Optimizing surfactant templating of yttria-stabilized zirconia aerogels for high-temperature applications: Effect of cationic surfactant

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Aerogel Background

Gel in which all of the liquid has been replaced with gas

95 – 99% air by volume, lightest synthetic solid in existence

Mesoporous solid made of connecting nanostructures

Pores between 2 and 50 nm

Exhibit many extreme material properties

- Low bulk density
- High specific surface area
- High porosity
- **Low thermal conductivity**

Thermal Management

http://www.aerogel.org

Aerogels as Thermal Insulators

Excellent insulators due low thermal conductivity (*k*)

- High porosity, high amounts of air (low *k*)
  - **Large pore volume/surface area, mesoporous structure → high porosity**
  - Higher porosity → lower *k*
- Small pores inhibit gas movement, suppress gas convection
- Tortuous path for heat transfer through solid pore walls
- Made from insulating solids (ex: YSZ)

  Composite of air + YSZ, both have low *k*
- Low amounts of solid for conduction

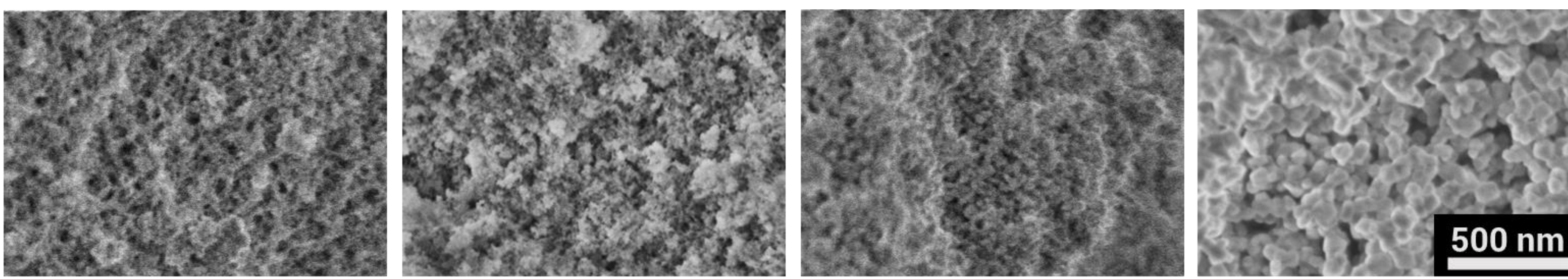
Material	*k* (W/m·K)
Air	0.02 – 0.03
YSZ	0.50 – 2.36
Zr Aerogel	0.02 – 0.18
Si Aerogel	0.01 – 0.02

Aerogels at High-Temperature

High-temperature exposure leads to sintering and densification of aerogels

- Pore collapse, surface area reduction
- Conduction increases → Effectiveness as insulators decreases
- Must **optimize the aerogel formulation** to retain mesoporous structure and high surface area upon high-temperature exposure to increase effectiveness at high temperature

Temperature Increases →



As-dried, 407 m^2/g, 1.43 cm^3/g | 600°C, 181 m^2/g, 0.88 cm^3/g | 1000°C, 47 m^2/g, 0.21 cm^3/g | 1100°C, 21 m^2/g, 0.02 cm^3/g

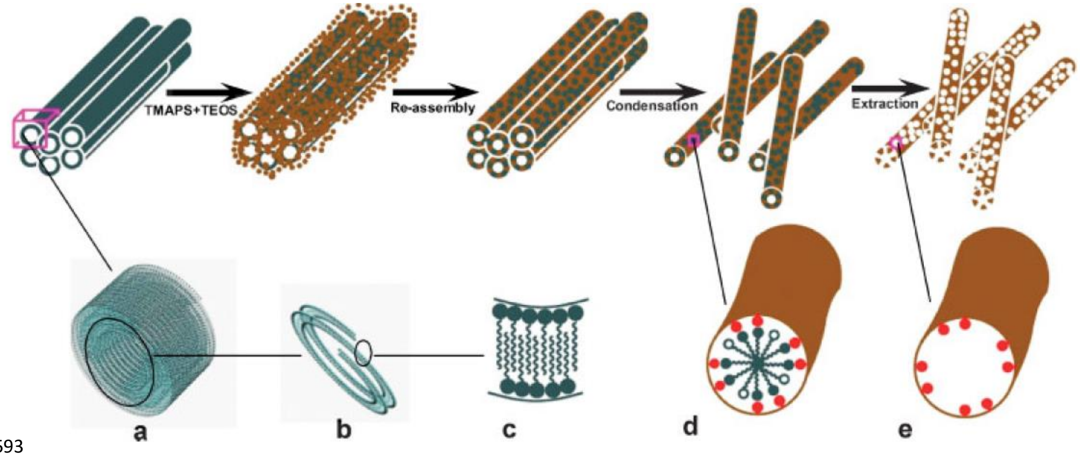
Surface Area, Pore Volume Decreases →

Templating Methods

Structure directing agents can be used to control the pore structure of materials in the mesopore range

- Leads to well-ordered structures, uniform pore diameters
- Hard (porous membrane) vs. Soft (surfactant) templates
- Used to produce hollow spheres or fibers, nanotubes, mesoporous silica, gels, aerogels, etc.

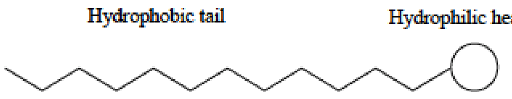
Example: Formation of mesoporous silica nanotubes



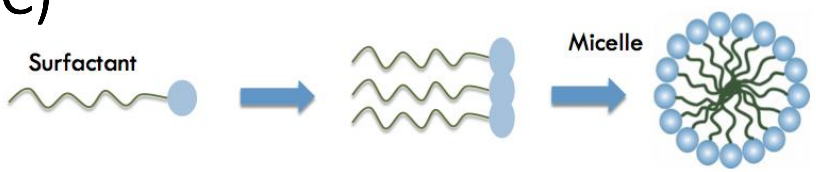
Yu et al., https://doi.org/10.1002/adfm.200700593

Surfactant Templating

Surfactants (Surface-active-agent)



- Amphiphilic molecules, preferentially adsorbing at an interface
- Assemble at interfaces and in the bulk, forming micelles at the critical micelle concentration (CMC)



Micelles can be used as templating agents for aerogels

Enable retention of mesoporous structure and high specific surface area, minimize shrinkage at high-temperature

Surfactant interaction with aerogel matrix could be a potential negative consequence of surfactant templating

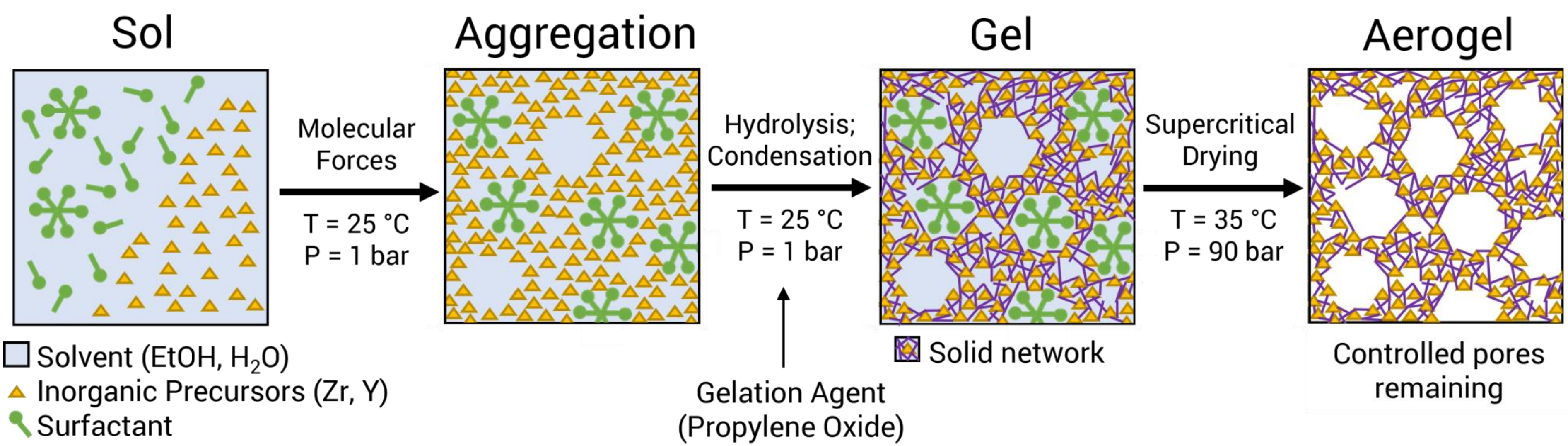
Surfactants control precursor size and crystalline growth via capping effect

https://www.stolaf.edu

Surfactant Templating

Surfactants template the aerogel structure

- Added to sol prior to gelation (multiple of CMC)
- Washed out during supercritical drying and oxidized during heat treatment, leaving pores behind
- Not all pores are directly templated by surfactant

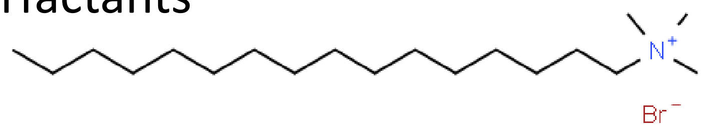


Cationic Surfactants

Prior work: Cationic surfactant

- Hydrophilic head has a positive charge
- Chosen surfactant: Cetrimonium Bromide (CTAB)

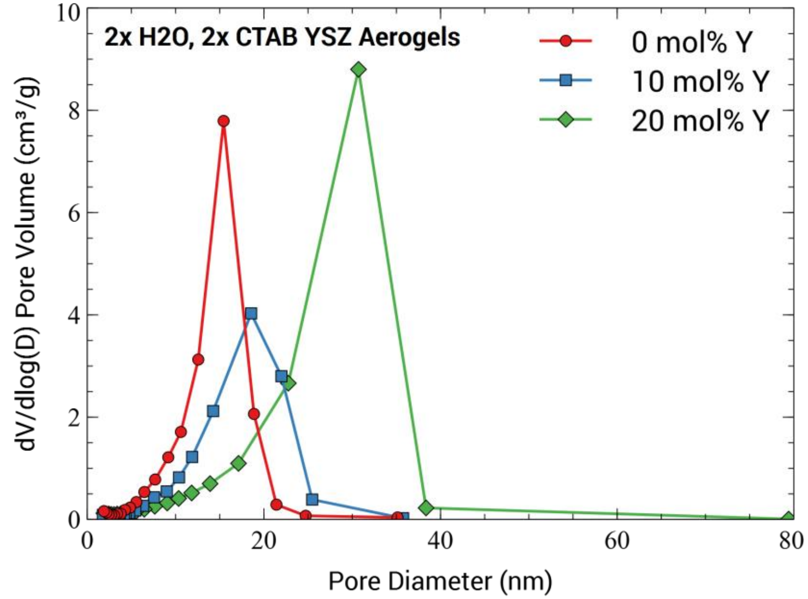
Motivation: Known to form smaller nanoparticles with higher surface area after heat-treatment compared to other surfactants



Experimental: Synthesis & characterization of YSZ aerogels with 0x, 0.5x, and 2x CTAB with various heat-treatment

Results: 0.5x CTAB synthesized aerogels with higher surface area and pore volume following exposure to 600°C and 1000°C

YSZ Aerogel Formulation



20 mol% Y → increasing Y content increased pore size, as well as retained mesoporous structure and smaller particle size after high-temperature exposure compared with lower dopant levels (Hurwitz)

2x H_2O → synthesized aerogels with higher surface area and pore volume at high temperature than 6x H_2O

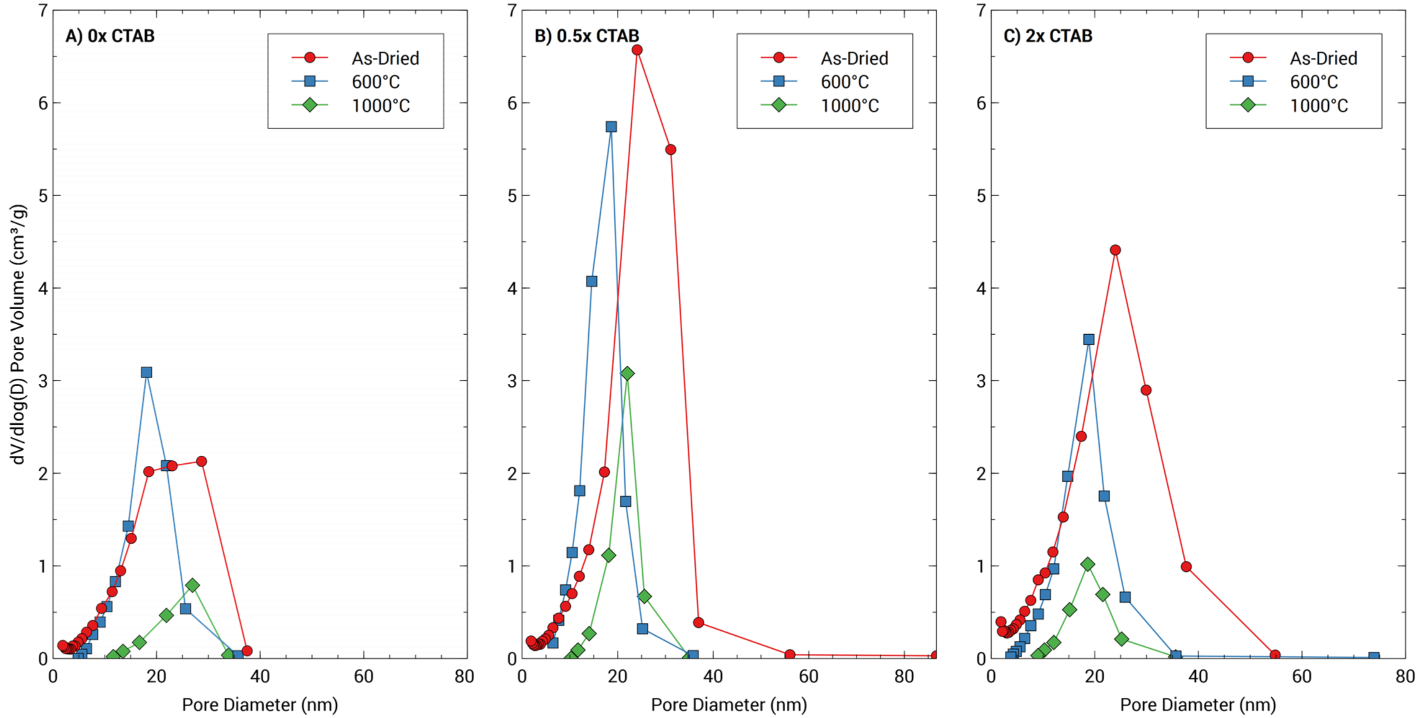
20% Y, 2x H_2O

	BET Surface Area (m^2/g)		BJH Desorption Cumulative Pore Volume (cm^3/g)	
CTAB	**0.5x**	**2x**	**0.5x**	**2x**
As-Dried	403	260	1.95	1.22
600°C	257	181	1.35	0.88
1000°C	52	47	0.36	0.21

20% Y, 6x H_2O

	BET Surface Area (m^2/g)		BJH Desorption Cumulative Pore Volume (cm^3/g)	
CTAB	**0.5x**	**2x**	**0.5x**	**2x**
As-Dried	434	393	1.63	1.89
600°C	148	107	0.83	0.49
1000°C	37	43	0.09	0.11

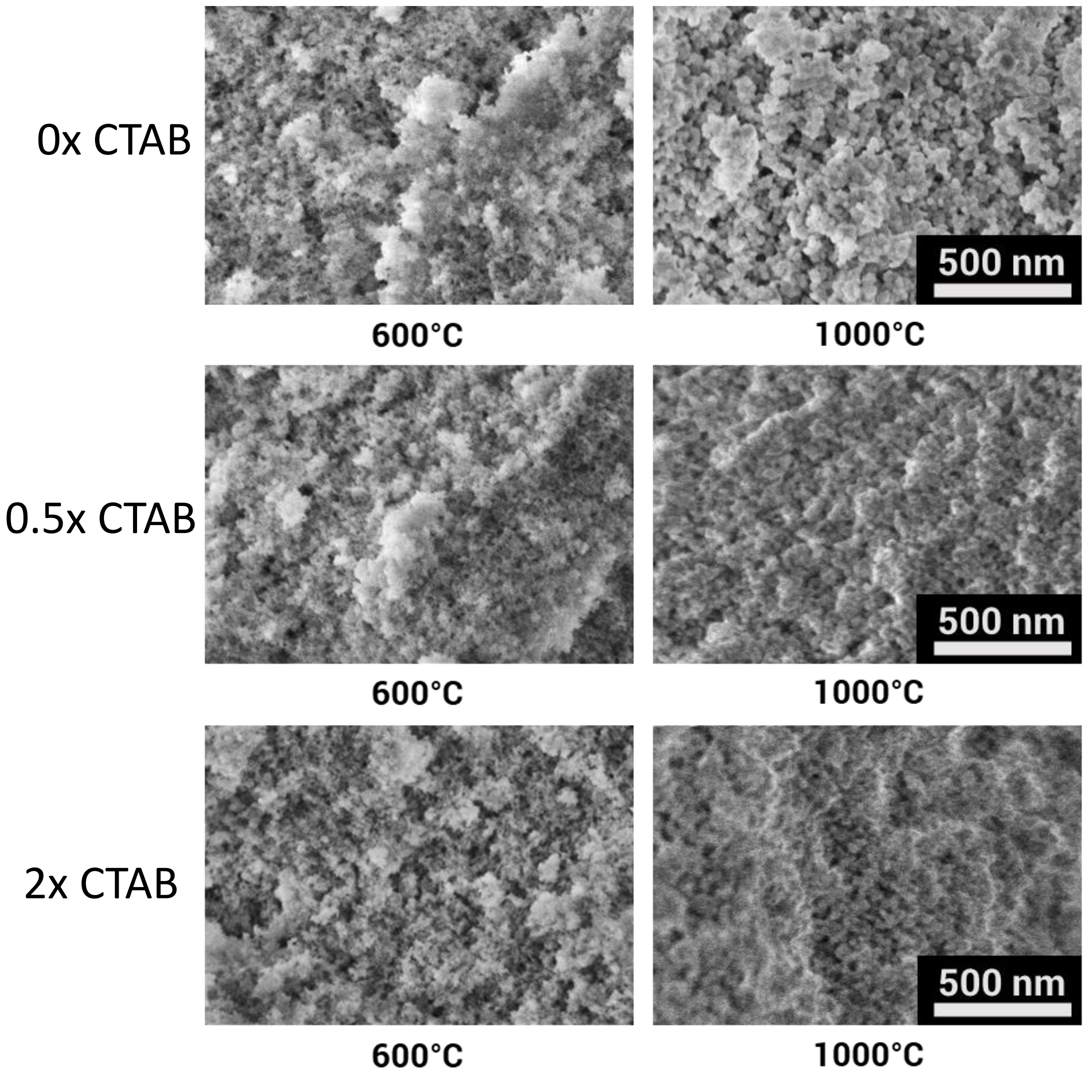
Surface Area & Pore Volume



	BET Surface Area (m²/g)			BJH Desorption Cumulative Pore Volume (cm³/g)		
	0x CTAB	**0.5x CTAB**	**2x CTAB**	**0x CTAB**	**0.5x CTAB**	**2x CTAB**
As-Dried	263	403	407	0.97	1.95	1.43
600°C	149	257	181	0.77	1.35	0.88
1000°C	37	52	47	0.2	0.36	0.21

0.5x CTAB had the highest surface area and the highest pore volume of heat-treated aerogels

Pore Structure

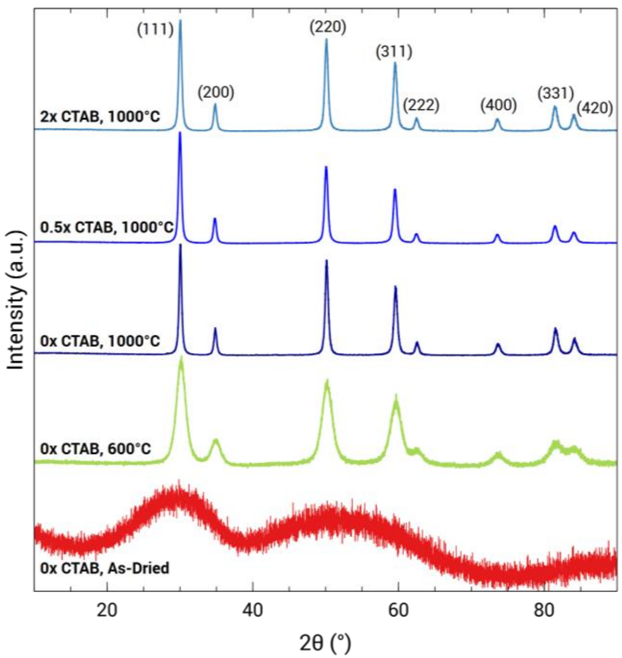


Sintering and densification is evident, especially at 1000°C.

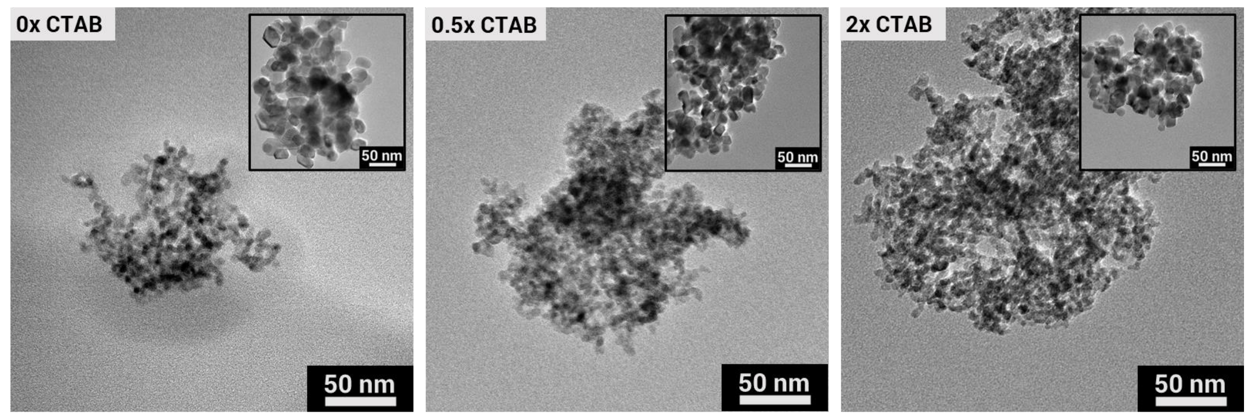
With the addition of CTAB, the aerogels are less dense or coarse, particularly at 1000°C.

Differences of the pore size in aerogels without CTAB and aerogels with CTAB were difficult to distinguish.

Crystalline Structure



CTAB inhibited crystallite growth at 1000°C, which may have hindered surface area and pore volume decrease, as well as shrinkage

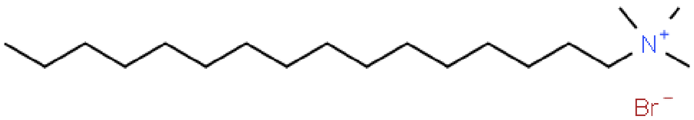


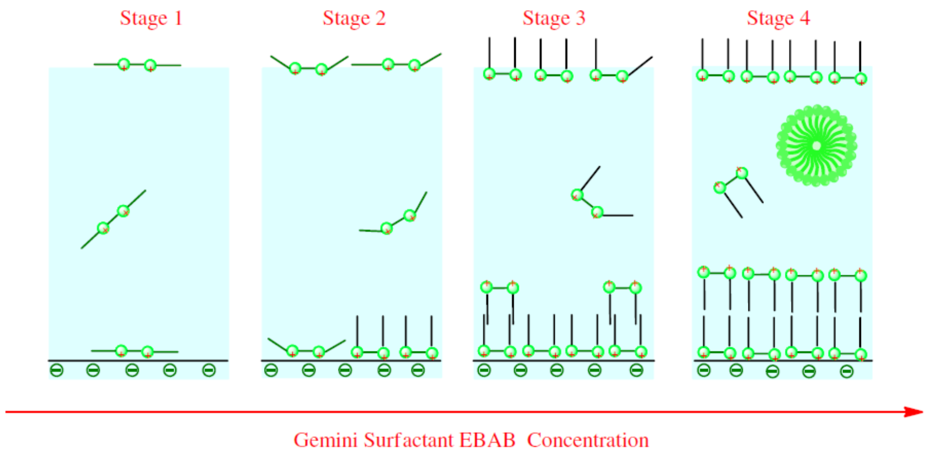
TEM images (100k magnification) heat-treated at 600°C and 1000°C (inset)

		Average Crystallite Size (Å)				
CTAB	**Temperature (°C)**	**Scherrer**	**Monshi-Scherrer (M-S)**	**Williamson-Hall (W-H)**	**Size-Strain-Plot (SSP)**	**TEM Analysis**
0x	**600**	55	60	68	63	61
	1000	197	227	283	250	270
0.5x	**600**	56	60	65	62	73
	1000	195	210	225	205	217
2x	**600**	55	59	64	60	76
	1000	193	200	207	201	210

Surfactant Interaction

0.5x CTAB showed the overall highest surface area and pore volume following heat-treatment, which was unexpected





Result influenced by?

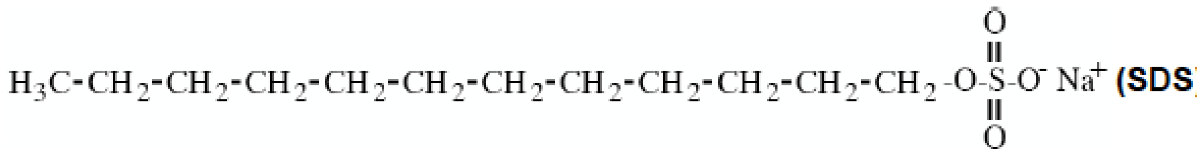
- Estimation of the critical micelle concentration of CTAB
- Adsorption could have constrained gelation, reducing the aerogel skeleton strength and increasing shrinkage

Gemini surfactant (+) adsorbed onto quartz surface (-); increasing surfactant concentration led to build-up on surface through, first, electrostatic interactions and, then, hydrophobic chain interactions

Huang et al., https://doi.org/10.1016/j.cej.2014.07.057

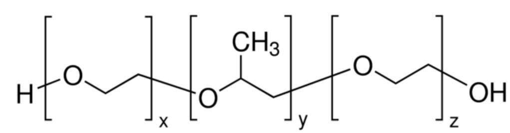
Charge Effects with Precursor

Proposed work: understand interactions of surfactants with the zirconia aerogel matrix



Experimental: anionic and nonionic surfactants added to YSZ aerogels; QCM experiments to understand interactions

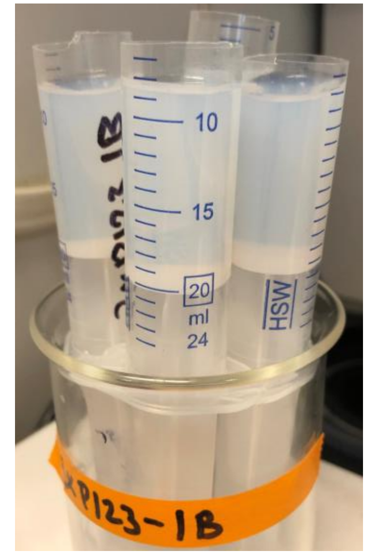
- Anionic (negative charge): Sodium dodecyl sulfate (SDS)
- Nonionic (no apparent ionic charge): Pluronic® P-123



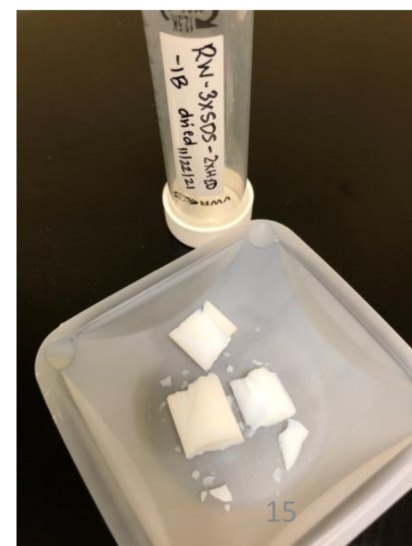
Results: Is surface area & mesoporous structure retained in YSZ aerogels after heat-treatment?

Preliminary Experiments

Sample	Gel?	Aerogel?	Shrinkage (%)	Density (g/cm³)
No surfactant			17.39	0.23
SDS, Below CMC*				
SDS, Above CMC*			17.54	0.25
SDS, Above CMC**				
P-123, Below CMC*				
P-123, Above CMC*			16.79	0.27
CTAB, Above CMC*			20.38	-----



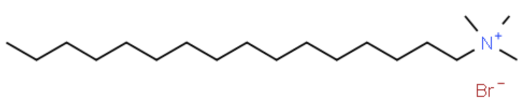
20 mol% Y, 2x H2O YSZ aerogels
*CMC in water
**CMC in 30 wt% solvent EtOH

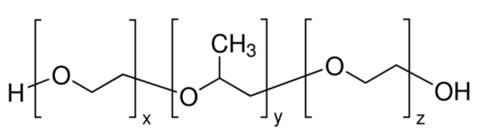


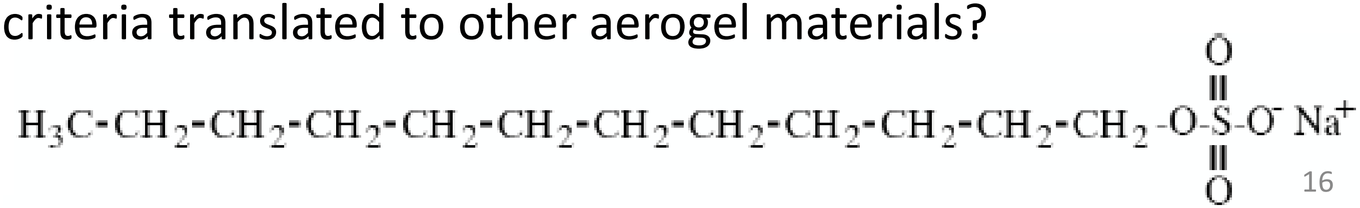
Project Goal Summary

Project Goal: Optimize the formulation of YSZ aerogels using surfactant templating

- Synthesize surfactant-templated aerogels with high porosity
  - Cationic, anionic, and nonionic surfactant templates
  - Higher porosity → lower thermal conductivity
  - Increased effectiveness when used as thermal management systems
- **Determine surfactant selection criteria**
  - Use a set of experiments in a limited sub-space
  - Characterize results
  - How is this criteria translated to other aerogel materials?







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- Dr. Wayne Jennings (SEM)
- Jessica Cashman (Synthesis)

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Supplemental Slides

Charge Effects with Precursor

Proposed work: Quartz Crystal Microbalance Experiments

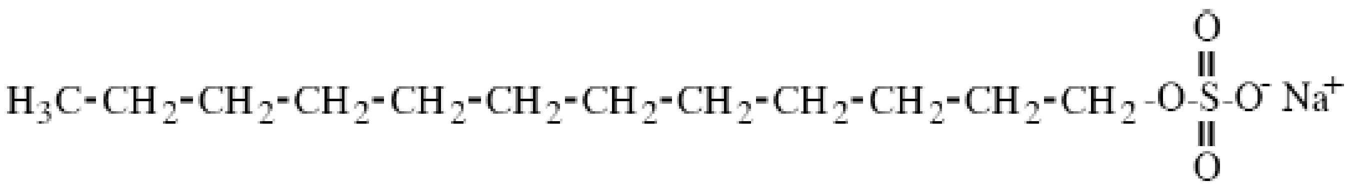
- Zirconia-sputtered QCM sensors will be placed in the sol solution containing the surfactant
- The gel will form around the QCM sensor
- Using cationic, anionic, and nonionic surfactants
- Are the surfactants solely forming micelles? Or are the surfactants interacting with zirconia through adsorption onto the gel?
- Following an enhanced understanding of surfactant interaction with the zirconia matrix, selected surfactants will be used in the synthesis of zirconia aerogels

Anionic Surfactants

Proposed work: Anionic surfactants

- Hydrophilic head has a negative charge
- Chosen surfactant: Sodium dodecyl sulfate (SDS)

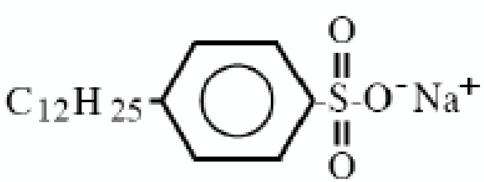
  Motivation: maintained high surface area and pore size in silica aerogels at 600°C; also lowered density and thermal conductivity



(SDS)

- Additional surfactant: Sodium dodecylbenzene sulfonate (SDBS)

  Motivation: influenced the final structure of carbon aerogels



(SDBS)

Selecting Nonionic Surfactants

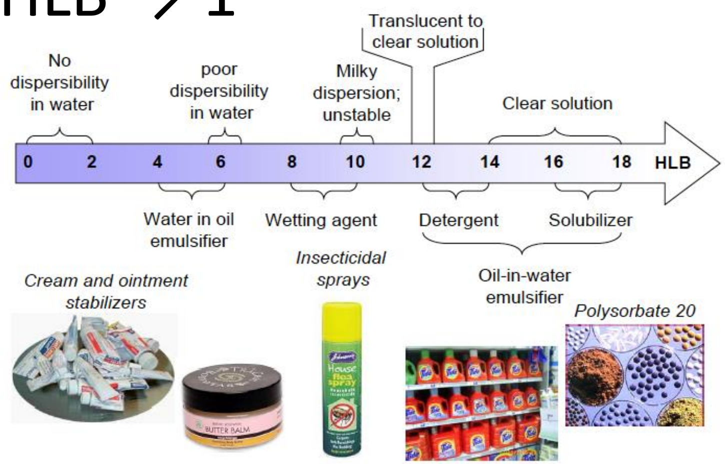
Hydrophilic–lipophilic balance (HLB) reflects surfactant’s partitioning behavior between polar and non-polar medium

- Agreed-upon method used to compare surfactants
- Useful index for non-ionic surfactants

HLB value = Σ(Hydrophilic groups) + Σ(Lipophilic groups) + 7

- Strongly hydrophilic surfactant, HLB → 40
- Strongly lipophilic surfactant, HLB → 1

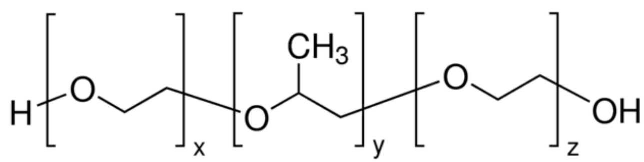
HLB may be used as a predictive parameter to compare surfactant influence on aerogel properties



Nonionic Surfactants

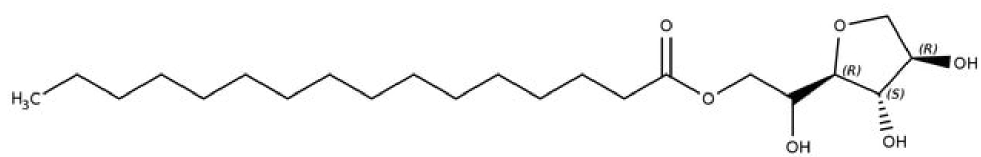
Proposed work: Nonionic surfactants

- Surface-active portion bears no apparent ionic charge
- Chosen surfactant: Pluronic® P-123 (*HLB: 7 - 9*)



- Additional surfactant: Brij® 52 (*HLB: 5*)

- Additional surfactant: Span® 40 (*HLB: 6*)



- Motivation: low Hydrophilic-Lipophilic Balance (HLB) value