger than the monolith's volume.

To reduce processing time, drying techniques have been developed which do not require solvent exchange. Loy *et al.*[16] fabricated aerogels by reacting alkoxides and formic acid in supercritical CO_2. Gross *et al.*[17] heated a pressure vessel filled with an ethanolic precursor solution and vented it once the supercritical point was reached. Anderson *et al.*[18] subjected an alcogel to uniaxial pressure, heated the vessel and vented it once it reached the supercritical temperature of ethanol. These techniques do facilitate the rapid fabrication of aerogels, but they cannot produce aerogels with custom shapes, since the mold is the pressure vessel itself. Probably for this reason, none of these techniques has been widely accepted. Another promising method was developed by Sharp *et al.*,[19] who synthesized gels without adding water and using formic acid as catalyst; however, the reaction by-products included water, which required solvent exchange prior to supercritical drying.

Fabrication is even slower for mechanically strong aerogels. As shown in pioneering work by the group of N. Leventis, the mechanical strength of aerogels can be increased by cross-linking the skeletal oxide nanoparticles with a polymer.[20] Typically, cross-linking of aerogels is achieved by derivatizing the pore walls of alcogels by adding to the initial gelation solution an alkoxide carrying a suitable moiety, such as an amine or an acrylic group. The gelation solvent is then exchanged with a solution of a monomer and a polymerization initiator. When

polymerization is initiated, the monomer engages the surface moiety. The resulting cross-linking of the skeletal oxide nanoparticles increases the mechanical properties of the monoliths without overly compromising their porosity.[20] Since exchanging the gelation solution with a monomer solution is time-consuming, several groups, including ours, have developed one-pot approaches where part of the gelation solvent is replaced by a monomer. Leventis et al.[21] added acrylonitrile to a methanolic solution of an alkoxide and a catalyst. Meador et al.[22] used an epoxy monomer, our own group used an acrylic monomer,[23] and Duan et al. used a custom-synthesized, water-dispersible urethane oligomer.[24] In all these reports, however, exchange with dry solvents was required prior to drying, which lengthened the fabrication process. To date, fabrication times for cross-linked aerogels are of several days[24] even when one-pot synthetic recipes are employed.

A drying route exists which makes use of supercritical organic solvents and has the promising advantage of not requiring solvent exchanges.[6,25] Supercritical solvent drying has been used in one of the most successful aerogel applications, the star dust project,[25] but it is not frequently utilized. One often-mentioned reason is flammability. To prevent evaporation of the gelation solution before the supercritical point is reached, the wet gel must be placed in a vessel containing excess solvent, which can pose flammability hazards. These hazards, can be greatly alleviated by pre-pressurization of the vessel with inert gas, which can reduce the volume of excess solvent to less than 10% of the volume of the drying vessel.[5,26,27] Another relevant and only partially addressed issue of supercritical solvent drying is that the gelation solvent used in most formulations contains water for up to 35% by weight. Since water has high supercritical temperature (647.1 K) and pressure (22.06 MPa), the critical point of a water-solvent mixture can be substantially higher than that of the dry solvent. The increased drying temperature can induce a series of unwanted reactions such as esterification, pore wall derivatization with hydrocarbon fragments and silica dissolution.[6] Among these reactions silica dissolution is the most undesirable since it can induce monolith shrinkage by up to 20%.[27,28] Exchange of the gelation solution with dry solvents is therefore often necessary to reduce the drying temperature and thus the rate of the undesirable reactions.[27]

Here we show that native and cross-linked aerogel monoliths can be fabricated in one pot and dried supercritically without need for solvent exchange. The key to our technique is the use of an ethanol-water azeotrope mixture as a gelation solvent, which contains 4.4% water by volume. The small water content allows for drying at temperatures close to the supercritical temperature of the dry solvent, where reactions such as silica dissolution and polymer degradation are negligible. Starting from the sol, both native oxide and cross-linked aerogels can be fabricated in a matter of hours. These results are of particular importance since they dramatically shorten fabrication times of native and, most importantly, cross-linked aerogel monoliths.

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2.   **Experimental**

2.1 Chemicals

Reagent-grade Tetraethyl Orthosilicate (TEOS), Tetramethyl Orthosilicate (TMOS), Aluminum Chloride Hexahydrate (AlCl$_3$•6H$_2$O), Trimethoxysilylpropyl methacrylate (MTMS), Methyldiethanolethylamine (Amine), Eosin Y were purchased from Acros Organics. Hexanedioldiacrylate (HDDA) was purchased from Sigma-Aldrich. A sample of Acrylated Dipentaerythritol (DPHA) was provided by Allnex SA, Belgium. The structure of the monomers is shown in Scheme 1. All reagents were used as-received. The ethanol/water azeotrope mixture (containing 4.4% water and 95.6% pure ethanol by volume) was used as gelation solvent and as supercritical fluid in the drying process. Unless stated otherwise, all references to ethanol in this manuscript indicate this ethanol-water azeotrope mixture.
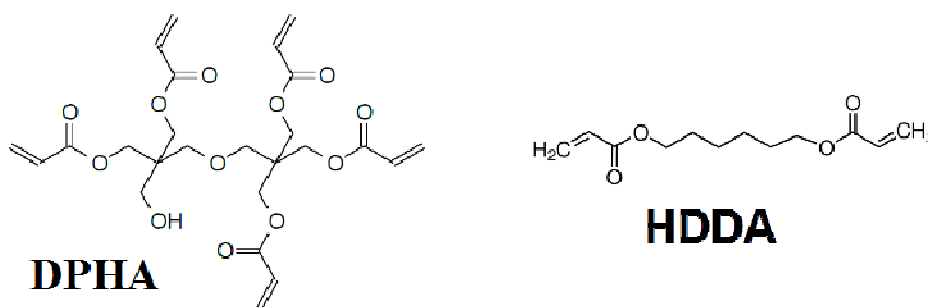
Scheme 1. Cross-linking monomers.

2.2 *Base-catalyzed synthesis of silica aerogels*

TMOS was added to a 0.13 mol• l^{-1} diethanolmethylamine ethanolic solution in a volume fraction between 6% and 25%. The solutions were thoroughly mixed and poured into molds. Gelation occurred within 30 minutes. From here forth, gels with the lowest (6% v/v) TMOS concentration will be referred to as low-density (LD) gels, and gels with the highest concentration will be referred to as high-density (HD) gels. The TMOS/ethanol/H$_2$O mole ratio was 1/31.2/4.6 for the LD gels and 1/7.5/1.1 for the HD gels. During experimentation, a LD gel was made by adding 0.5 ml of TMOS to a mixture of 3ml of ethanol and 0.045 ml of diethanolmethylamine.

2.3 *Acid-catalyzed synthesis of silica aerogels*

TMOS is a popular precursor for laboratory applications, mostly because of its rapid gelation. The experiments presented in this manuscript are no exception, and were carried out,

for the most part, using TMOS as an alkoxide precursor. However, TMOS can hardly be employed on a large scale because it is very hazardous and expensive. For large scale applications TEOS is preferred, because it is less hazardous and considerably cheaper. Since our azeotrope-based technique may have industrial relevance, we extended it to the fabrication of native aerogels using TEOS as a precursor. The experiments carried out with TEOS, were limited in scope because they were meant as proof-of-concept. To facilitate readability, all figure captions in the manuscript body report the alkoxide used for the synthesis. The gelations of alcogels made with TEOS occurs very slowly in a basic environment, in our experiments after a minimum of 16 days, and produces gels with a significantly reduced surface area, in our experiments 110 $m^2 \cdot g^{-1}$. Therefore, we decided to employ acid catalysis. To minimize the amount of water added to the gelation solution, we used a metal salt (aluminum chloride) to lower the pH. A stock solution with a concentration of $1.4 \cdot 10^{-3}$ $mol \cdot l^{-1}$ was prepared by dissolving $AlCl_3 \cdot 6H_2O$ in ethanol. The pH value of this solution was measured with a calibrated pH meter to be 2.4. Because of the low water concentration of the solution, this value must be considered to be approximate and with an uncertainty of up to one pH unit[28-30]. Experimental error notwithstanding, the measured pH of 2.4 is consistent with titration experiments conducted by Sjoblom *et al.*[30], which showed that Al salts dissolved in ethanol are strong acids with a titration point of three moles of strong base per mole of Al salt. Once TEOS was added to the $AlCl_3$ solution, gelation did not occur within a time frame of several days, and suggested that the pH of the solution was too acidic. This finding is in agreement with the work of Ref.[30], where gelation was found to require months when Al salts were used as acid catalysts. Therefore, we decided to add a base to raise the pH and accelerate gelation. Two solutions were subsequently prepared: Solution A was prepared by adding TEOS to the aluminum chloride stock solution in a concentration between 6.6% and 25% v/v, and left inside a hermetically closed container for a minimum of one hour to allow hydrolysis of the alkoxide. Solution B was a 0.142 $mol \cdot l^{-1}$ diethanolmethylamine ethanolic solution. The solutions were thoroughly mixed and poured into molds. The TEOS/ethanol/H_2O mole ratio was 1/15/2.2 for the gels with the highest TEOS concentration. The concentrations of $AlCl_3$ and diethanolmethylamine in the gelation solution were $1.05 \cdot 10^{-3}$ $mol \cdot l^{-1}$ and $1.376 \cdot 10^{-3}$ $mol \cdot l^{-1}$, respectively. The amine increased the pH to about 8.5 and gelation occurred within 30 minutes. In another control experiment, we also prepared alcogels using acid-catalysis of TMOS. The synthesis was carried out as described above but with the TEOS replaced by TMOS in the same concentration. The gelation solution gelled within two hours and produced an aerogel that, while having a surface area of 760 $m^2 \cdot g^{-1}$, shrank by 20%. We also note that the $AlCl_3$ concentration was very small ($mmol \cdot l^{-1}$) compared with the alkoxide concentration($\sim$1 $mol \cdot l^{-1}$). XRD analysis of aerogels yielded a broad peak characteristic of silica but no peaks of Al oxides or hydroxides.

2.4 *Base-catalyzed synthesis of cross-linked aerogels*

A stock solution of ethanol and the photoinitiator Eosin Y was first prepared with an Eosin concentration of 4 g·l^{-1}. Solution A consisted of ethanol (1.35 ml), Eosin stock solution (0.15 ml), TMOS (0.88 ml) and MTMS (0.04 ml). Solution B had a fixed volume of 1.62 ml and contained diethanolmethylamine (0.05 ml), ethanol and the acrylic monomer HDDA. The volume of the monomer was varied to yield a weight concentration between 10% and 40% of the gelation solvent, and the volume of ethanol of solution B was varied accordingly in order to maintain a constant volume. So, for example, 40% by weight HDDA samples were prepared with solution B containing 1.12 ml of HDDA, 0.45 ml ethanol and 0.05 ml diethanolmethylamine. Solutions A and B were thoroughly mixed and poured into molds. Gelation occurred within 60 minutes.

2.5 Photopolymerization

Monomer-containing alcogels were cross-linked by photopolymerization. Photopolymerization was preferred to thermal polymerization because heating introduces solvent evaporation issues which are difficult to tackle when large monoliths are being fabricated. As we showed in previous work,[31] ultraviolet (UV) photoinitiation is not recommended; UV light is strongly absorbed by the organics in the gelation solution and penetration is typically less than 10 mm. For this reason, Eosin Y, a photoinitiator which absorbs in the green region of the visible spectrum, was employed to ensure that light could penetrate through alcogels of any thickness. Upon light absorption, charge is transferred between the Eosin Y dye and the coinitiator dimethanolmethylamine, resulting in a reduced radical dye species and a coinitiator radical capable of initiating polymerization.[32,33] The illumination system consists of eight green light-emitting diodes (LEDs) which are arranged symmetrically around the sample. The LEDs have a power of 1 Watt and the luminous intensity, measured with a power meter (Thor Labs), is 30 mW·cm^{-2} at the sample location. LEDs were mounted on optical mounting posts (Newport M-MSP-2) inserted into post holders (Newport BPH-4). With this arrangement, LEDs could be placed symmetrically around samples and moved vertically with a travel of 50 mm. A digital camera image of the exposure array (mounted on an optical table) is shown in Figure S1. Typical exposure times were 30 minutes and the samples were rotated every 10 minutes within the diode array to ensure homogeneous illumination. The effect of exposure times was also investigated. Density and modulus of the monoliths both increased for exposure times below about 15 minutes, and remained constant afterwards, as shown in Figure S2. This result indicates that the exposure times used in our experiments (30 minutes) ensured complete polymerization. NMR results presented in Figure 6 confirm that polymerization was completed for exposures of 30 minutes. For shorter exposures, samples were washed twice in excess (10x[15]) ethanol, 8 hours per washing.

Hazard warning: LEDs with a power of 1 W and higher are very intense light sources. Permanent eyesight damage may occur if these lights are directly stared into at close range. Use of protective eyewear is recommended.

A series of trials were conducted to determine the optimum Eosin Y concentration. Excessive concentrations of Eosin Y prevented light penetration through the alcogels and led to polymerization only in the outer layers of the gels. Low Eosin Y concentrations led to mechanically weak monoliths, indicating partial polymerization. The Eosin Y concentration reported in Section 2.4 ensured light penetration for about 15 mm. By illuminating from all sides for 30 minutes, uniformly polymerized monoliths with sizes up to 25 mm could be obtained.

2.6 *Supercritical drying of alcogels in ethanol/water azeotrope mixture*

After gelation, the alcogels were aged for a minimum of two hours inside hermetically sealed molds. For most samples used in our experiments, molds were propylene syringes with a diameter of 13 mm and the needle side cut off. To produce parallelepipeds, two-part silicone molds were fabricated, as shown in Figure S3. Molds were typically coated with silicone grease as a mold-release agent. Shorter aging times resulted in extremely weak, crack-prone monoliths; longer aging times of up to 3 days yielded monoliths with density, surface area and modulus which nearly coincided with those of monoliths aged for two hours. The alcogels were removed from the molds after aging and placed inside the supercritical dryer, a Parr Instruments model 4602 pressure vessel with a capacity of 2 liters. The pressure vessel was equipped with a thermowell and it was heated by three ceramic heaters, each with a power of 800 W. Heating rates were controlled by varying the power delivered to the heaters with a variac. To prevent solvent evaporation from the alcogels before the supercritical point was reached, an excess volume (500 ml) of ethanol (azeotrope) was poured into the drying vessel. The pressure vessel was heated to reach the supercritical temperature and pressure of the ethanol-water azeotrope mixture (P_c = 7.31 MPa, T_c = 526 K), kept at supercritical conditions for 20 minutes, and then vented. The vessel was deliberately not pre-pressurized with inert gas, and the excess ethanol was kept constant at 500 ml. Pre-pressurization reduces the amount of excess solvent (and thus the hazards) necessary for solvent supercritical drying; however, density, shrinkage and pore texture of dried monoliths depend on the pre-pressurization pressure and the volume of excess solvent[34]. Given the proof-of-concept character of our experiments, we decided to avoid introducing additional degrees of freedom (initial pressure and volume of excess solvent) into our investigation.

Hazard note: Since the molar volume of supercritical ethanol is about four times the molar volume of liquid ethanol, the volume of solvent added to the pressure vessel should be calculated carefully. Excess solvent can induce a large pressure increase at the supercritical point which may exceed the pressure rating of the vessel. See also Parr's user manual, especially the section entitled "I did not know it was loaded."[35] Should an experimentalist elect to use pre-

pressurization methods to reduce the amount of excess supercritical drying solvent, the pressurization tubing should be built and secured according to regulatory code. Also, venting releases hot ethanol vapor. It is recommended to place the exhaust tube inside a large vessel with the end of the tube submerged in water or to use a condenser coil.

To further reduce the drying temperature we attempted to use dry ethanol as the drying fluid; however, supercritical drying in pure ethanol yielded small monoliths which were crack-free and large monoliths with a cracked core. Cracking was likely caused by the supercritical temperature (T_c) of the water-ethanol azeotrope mixture inside the alcogels, which was higher than the T_c of the dry ethanol surrounding the alcogels. When the dry ethanol had reached its critical temperature, the fluid inside the alcogel was 20-30 K away from its critical temperature. When the fluid inside the alcogel transitioned from liquid to vapor, it caused capillary stresses. These stresses were less evident in small monoliths, since the dry solvent probably had sufficient time to diffuse inside the monoliths while the vessel was being heated.

2.7   *Characterization.*

Raman Spectra were measured using a Horiba LabRam Evolution with an excitation line of 532 nm and a power of 5 mW measured at the sample position. The acquisition time was 3 minutes. FT-IR Spectroscopy was carried out using a Thermo Scientific Nicolet 6700. A smart iTR diamond ATR accessory was used to eliminate the use of KBr pellets. 32 scans were taken with data spacing of 0.482 cm^{-1} and a resolution of 4 cm^{-1}. Surface areas and pore size distributions were measured with a Micromeritics ASAP 2020 analyzer. Samples with an average weight of 40 mg were outgassed in vacuum for 24 hours at 120 ˚C. 48 adsorption/desorption points were taken with 3 minutes of equilibration time between each measurement and tolerance of 0 at 77.2K (sample holder submerged in liquid nitrogen). These 48 points were plotted as a linear isotherm. The surface area values are calculated according to the BET model using the first 5 points of the adsorption curve and pore sizes were calculated according to the BJH model using the desorption curve values. CPMAS-TOSS solid-state NMR was acquired on a Bruker DRX300WB spectrometer equipped with a 7-mm CPMAS probe. Each sample was packed into a 7-mm Zirconia rotor with Kel-F cap and then spun at 5 kHz at room temperature. The operating frequency was 75.48 and 59.62 MHz for ^{13}C and ^{29}Si, respectively. The contact time was 5 ms for ^{29}Si and 1 ms for ^{13}C and repetition time was 2 s for both nuclei. The experiment time was sample dependent, with number of scans ranging from 300 to 2,000 for ^{13}C and 1,000 to 2,000 for ^{29}Si. A line-broadening of 60 Hz (^{13}C) and 100 Hz (^{29}Si) were each applied before Fourier Transformation. Chemical shift was externally referenced to glycine (C=O carbon at 176.03 ppm) and DSS (sodium salt of 2,2-dimethyl-2-silapentane-5-sulphonic acid, ^{29}Si at 0 ppm). TGA was performed with a TA Instruments Model 2950 using a temperature ramp rate of 10 °C·min^{-1} under air. For compression testing, we employed an Insight 30 using a 50N load cell and compression velocity 0.254 cm·min^{-1}. Sample contact surfaces were cut parallel, and the

samples were tested following ASTM D695. Even though the standard calls for a sample height/diameter ratio of about 4, we kept this ratio to about 3 to prevent buckling.[20,21]

3.   Results and Discussion

3.1 Fabrication procedure.

Our fabrication method requires a single wet-chemistry step and produces alcogels that can be dried supercritically without requiring any solvent exchanges. The key to our method is the use of an ethanol-water azeotrope mixture as both gelation solvent and supercritical drying fluid. The water concentration (4.4% by volume) of the ethanol-water azeotrope is lower than the water concentrations typically employed for alkoxide hydrolysis-condensation (up to 35% by weight). Because of the lower water concentration, gelation is about two times slower than with conventional methods. The longer gelation time is, more than compensated by two major advantages. The most important advantage is that the low water concentration reduces the drying temperature.   Bazaev et al.[36] have shown that the critical temperature (T_c) and pressure (P_c) point of ethanol-water mixtures with an ethanol mole fraction x can be calculated with an accuracy of a few percent using the following equations:

$$T_c = 647.1 - 239\,x + 177.76\,x^2 - 71.93\,x^3 \quad (1)$$

$$P_c = 22.06 - 37.37x + 37.15\,x^2 - 15.72\,x^3 \quad (2)$$

Typical gelation solutions used by other groups contain water in a concentration between 15 and 35% by weight.[37] For these water concentrations, Eqs. (1) and (2) yield T_c between about 540 and 560 K and P_c between about 8.5 and 10.5 MPa, respectively. The water-ethanol azeotrope mixture has an ethanol mole fraction $x = 0.87$, for which Eqs. (1) and (2) yield $T_c = 526$ K and $P_c = 7.31$ MPa.   Since the reaction rate of the solvent with the silica framework increases exponentially with temperature,[19] the lower drying temperature of our technique reduces silica dissolution, monolith shrinkage, pore derivatization with hydrocarbons and other undesirable by-products. In most previous reports,[5,26,27,31] the gelation solvent contained a high water concentration; it had to be exchanged with a dry solvent to lower the drying temperature and hence the rate of the undesired reactions. With our technique reported here, drying can be carried out right away. In addition, our mold-free drying greatly accelerates and simplifies the drying process. When alcogels are dried within their molds, mechanical stresses can arise during heating because of the different expansion coefficients of glass, solvent and gel skeleton. In addition, molds limit the surface from which vapors can escape during venting. Not surprisingly, groups that dry gels within their molds report long aging times (which increase the mechanical strength of the gels) and slow heating and venting rates (requiring up to two days to complete the process)[5]. Our mold-free drying allowed fabrication of crack-free aerogel samples of different sizes with an aging time of two hours. In addition, we could produce crack-free monoliths with

heating rates as high as 125 ^{o}C·h^{-1} and venting rates as high as 0.4 MPa per minute, though such a high venting rate, is not recommended because of an increased risk of hot solvent spraying from the collection vessel. A further advantage of our technique is that the low water content of the gelation solution alleviates monomer solubility issues. Solubility issues are very relevant for the synthesis of cross-linked aerogels and they will be discussed in Section 3.3. We will now show that native and cross-linked aerogels produced with our technique have densities, surface areas, and moduli agreeing with expectations.
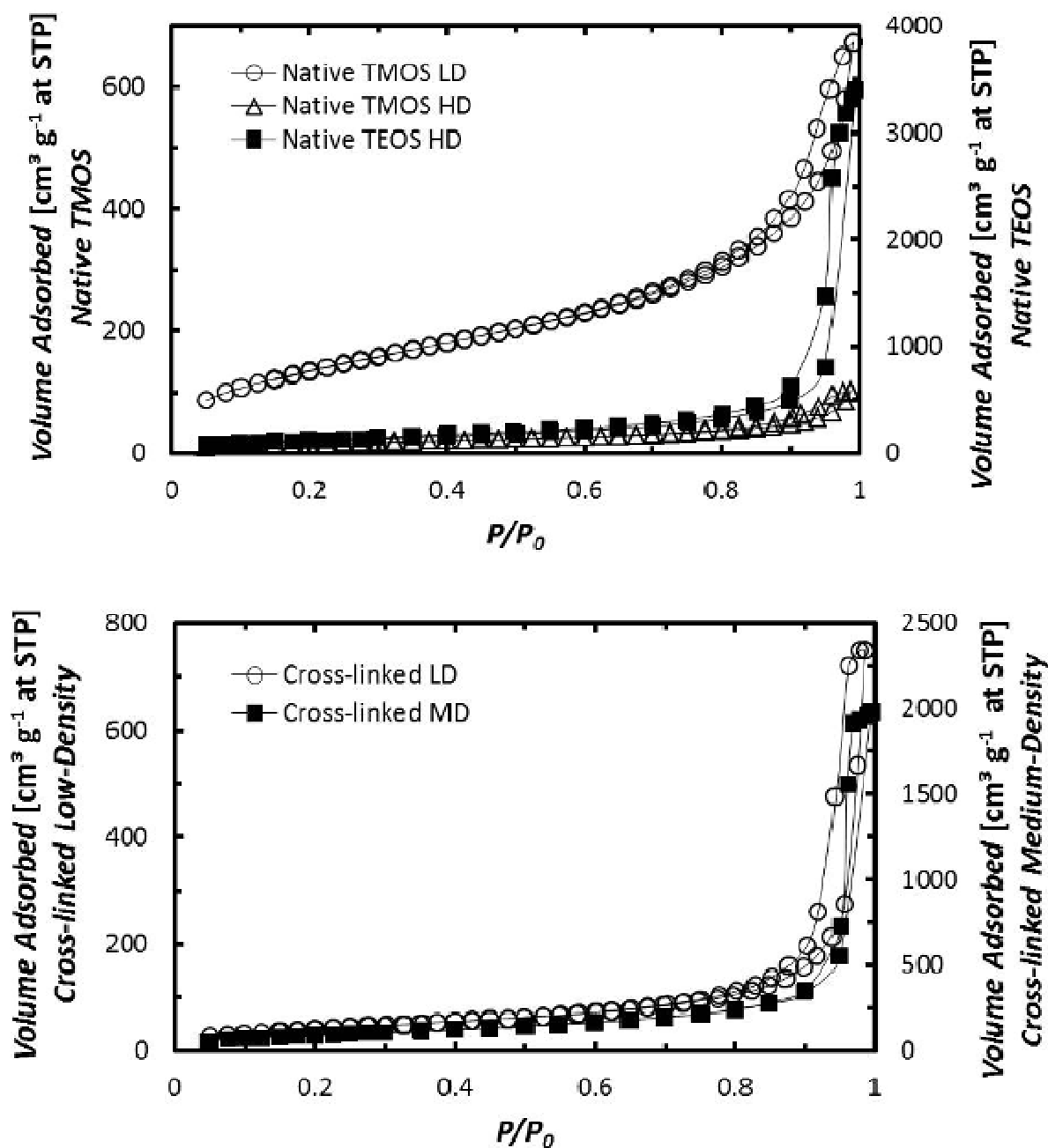
3.2. Native oxide aerogels.

As detailed in Table 1 and Figures 1 and 2, native oxide aerogels fabricated with our technique have surface areas of several hundred square meters per gram, mean pore sizes of tens of nanometers and densities below about 0.2 g·cm^{-3}. These values are expected for monoliths dried in supercritical solvents. Supercritical solvent drying is, in essence, a hydrothermal process which leads to Ostwald ripening of the skeletal oxide nanoparticles and to a reduced micropore volume.[6,38-44] Typically, aerogels dried in supercritical solvents have 20-30% less surface area and 2-3 times larger mean pores than their counterparts dried at or near room temperature.

Aerogel class	Alkoxide, monomer concentration in gelation solution [% volume]	BET surface area [m^2·g^{-1}]	BJH mean pore size [nm]	Linear shrinkage after drying [%]	Density [g·cm^{-3}]	Young's modulus [MPa]
Native silica (LD)	TMOS 5.5, HDDA 0	510	28	5	0.03	Not measurable (monolith cracked when contacted by anvil)
Native silica (HD)	TMOS 22, HDDA 0	310	40	5	0.11	0.48
Native silica (HD)	TEOS 25, HDDA 0	450	45	21	0.17	Not measurable (monolith cracked when contacted by anvil)
Cross-linked (LD)	TMOS 27, HDDA 7	350	46	13	0.27	10
Cross-linked (MD)	TMOS 22, HDDA 27	154	35	8	0.46	43

Table 1: Physical characteristics of native and cross-linked aerogels.

Figure 1: *Top*: Adsorption isotherms of three native oxide aerogels fabricated in our experiments. Open circles: low density (LD) native oxide aerogels, prepared using a 5.5% (by volume, v/v) TMOS concentration in the gelation solution. Open Triangles: high density (HD) native oxide aerogels, prepared using a 22% v/v TMOS concentration. Filled squares: high density (HD) native oxide aerogels, prepared using a 25% v/v TEOS concentration. *Bottom*: Adsorption isotherm of two cross-linked aerogels fabricated in our experiments. Open circles: (LD) cross-linked aerogels, 7% v/v monomer concentration. Filled squares: (MD) cross-linked aerogels, 27% v/v monomer concentration.
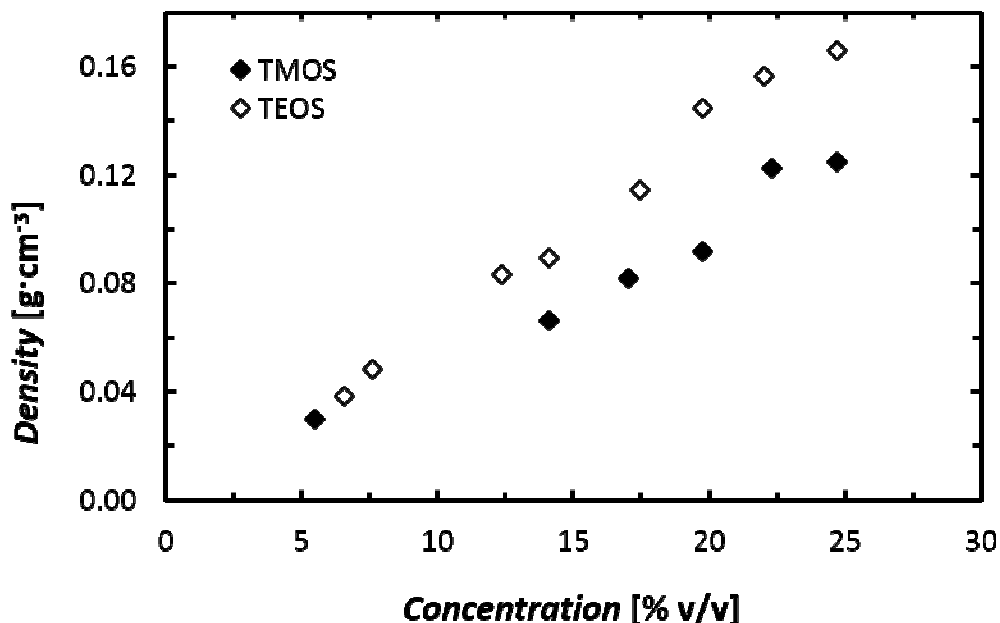
Figure 2: Density of aerogels as a function of alkoxide concentration in the gelation solution for TMOS (base-catalyzed) and TEOS (acid-catalyzed).

We also observed monolith shrinkage, which for base-catalyzed gels was on the order of 5%. This shrinkage is comparable to the shrinkage observed for monoliths dried in supercritical CO_2, but it is considerably smaller than the shrinkage reported by previous work which employed supercritical solvent drying.[5,26,27] For example, Kocon *et al.*[26] and Yoda and Oshima[27] reported a shrinkage of up to 20% using methanol which was attributed to the increased solubility of silica in methanol at high temperatures. In our experiments, shrinkage was not observed for two reasons: the supercritical fluid was ethanol, for which silica solubility is about 7 times lower than for the methanol used in Refs.[26,27] and our drying temperatures were about 30 K lower. Higher shrinkage (~20%) and, consequently, higher densities, were observed for acid-catalyzed aerogels, as shown in Figure 2 and Table 1. The higher shrinkage is attributed to the different morphologies of acid- and base-catalyzed alcogel skeletons. Acid catalysis yields highly branched skeletal nanoparticles which are prone to collapse, especially when subject to the elevated temperatures of supercritical drying. In comparison, base catalysis yields dense and morphologically stable spherical nanoparticles.[45,46]

Solid-state NMR analysis, presented in Figure 3, further confirmed that our aerogel samples did not present any anomalies, for example those due to incomplete hydrolysis-condensation reactions. Two pairs of alcogels were fabricated using TMOS (respectively, TEOS) as a precursor. For each pair, one alcogel was dried supercritically and the other was dried in air. The ^{29}Si spectra of TMOS samples (Fig. 3, top panel) exhibit peaks at -102 ppm (silanol)[47], -111 ppm (siloxane)[48], and at -67 ppm (tridentate bonding of MTMS to silica)[49]. The peak at -

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67 ppm is asymmetric and points to the presence of mono- and bidentate bonding of MTMS to the silica framework, which yields peaks at -52 ppm and -59 ppm, respectively[48]. Figure 3, bottom panel, also reports the ^{29}Si spectra of acid-catalyzed samples. The peaks coincide with the peaks observed for base-catalyzed gels with the exception of a weak peak in air-dried samples at -93 ppm, related to Si atoms with bidentate bonding to the silica matrix and carrying two OH groups[48]. Area integration shows that Si with bidentate bonds represent a small fraction (~5%) of the total Si atoms. The bidentate bonds disappear in supercritically dried samples. Overall, NMR analysis shows that air-dried and supercritically dried samples exhibit very similar characteristics, with peaks that coincide with those reported in the literature for silica aerogels synthesized following more conventional pathways.
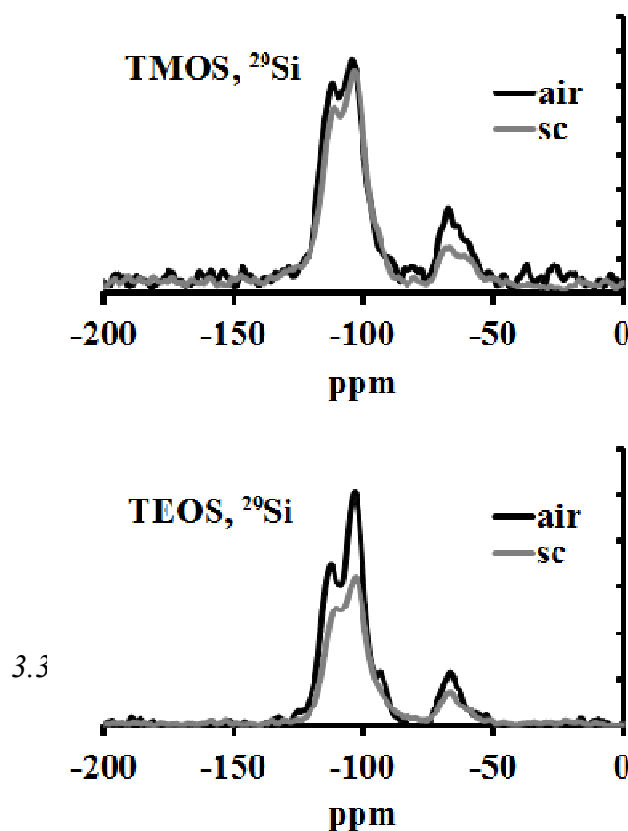

Figure 3: ^{29}Si NMR spectra of samples prepared with the precursors indicated in the legend. Black lines: air-dried samples. Grey lines: supercritically dried samples. Pore walls were derivatized with MTMS in all cases.

In this work, we followed the general principles of aerogel cross-linking and derivatized the pore walls with an acrylic group by adding trimethoxysilylpropyl methacrylate (MTMS) to the gelation solution. As briefly mentioned in Section 3.1, the use of the ethanol-water azeotrope mixture as a gelation solvent alleviated monomer solubility issues and simplified processing. In our previous work,[23] for example, we noticed that the high water concentration of the gelation

solution imposed the use of monomers that were at least partially water-dispersible, such as methyl methacrylate, usually in a concentration below about 10% by weight. By using the ethanol-water azeotrope mixture, gelation solutions could be prepared using a highly hydrophobic monomer such as HDDA in a concentration as high as 40% by weight which gelled in approximately one hour. After aging for two hours, wet gels were cross-linked by visible light photopolymerization as described in the experimental section 2.5. HDDA was chosen because it is a highly reactive monomer which is often used as a benchmark in photopolymerization.[51-53] The homogeneity of the samples was confirmed by measuring densities, surface areas and pore sizes from multiple regions of samples. These measurements did not show a dependence on the region from where the sample was taken (e.g., outer regions versus core). In addition, samples that were deliberately brought to rupture in compression measurements did not show any preferential failure region or direction. The only exception were samples that contained a high concentration of Eosin. In these samples, light penetrated only the outer regions. Consequently, the outer regions, which had a higher polymer concentration than the core, had a lower surface area, higher density, and tended to fail after the core in compression. Figures 1 and 4 and Table 1 show that the cross-linked aerogels produced with our one-pot method had physical characteristics that met expectations for cross-linked aerogels. Surface areas were on the order of 100-300 $m^2 \cdot g^{-1}$; pore sizes were on the order of tens of nanometers because of syneresis; and densities were between about 0.2 and 0.5 $g \cdot cm^{-3}$. Shrinkage was between 7 and 10%, which is typical for cross-linked monoliths. Shrinkages between about 7% and 28% have been reported by previous work and are attributed to compression of the skeletal secondary particles by the cross-linking polymer.[21,53] Moduli were between about 10 and 30 MPa and increased with the concentration of monomer in the gelation solution, as may be seen in Figure 4. The observed linear increase is in agreement with reports by the Leventis group,[54] and more recently, by Meador et al.[22]

The measured moduli may appear low when compared to the moduli of several hundred of MPa which are often reported for cross-linked aerogels.[18] This discrepancy is due to our choice of monomer. HDDA is a very flexible molecule, which leads to polymers with a modulus between about 10 and 50 Mpa.[55,56] Thus, the modulus of our aerogels agrees with expectations for a polymer synthesized from HDDA. Preliminary results indicate that monoliths with a modulus of up to 400 MPa can be fabricated using the pentacrylate DPHA, whose structure is reported in Scheme 1. The reason for this large difference in moduli is due to the penta-functionality of DPHA monomers that produces three-dimensional network structures. When compared to the modulus of HDDA, a bi-functional molecule that can only form linear polymer chains, the high modulus of DPHA-cross-linked aerogels confirms formation of a network structure. A full report on the relationship between the monomer structure and the modulus of the materials is in preparation.[57]
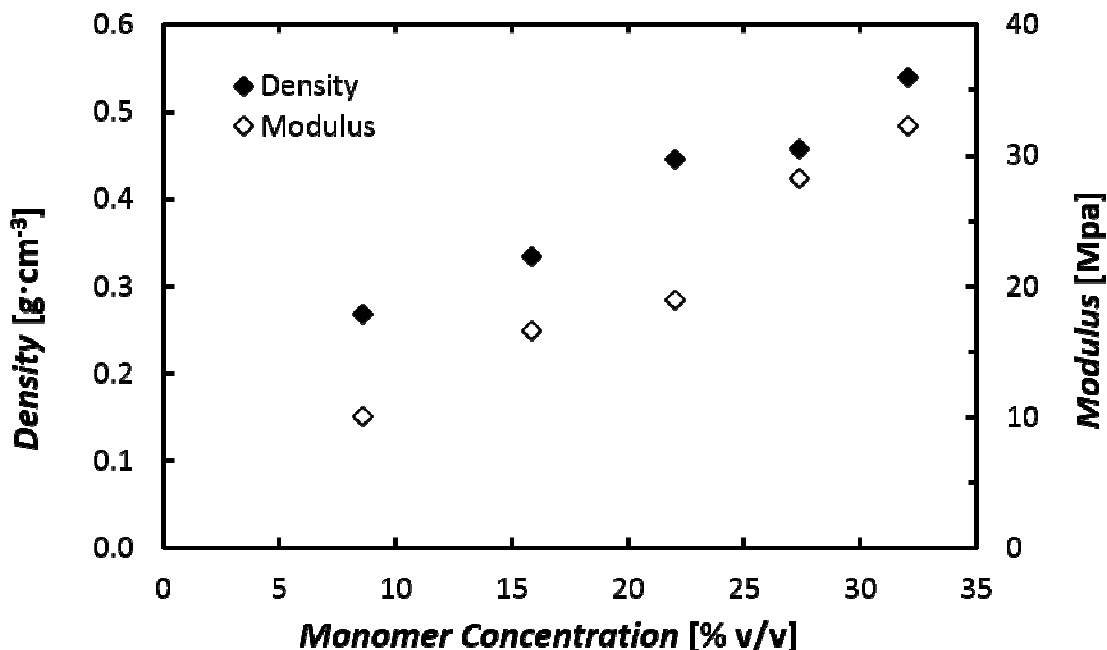
Figure 4: Dependence of Young's modulus and density of cross-linked aerogels on HDDA concentration. An exposure time of 30 minutes in samples with 0.6 mg of Eosin Y each was used to guarantee homogeneous polymerization of each sample. Alkoxide: TMOS, base-catalyzed.

Derivatization and engagement of the surface acrylic moiety during polymerization were confirmed by FT-IR analysis, reported in Figure 5. In native silica gels broad peaks at about 800 cm^{-1} and 1063 cm^{-1} were observed, which corresponded to the Si-O stretch and the Si-O-Si stretch respectively.[58] In silica aerogels that had been derivatized with MTMS but had not been cross-linked, additional peaks were evident at 1395, 1449, 1636 and 1722 cm^{-1}. Peaks in the 1390–1450 cm^{-1} region are due to sp^3 C–H bending. The weak peak at 1636 cm^{-1} and a relatively large peak at 1720 cm^{-1} are attributed to C=C stretch and the C=O stretch, respectively. In cross-linked aerogels the peak at 1636 cm^{-1} was absent, indicating engagement of the surface moiety by the polymerization process.[31,32] The FT-IR data was collected after supercritical drying and it provided a first indication that the cross-linking polymer had not been affected by the high temperatures. For example, the presence of the C=C stretch in MTMS-derivatized aerogels indicated that the surface acrylic moiety was not attacked during drying; the absence of the C=C stretch peak in cross-linked aerogels indicated that polymer attachment to the silica walls was not affected by drying.
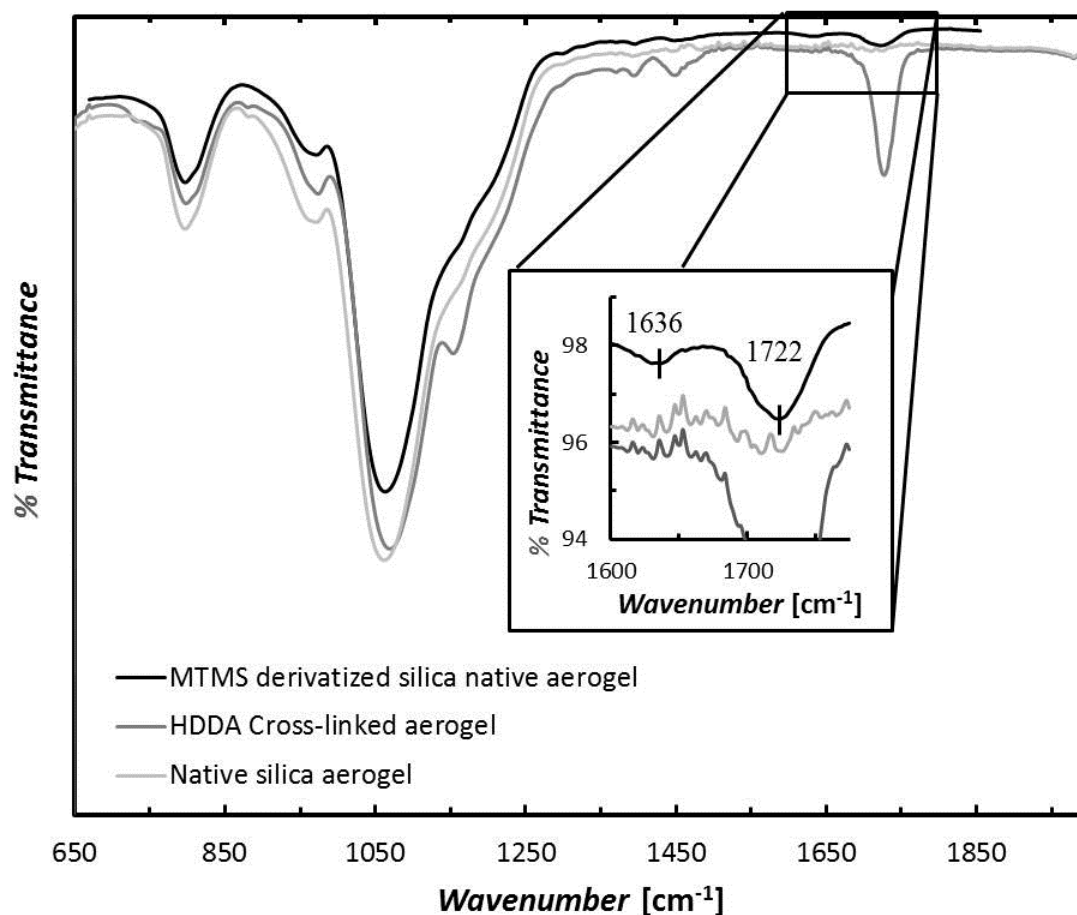
Figure 5: FT-IR spectra of aerogel monoliths after supercritical drying.

Figure 6 shows ^{13}C and ^{29}Si solid-state NMR spectra for air- and supercritically-dried cross-linked aerogels. The [29]Si spectra exhibit the silanol and siloxane peaks at -102 and -111 ppm which were observed also in native aerogels (Figure 3). Air-dried samples also exhibited a peak at -44 ppm, which is attributed to Si atoms with monodentate bonding to the silica matrix and also bound to (unhydrolyzed) methoxy groups and the derivatizing propylacrylate group[48]. Supercritically dried samples exhibit a peak at -52 ppm which can be reconciled with Si atoms with monodentate bonding carrying two OH groups and the propylacrylate group, indicating that hydrolysis (but not condensation) took place during supercritical drying. Mono- and bidentate bonds of the derivatizing moiety are not surprising, since the silane carrying the moiety is anchored to the surface where coordination tends to be lower than in the bulk. Mono-and bidentate bonds have been reported, for example, by Maciel and Sindorf, who investigated reactions of methylchlorosilane with a silica gel[59], and by the Leventis group, who derivatized silica alcogels with aminopropyl triethoxysilane[60]. Peak area integration showed that the concentration of partially reacted silanes was between about 11 and 12% in both air- and

supercritically-dried samples, indicating that Si atoms with monodentate bonds were not removed from the monolith by supercritical drying. As for ^{13}C, peaks were measured at 26, 28, 40, 64, and 174 ppm which are reconciled with aliphatic carbons of polymerized HDDA[49]. Polymer formation is clearly demonstrated by the strong C=O carbon signal at 174 ppm in the ^{13}C CPMAS spectrum in both air-dried and supercritically dried samples. In the HDDA monomer, the C=O peak is located at 167 ppm, and shifts to 174 ppm upon polymerization[48]. The air-dried sample shows also a small peak at 129 ppm which is from the unsaturated C=C carbon of unreacted monomer. We used peak area (integration values) to estimate how much unreacted monomer was left in the air-dried sample. The percentage of C=O carbon in each sample was calculated by dividing the peak area of C=O carbon by the sum of peak areas of all of the carbons. The % C=O carbon is 17.6 for the supercritically dried sample and 16.7 for the air-dried sample, indicating a difference of 1%, which is the amount of unreacted monomer left in the air-dried sample. Except for the weak C=C resonance, the NMR peaks coincide for air- and supercritically dried samples, indicating that supercritical drying had little or no effect on the polymer.
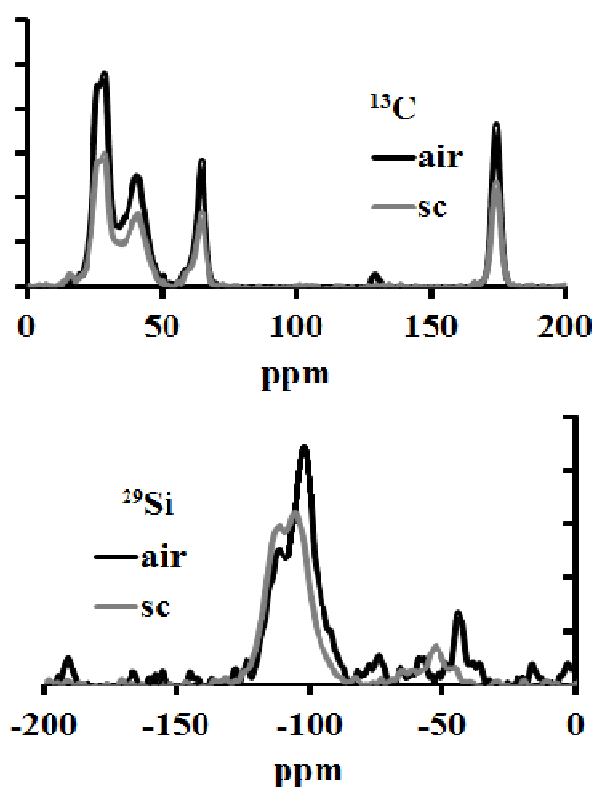

Figure 6: ^{13}C (top) and ^{29}Si (bottom) NMR spectra of cross-linked aerogels. Black lines: air-dried. Grey lines: supercritically dried. The alkoxide precursor was TMOS, base-catalyzed.

Further tests were carried out to demonstrate that drying did not affect the cross-linking polymer. In one test, an ethanolic solution of HDDA and the initiator Eosin was prepared which had the same composition of the gelation solution, except that the alkoxide had been replaced by

an equivalent volume of ethanol. The solution was poured into two transparent molds which were exposed to green light until solid cylindrical monoliths were obtained. After exposure, both samples were washed. One sample was then dried in air and the other dried supercritically. Density, surface area and modulus of these polymer monoliths were comparable and further suggested that supercritical drying did not substantially affect the polymer. The air- dried sample exhibited a 5.5% shrinkage, a density of 0.410 $g \cdot cm^{-3}$, a surface area of about 20 $m^2 \cdot g^{-1}$ and a Young's modulus of 29.7 MPa. The supercritically dried sample shrank by 3.5%, had a density of 0.406 $g \cdot cm^{-3}$, a surface area of about 15 $m^2 \cdot g^{-1}$ and a Young's modulus of 29.2 MPa. Figure 7 compares the Raman spectra, of these air- and supercritically- dried polymer samples. With two minor exceptions, the spectra exhibited the same peaks in the two samples and confirmed that the polymer was not affected by supercritical drying. One exception was that the air-dried sample exhibited a luminescent background. This background likely originated from residual Eosin Y, which is a strongly luminescent molecule. The second exception was that the supercritically dried sample also exhibited a peak at 1659 cm^{-1} which is within the range of the C=C stretch. The signal may arise from an unpolymerized end of the diacrylate HDDA molecule. In the air-dried sample the weak C=C peak was probably covered by the luminescent background.
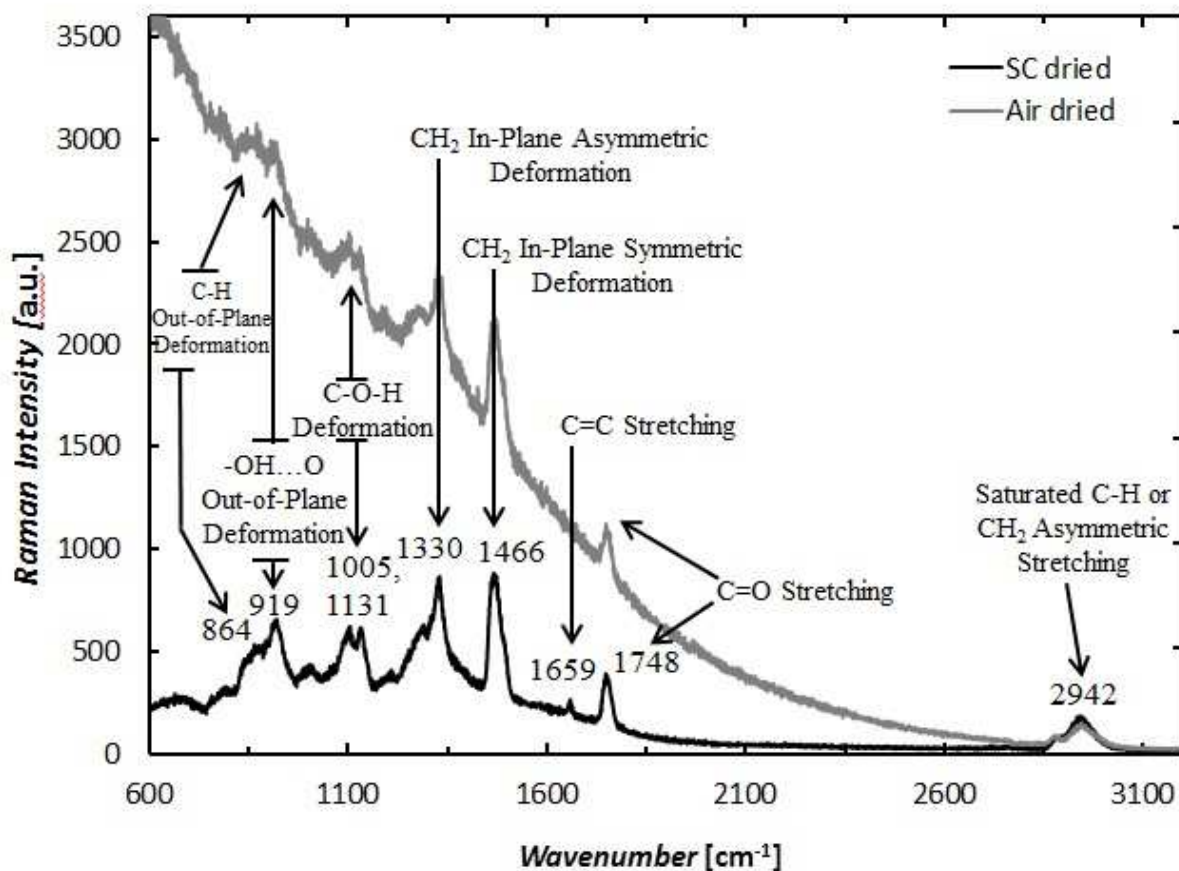
Figure 7: Raman spectra of HDDA polymer monoliths prepared by photoinitiated polymerization, one dried in air and one dried supercritically. Excitation: 532 nm.

Figure 8 reports TGA analysis of native and HDDA cross-linked aerogels. In native samples, a ~25% weight decrease is evident starting at about 160 ^{0}C, which is likely due to desorption, and, possibly, combustion of gelation residues [61-63]. As for the cross-linked sample, a weight difference of about 78% can be calculated between the weight at room temperature and at 600 ^{0}C. This weight loss is in agreement with the 76% polymer weight that can be calculated from the composition of the gelation solution. The 72% weight loss is also in agreement with reports by Katti et al.,[60] and by Duan et al.,[24] where a polymer content of about 70% by weight was measured for cross-linked aerogels using TGA. The polymer content figures are interpreted as additional confirmation that drying in supercritical ethanol-water azeotrope does not substantially affect the cross-linking polymer.
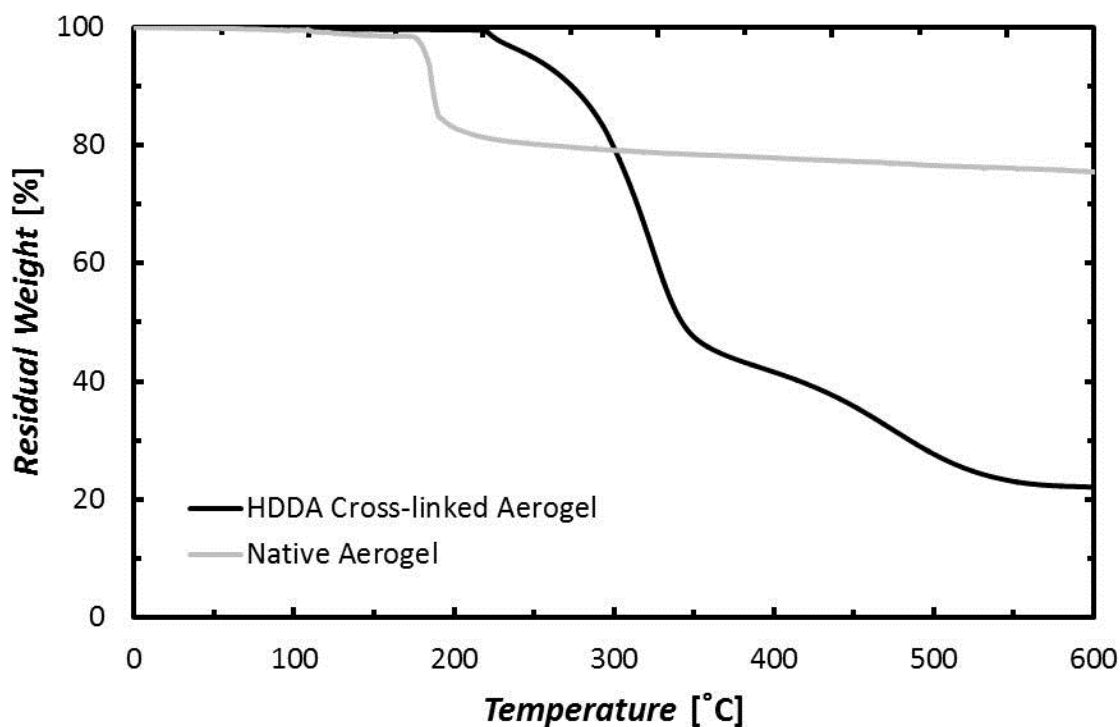
Figure 8: TGA measurements of native and HDDA cross-linked aerogels. Precursor: TMOS, base-catalyzed.

Figure 9a shows a native oxide monolith in the shape of a cube with each side measuring 25 mm and Figure 9b shows a cross-linked parallelepiped with a size of 12 x 25 x 25 mm each produced using our one-pot synthesis method and super critical ethanol drying method. Starting from the sol, both monoliths were fabricated in less than 6 hours, the same amount of synthesis time as the cylindrical monoliths with a ~13mm diameter. We also note that the monolith of Figure 9b could be glued to a concrete cinder block (grey background) without any noticeable shearing.
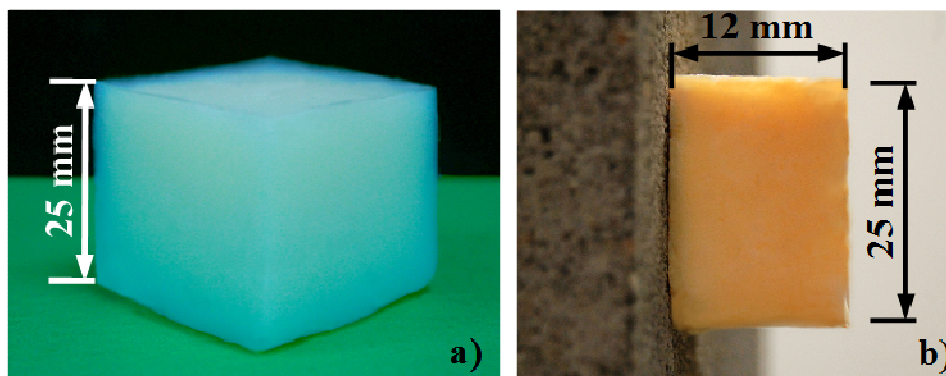
Figure 9: Examples of aerogel monoliths produced with our technique. a) Native oxide aerogel monolith in the shape of a cube with a size 25 mm using the acid catalyzed synthesis method. b) A cross-linked monolith glued to a concrete block. Precursor: TMOS, base-catalyzed.

4.   Conclusions

We report an important improvement in aerogel fabrication. Aerogel synthesis is in one pot for native and cross-linked alcogels and no solvent exchanges are necessary. Monoliths can be fabricated in a few hours independent of their type (native or cross-linked), and large volumes of fresh solvent are not required by the process.

Acknowledgements

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