

Video Article

# Preparing Silica Aerogel Monoliths via a Rapid Supercritical Extraction Method

Mary K. Carroll<sup>\*1</sup>, Ann M. Anderson<sup>\*2</sup>, Caroline A. Gorka<sup>1</sup>

<sup>1</sup>Department of Chemistry, Union College

<sup>2</sup>Department of Mechanical Engineering, Union College

\*These authors contributed equally

Correspondence to: Mary K. Carroll at [carrollm@union.edu](mailto:carrollm@union.edu)

URL: <https://www.jove.com/video/51421>

DOI: [doi:10.3791/51421](https://doi.org/10.3791/51421)

Keywords: Chemistry, Issue 84, Aerogel fabrication, Silica aerogels, Aerogel monoliths, Rapid supercritical extraction, Hot press, Tetramethylorthosilicate (TMOS)

Date Published: 2/28/2014

Citation: Carroll, M.K., Anderson, A.M., Gorka, C.A. Preparing Silica Aerogel Monoliths via a Rapid Supercritical Extraction Method. *J. Vis. Exp.* (84), e51421, doi:10.3791/51421 (2014).

## Abstract

A procedure for the fabrication of monolithic silica aerogels in eight hours or less via a rapid supercritical extraction process is described. The procedure requires 15-20 min of preparation time, during which a liquid precursor mixture is prepared and poured into wells of a metal mold that is placed between the platens of a hydraulic hot press, followed by several hours of processing within the hot press. The precursor solution consists of a 1.0:12.0:3.6:3.5 x 10<sup>-3</sup> molar ratio of tetramethylorthosilicate (TMOS):methanol:water:ammonia. In each well of the mold, a porous silica sol-gel matrix forms. As the temperature of the mold and its contents is increased, the pressure within the mold rises. After the temperature/pressure conditions surpass the supercritical point for the solvent within the pores of the matrix (in this case, a methanol/water mixture), the supercritical fluid is released, and monolithic aerogel remains within the wells of the mold. With the mold used in this procedure, cylindrical monoliths of 2.2 cm diameter and 1.9 cm height are produced. Aerogels formed by this rapid method have comparable properties (low bulk and skeletal density, high surface area, mesoporous morphology) to those prepared by other methods that involve either additional reaction steps or solvent extractions (lengthier processes that generate more chemical waste). The rapid supercritical extraction method can also be applied to the fabrication of aerogels based on other precursor recipes.

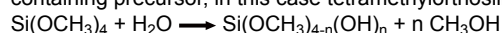
## Video Link

The video component of this article can be found at <https://www.jove.com/video/51421/>

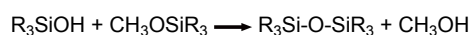
## Introduction

Silica aerogel materials have low density, high surface area, and low thermal and electrical conductivity combined with a nanoporous structure with excellent optical properties. The combination of these properties in one material makes aerogels attractive in a large number of applications<sup>1</sup>. In a recent review article, Gurav *et al.* describe in detail the current and potential applications of silica aerogel materials, both in scientific research and in development of industrial products<sup>2</sup>. For example, silica aerogels have been used as absorbents, as sensors, in low-dielectric materials, as storage media for fuels, and for a wide array of thermal insulating applications<sup>2</sup>.

Aerogels are typically fabricated using a two-step process. The first step involves mixing appropriate chemical precursors, which then undergo condensation and hydrolysis reactions to form a wet gel. To prepare silica gels, the hydrolysis reactions occur between water and a silica-containing precursor, in this case tetramethylorthosilicate (TMOS, Si(OCH<sub>3</sub>)<sub>4</sub>), in the presence of acid or base catalyst.



TMOS is insoluble in water. In order to facilitate hydrolysis, it is necessary to include another solvent, in this case methanol (MeOH, CH<sub>3</sub>OH), and to stir or sonicate the mixture. Base-catalyzed polycondensation reactions then occur between the hydrolyzed silica species:



The polycondensation reactions result in the formation of a wet gel, comprised of a porous SiO<sub>2</sub> solid matrix, in which the pores are filled with the solvent byproducts of the reaction, in this case methanol and water. The second step involves drying the wet gel to form an aerogel: removing the solvent from the pores without altering the solid matrix. The drying process is critically important to the formation of the aerogel. If not carried out correctly the fragile nanostructure collapses and a xerogel is formed as illustrated schematically in **Figure 1**.

There are three basic methods for drying sol-gel materials to produce aerogels: supercritical extraction, freeze drying and ambient pressure drying. The supercritical extraction methods avoid crossing the liquid-vapor phase line so that surface tension effects do not cause the

nanostructure of the gel to collapse. Supercritical extraction methods can be performed at high temperature (250–300 °C) and pressure with direct extraction of the alcohol solvent byproduct of the condensation and hydrolysis reactions<sup>3–7</sup>. Alternatively, one can perform a set of exchanges and replace the alcohol solvent with liquid carbon dioxide, which has a low supercritical temperature (~31 °C). The extraction can then be performed at relatively low temperature<sup>8,9</sup>, albeit at high pressure. Freeze drying methods<sup>10,11</sup> first freeze the wet gel at low temperature and then allow the solvent to sublime directly to a vapor form, again avoiding crossing the liquid-vapor phase line. The ambient pressure method uses surfactants to reduce the surface tension effects or polymers to strengthen the nanostructure, followed by drying of the wet gel at ambient pressure<sup>12–16</sup>.

The Union College Rapid Supercritical Extraction (RSCE) process is a one-step (precursor to aerogel) method<sup>17–19</sup>. The method employs high-temperature supercritical extraction, which allows fabrication of monolithic aerogels in hours, rather than the days to weeks required by other methods. The method utilizes a confined metal mold and a programmable hydraulic hot press. Chemical precursors are mixed and poured directly into the mold, which is placed between the platens of the hydraulic hot press. The hot press is programmed to close and apply a restraining force to seal the mold. The hot press then heats the mold at a specified rate to a temperature,  $T_{\text{high}}$ , above the critical temperature of the solvent (see **Figure 2** for a plot of the process). During the heatup period the chemicals react to form a gel and the gel strengthens and ages. As the mold is heated the pressure also rises, eventually reaching a supercritical pressure. Upon reaching  $T_{\text{high}}$ , the hot press dwells at a fixed state while the system equilibrates. Next the hot press force is decreased and the supercritical fluid escapes, leaving behind a hot aerogel. The press then cools the mold and its contents to room temperature. At the end of the process (which can take 3–8 hr) the press opens and monolithic aerogels are removed from the mold.

This RSCE method offers significant advantages over other aerogel fabrication methods. It is fast (<8 hr total) and not very labor intensive, typically requiring only 15–20 min preparation time followed by 3–8 hr processing time. It does not require solvent exchanges, which means that relatively little solvent waste is generated during the process.

In the section that follows, we describe a protocol for preparing a set of cylindrical silica aerogel monoliths via the Union RSCE method from a precursor mixture comprised of TMOS, methanol, and water with aqueous ammonia employed as the catalyst for the hydrolysis and polycondensation reactions (with a TMOS:MeOH:H<sub>2</sub>O:NH<sub>3</sub> molar ratio of 1.0:12:3.6:3.5 × 10<sup>−3</sup>). We note that the Union RSCE method can be used to prepare aerogels of various different sizes and shapes, depending on the metal mold and hydraulic hot press employed. This RSCE method has also been used to prepare other types of aerogels (titania, alumina, etc.) from different precursor recipes<sup>20</sup>.

## Protocol

**Safety Considerations:** Safety glasses or goggles should be worn at all times during the preparative work with solutions and the hydraulic hot press. Laboratory gloves should be worn when preparing the chemical reagent solution and when pouring the solution into the mold in the hot press. TMOS, methanol and concentrated ammonia, and solutions containing these reagents, must be handled within a fume hood. The supercritical extraction process releases hot methanol, so it is necessary both to vent the hydraulic hot press, and to ensure that there are no ignition sources within the vent path of the hot press. In addition, we recommend installation of a safety shield around the hot press. In the event of a gasket failure, the shield will help contain the resulting gasket pieces and thereby protect anyone working near the hot press.

## 1. Prepare Reagents and Other Supplies

1. Gather the reagents needed for the recipe: tetramethylorthosilicate, methanol, deionized water, and ammonia.
2. Make 100.0 ml of a 1.5 M ammonia solution. To do so, dilute 10.1 ml of 14.8 M concentrated ammonia to 100 ml with deionized water.
3. Acquire a square stainless steel mold, 12.7 cm x 12.7 cm x 1.9 cm high, with 9 circular wells of 2.2 cm diameter (see **Figure 3**). Wipe the mold with a clean, damp rag to remove any surface oil or dust. Spray inside of each circular well with high-temperature mold release spray to ease in removal of aerogels from the mold after processing.
4. Prepare three sets of sealing gaskets from 1/16 in (1.6 mm) thick graphite sheet and 0.0005 in (0.012 mm) thick stainless steel foil. Cut three pieces of each material sufficient to cover the mold completely (>12.7 cm x >12.7cm).

## 2. Prepare Instruments

1. Program the hot press sealing and extraction programs. First set up a sealing program that will be used to seal the bottom of the open mold. See **Table 1** for the necessary program values. Next set up the extraction program with the correct parameters for the silica aerogels using the mold described above. See **Table 2** for these parameters.
2. Prepare glassware. To avoid contamination, four glass beakers will be needed, one 250 ml beaker labeled 'precursor solution,' one 100 ml beaker labeled 'methanol,' one 20 ml beaker labeled 'DI water,' and one 10 ml beaker labeled '1.5 M ammonia.' Make sure all beakers are clean and dry.
3. Prepare pipettes. Digital pipettes should be used for ease. A 10 ml digital pipette and a 1,000 µl pipette will be used. Make sure multiple pipette tips are available.
4. Prepare sonicator by adding water to the fill line.

## 3. Seal Mold Bottom

1. Place mold and gasket material in hot press. First center a graphite sheet on the lower platen, add a sheet of stainless steel foil and place the mold on top of the stainless steel foil. Add another set of gasket material (stainless steel then graphite) on top of the mold. (Note: used gasket material can be used on the top in this step, but new gasket material must be used on the bottom.)
2. Start the hot press sealing program, using the parameters shown in **Table 1**. This program seals the bottom of the mold to prevent the liquid precursor chemicals from leaking when the mold is filled with precursor solution.

## 4. Make Precursor Solution

The recipe for TMOS-based silica aerogels is shown in **Table 3**. All solution preparation work is performed in a fume hood.

1. First pipette aliquots of TMOS totaling 17.0 ml from the reagent bottle into the 250 ml glass beaker labeled 'precursor solution'.
2. Pour some methanol into the 100 ml glass beaker and then pipette aliquots of methanol totaling 55.0 ml into the 250 ml glass beaker labeled 'precursor solution.'
3. Pour some deionized water into the 20 ml beaker labeled 'DI water' and from that beaker pipette 7.2 ml of water into the 250 ml beaker.
4. Lastly, pour some 1.5 M  $\text{NH}_3$  into the 10 ml beaker and from that beaker pipette 270  $\mu\text{l}$  of the solution into the 250 ml beaker.
5. Seal the beaker with plastic paraffin film.
6. Mix reagents to ensure that hydrolysis occurs by sonicating the precursor solution for at least 5 min. Prior to sonication, two liquid layers are sometimes visible in the precursor mixture. Following 5 min of sonication, the solution should appear to be monophasic. If it does not, sonicate the mixture for an additional 5 min.

## 5. Pour Precursor Solution into the Mold in the Hot Press

1. At the end of the mold sealing program the hot press platens will open. Remove the top-side gasket material and set aside. Leave the mold as is in the hot press so that the bottom side of the mold remains sealed.
2. Fill each well of the mold completely with the precursor solution. (Note: there will be about 10 ml of aerogel precursor solution left over after filling the mold. This can be discarded or processed under ambient conditions to make xerogels.)
3. Put fresh gasket material on the top of the mold: the stainless steel foil first and then the graphite on top.
4. Run the hot press extraction program (shown in **Table 2**). This program seals the mold, heats the contents to a supercritical state, performs the supercritical extraction and then cools the mold.

## 6. Remove the Aerogels from the Mold

1. When the extraction process is complete, remove the mold and gasket material from the hot press.
2. Remove the top gasket material from the mold. Set this aside.
3. Gently loosen the mold from the bottom gasket material.
4. Carefully remove each aerogel from the mold, one at a time, by firmly pushing them through from one side with a gloved finger.
5. When the aerogels are removed from the mold, the process is complete.

## Representative Results

Following the procedure described here results in consistent batches of monolithic silica aerogels. **Figure 4** shows images of typical silica aerogels made via this process. Each aerogel takes on the shape and size of the well in the processing mold with no shrinkage. The images show that the silica aerogels are translucent.

The physical properties of these aerogels are summarized in **Table 4**. They are comparable to those of silica aerogels produced from similar precursor recipes using low temperature supercritical extraction<sup>21</sup>. **Figure 5** shows a typical pore distribution acquired by BJH analysis of the desorption isotherm acquired with a Micromeritics ASAP 2010. The aerogels are mesoporous with a peak in pore diameter near 20 nm.

Step #	Temp	Temp Rate	Force	Force Rate	Dwell time (min)	Step Duration (min)
1	off	--	20,000 lb (89 kN)	600 k lb/min* (2,669 N/min)	10	10
2	End Step					

**Table 1. Hot Press Mold Sealing Program Settings.**

\* this rate represents the maximum press rate

Step #	Temperature	Temp Rate	Press Force	Force Rate	Dwell time (min)	Step Duration (min)
1 - Seal Mold	90 °F (32 °C)	200 °F/min (111 °C/min)*	40,000 lb (178 kN)	600,000 lb/min (2,669 kN/min)*	2	2
2 - Heat and Equilibrate	550 °F (288 °C)	2 °F/min (1.1 °C/min)	40,000 lb (178 kN)	--	30	260
3 - Extract and Equilibrate	550 °F (288 °C)	--	1,000 lb (4.4 kN)	1,000 lb/min (4.4 kN/min)	30	69
4 - Cool Down	100 °F (38 °C)	3 °F/min (1.7 °C/min)	1,000 lb (4.4 kN)	--	1	151
5 - Finish	End Step				<b>Total Time:</b>	482 min (8 hr)

**Table 2. Hot Press Extraction Program Settings.**

\* these rates represent maximum press rates

Chemical	Amount (ml)
TMOS	17
MeOH	55
H <sub>2</sub> O	7.2
1.5 M NH <sub>3</sub>	0.27

**Table 3. Recipe for 80 ml Silica Precursor Solution.**

Property	Typical Value
Bulk Density	0.1 g/cm <sup>3</sup>
Skeletal Density	1.9 g/cm <sup>3</sup>
BET Surface Area	560 m <sup>2</sup> /g
Cumulative Pore Volume	3.9 cm <sup>3</sup> /g
Average BJH Desorption Pore Diameter	21 nm
Average BJH Adsorption Pore Diameter	27 nm

**Table 4. Properties of Silica Aerogels Prepared via RSCE Process.**

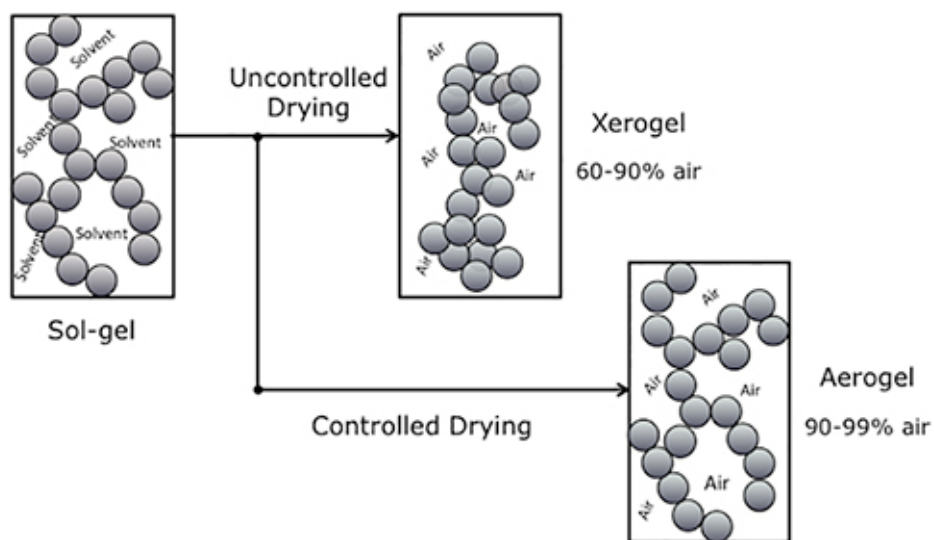


Figure 1. Schematic of sol-gel drying process.

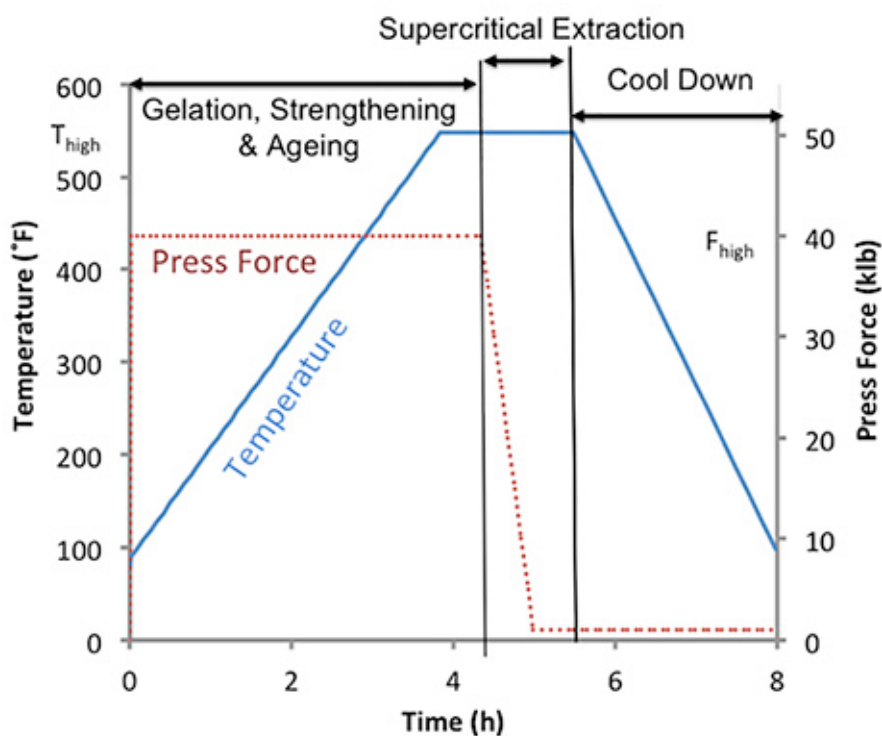
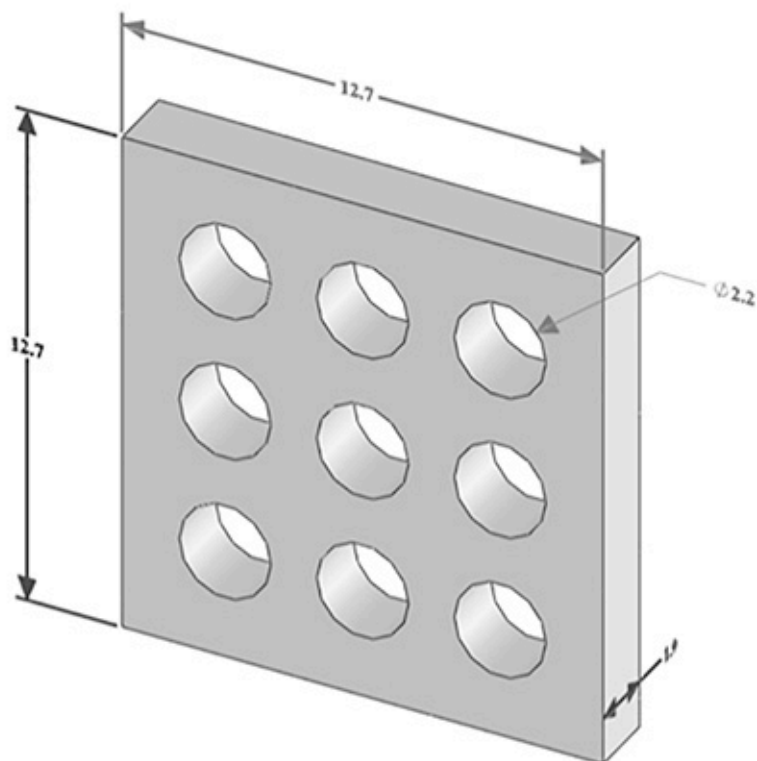
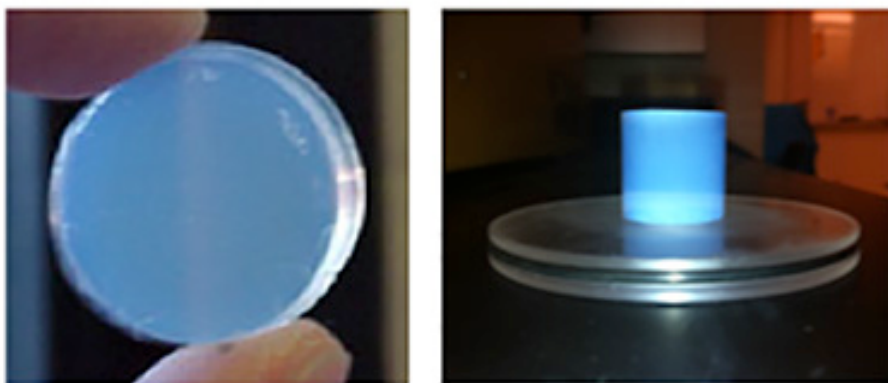


Figure 2. Hot press processing parameters used during RSCE process. (Note: English units are employed in this figure because the hot press is programmed in those units.)



**Figure 3. Schematic of mold used in RSCE process.** Aerogels are formed in each of the nine wells, which pass through the entire mold height (all dimensions are in cm).



**Figure 4. Images of silica aerogels prepared via this RSCE process.**

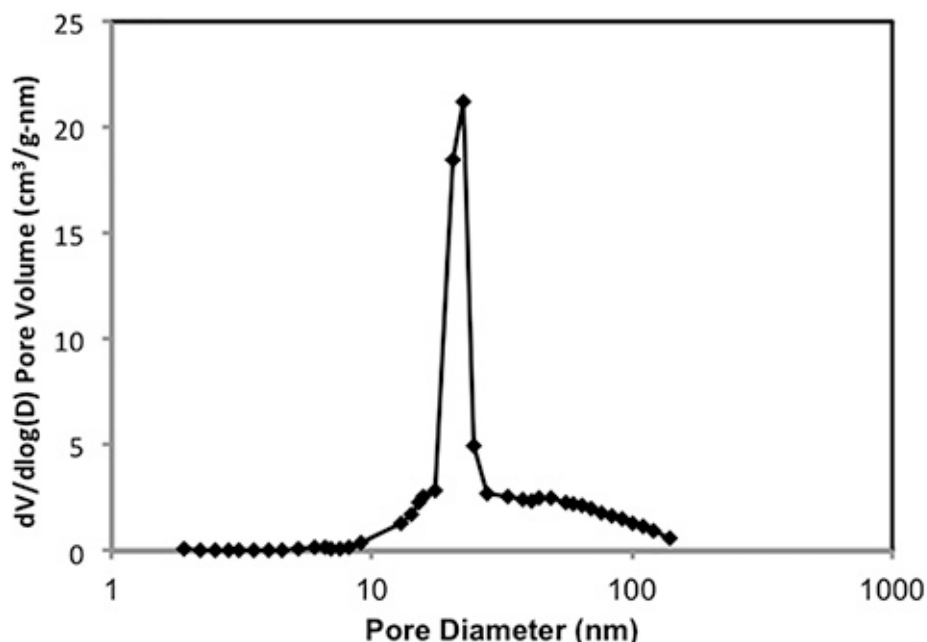


Figure 5. Typical BJH pore distribution (desorption) results for silica aerogel prepared via RSCE.

## Discussion

The RSCE method produces consistent batches of monolithic silica aerogels using an automated and simple process. The method as presented here requires an eight-hour processing step. It is possible to speed up the heating and cooling steps to make monolithic aerogels in as little as 3 hr<sup>22</sup>; however, when an 8 hr procedure is employed, more consistent batches of aerogel monoliths result. Small variations in the process parameters do not affect the physical properties of the resulting aerogels, indicating that the process is robust<sup>22</sup>.

The precursor recipe employed here results in monolithic silica aerogels; however, the rapid supercritical extraction process can be employed to make a variety of other types of aerogels<sup>20</sup> for a wide range of potential uses including hydrophobic silica aerogels<sup>23</sup> (for applications ranging from chemical spill cleanup to enhanced daylighting), titania and titania-silica aerogels<sup>24</sup> (for photocatalysis), and alumina and alumina-based aerogels<sup>25,26</sup> (for catalysis applications). It is possible to place a liquid precursor mixture, as in this work, or a previously prepared wet gel<sup>26</sup> in the wells of the mold for processing. The main limitation is that the chemicals involved in the formation of the sol-gel matrix not react with either the metal mold or gasket material at the temperatures employed in the extraction process. In addition, it is necessary to ensure that the supercritical point of the solvent or solvent mixture within the pores of the aerogel can be exceeded during the hot press process.

The aerogels can be doped with other chemicals (for example to make sensors as in Plata *et al.*<sup>27</sup>) by using a solution of the dopant molecule in methanol or water in place of pure solvent in the precursor mixture; however, the added chemicals must be thermally stable up to the maximum temperature employed in the hot press program in order to survive RSCE processing.

When using the Union RSCE process it is important to supply the appropriate amount of restraining force. Different sized and shaped molds can be used but the hot press restraining force must be adjusted accordingly<sup>28</sup>. If the force is too low, then the solvent will vent sub-critically and the wet gel will shrink within the mold. If the force is too high, then excessive pressure will build up in the mold and the aerogel will be destroyed upon extraction. The maximum aerogel size is limited by the maximum restraining force of the hot press. With a 24 ton hot press, we have prepared monoliths as large as 7.6 cm x 7.6 cm x 1.3 cm. Roth *et al.*<sup>28</sup> provide more information on appropriate processing conditions.

The maximum temperature used in this protocol is 288 °C, which is well above the critical temperature of methanol (240 °C) but below the supercritical temperature of water (374 °C). The wet gel likely contains some water so we have increased the maximum temperature in order to exceed the supercritical point of the solvent mixture. It is possible to heat to a lower maximum temperature (~250 °C) if needed; however, if this is done a longer dwell time (~60 min) in Protocol 2 of the hot press extraction program (see **Table 2**) is recommended to ensure that mold and wet gel reach a sufficiently high temperature.

If the processing steps are not consistently producing translucent monoliths, then use of an instrumented mold, equipped with pressure and temperature sensors (as in Anderson *et al.*<sup>22</sup> or Roth *et al.*<sup>28</sup>) is recommended to confirm in-mold conditions. If aerogel monoliths are observed to be cloudier than usual, consider preparing a fresh batch of catalyst solution. Over time, the 1.5 M ammonia solution can become less concentrated due to reaction of ammonia with atmospheric CO<sub>2</sub>. The lower-concentration solution of the ammonia catalyst results in longer gelation times, but this is not visually apparent when gelation occurs within the mold in the hot press.

We use a mold with wells that go completely through the block of metal. Such a mold allows for easy removal of intact monolithic aerogels after processing; it is also easier to machine than a mold in which each well has a solid, flat bottom. A disadvantage of this mold design is that if the mold is not properly sealed in Protocol 3 of the Procedure, the liquid precursors will leak from the bottom of the mold onto the lower hot press platen. When it is not important in the desired application to obtain intact monolithic aerogels, a mold with closed-bottom wells can be employed.



In this case, monoliths will still form in the mold, but because of the lack of shrinkage of the matrix, one will have to break the aerogels in order to remove them from the mold.

In summary, the Union College rapid supercritical extraction method for aerogel fabrication has several advantages. It is fast: the protocol described here results in high-quality silica aerogel monoliths in eight hours. It is environmentally friendlier and potentially more cost-effective than other aerogel fabrication methods that require solvent exchanges: the RSCE method is not labor-intensive, requiring less than 20 min of preparation time per batch of aerogels, and generates little solvent waste. Finally, this RSCE method has promise for automation and scale-up: hydraulic hot presses come in many sizes, from bench-top models to production line equipment.

## Disclosures

The authors declare that they have no competing financial interests.

## Acknowledgements

The authors thank undergraduate students Lutao Xie, for physical characterization of the aerogel materials, and Aude Bechu, for testing the draft procedure. We are grateful to the Union College Engineering Laboratory for machining the stainless steel mold. The Union College Aerogel Laboratory has been funded by grants from the National Science Foundation (NSF MRI CTS-0216153, NSF RUI CHE-0514527, NSF MRI CMMI-0722842, NSF RUI CHE-0847901, NSF RUI DMR-1206631, and NSF MRI CBET-1228851). This material is based upon work supported by the NSF under Grant No. CHE-0847901.

## References

- Aegerter, M. A., Leventis, N., Koebel, M. M. (ed). *Aerogels Handbook*, Springer, New York, New York, USA (2011).
- Gurav, J. L., Jung, I.-K., Park, H.-H., Kang, E. S., Nadargi, D.Y. Silica aerogel: Synthesis and applications. *J. Nanomater.* doi:10.1155/2010/409310 (2010).
- Kistler, S. S. Coherent expanded aerogels. *J. Phys. Chem.* **13**, 52-64 (1932).
- Phalippou, J., Woignier, T., Prassas, M. Glasses from aerogels. *J. Mater. Sci.* **25** (7), 3111-3117 (1990).
- Danilyuk, A. F., Gorodetskaya, T. A., Barannik, G. B., Lyakhova, V. F. Supercritical extraction as a method for modifying the structure of supports and catalysts. *React. Kinet. Catal. Lett.* **63** (1), 193-199 (1998).
- Pajonk, G. M., Rao, A. V., Sawant, B. M., Parvathy, N. N. Dependence of monolithicity and physical properties of tmos silica aerogels on gel aging and drying conditions. *J. Non-Cryst. Solids.* **209** (1-2), 40-50 (1997).
- Poco, J. F., Coronado, P. R., Pekala, R. W., Hrubesh, L. W. A rapid supercritical extraction process for the production of silica aerogels. *Mat. Res. Soc. Symp.* **431**, 297-302 (1996).
- Tewari, P. H., Hunt, A. J., Lofftus, K. Ambient-temperature supercritical drying of transparent silica aerogels. *Mater. Lett.* **3** (9), 363-367 (1985).
- Van Bommel, M. J., de Haan, A. B. Drying of silica aerogel with supercritical carbon dioxide. *J. Non-Cryst. Solids.* **186**, 78-82 (1995).
- Pajonk, G. M., Repellin-Lacroix, M., Abouarnadasse, S., Chaouki, J., Klavana, D. From sol-gel to aerogels and cryogels. *J. Non Cryst. Solids.* **121**, 66-67 (1990).
- Kalinin, S., Kheifets, L., Mamchik, A., Knot'ko, A., Vertigel, A. Influence of the drying technique on the structure of silica gels. *J. Sol-Gel Sci. Technol.* **15** (1), 31-35 (1999).
- Prakash, S. S., Brinker, C. J., Hurd, A. J. Silica aerogel films at ambient pressure. *J. Non-Cryst. Solids.* **190** (3), 264-275 (1995).
- Prakash, S. S., Brinker, C. J., Hurd, A. J., & Rao, S. M. Silica aerogel films prepared at ambient pressure by using surface derivatization to induce reversible drying shrinkage. *Nature.* **374**(6521), 439-443 (1995).
- Haereid, S., Einarsrud, A. Mechanical strengthening of TMOS-based alcogels by aging in silane solutions. *J. Sol-Gel Sci. Technol.* **3** (3), 199-204 (1994).
- Bhagat, S. D., Oh, C. S., Kim, Y. H., Ahn, Y. S., Yeo, J. G. Methyltrimethoxysilane based monolithic silica aerogels via ambient pressure drying. *Microporous Mesoporous Mater.* **100** (1-3), 350-355 (2007).
- Leventis N., Palczer A., McCorkle L., Zhang G., Sotiriou-Leventis C. Nanoengineered silica-polymer composite aerogels with no need for supercritical fluid drying. *J. Sol-Gel Sci. Technol.* **35** (2), 99-105 (2005).
- Gauthier, B. M., Bakrania, S. D., Anderson, A. M., Carroll, M. K. A fast supercritical extraction technique for aerogel fabrication. *J. Non-Cryst. Solids.* **350**, 238-243 (2004).
- Gauthier, B.M., Anderson, A.M., Bakrania, S.D., Mahony, M.K., Bucinell, R.B. *Method and Device for Fabricating Aerogels and Aerogel Monoliths Obtained Thereby*. US Patent No. 7,384,988 (2008).
- Gauthier, B.M., Anderson, A.M., Bakrania, S.D., Mahony, M.K., Bucinell, R.B. *Method and Device for Fabricating Aerogels and Aerogel Monoliths Obtained Thereby*. US Patent No. 8,080,591 (2011).
- Carroll, M. K., Anderson, A. M. Use of a rapid supercritical extraction method to prepare aerogels from various precursor chemistries. *Polymer Preprints.* **52** (1), 31-32 (2011).
- Pierre, A. C., Rigacci, A. SiO<sub>2</sub> aerogels. In Aegerter, M. A., Leventis, N., Koebel, M. M. (ed). *Aerogels Handbook*, Springer, New York, New York, USA (2011).
- Anderson, A. M., Wattley, C. W., Carroll, M. K. Silica aerogels prepared via rapid supercritical extraction: Effect of process variables on aerogel properties. *J. Non-Cryst. Solids.* **355** (2), 101-108 (2009).
- Anderson, A. M., Carroll, M. K., Green, E. C., Melville, J. T., Bono, M. S. Hydrophobic silica aerogels prepared via rapid supercritical extraction. *J. Sol-Gel Sci. Technol.* **53** (2), 199-207 (2010).
- Brown, L. B., Anderson, A. M., Carroll, M. K. Fabrication of titania and titania-silica aerogels using rapid supercritical extraction. *J. Sol-Gel Sci. Technol.* **62** (3), 404-413 (2012).



25. Bono, M. S., Anderson, A. M., Carroll, M. K. Alumina aerogels prepared via rapid supercritical extraction. *J. Sol-Gel Sci. Technol.* **53** (2), 216-226 (2010).
26. Dunn, N. J. H., Carroll, M. K., Anderson, A. M. Characterization of alumina and nickel-alumina aerogels prepared via rapid supercritical extraction. *Polymer Preprints.* **52** (1), 250-251 (2011).
27. Plata, D.L., Briones, Y.J., *et al.* Aerogel-Platform Optical Sensors for Oxygen Gas. *J. Non-Cryst. Solids.* **350**, 326-335 (2004).
28. Roth, T. B., Anderson, A. M., Carroll, M. K. Analysis of a rapid supercritical extraction aerogel fabrication process: Prediction of thermodynamic conditions during processing. *J. Non-Cryst. Solids.* **354** (31), 3685-3693 (2008).