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## Characterization of microporous silica-based membranes by calorimetric analysis

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# **Characterization of silica membranes by calorimetric analysis**

**Vittorio Boffa**

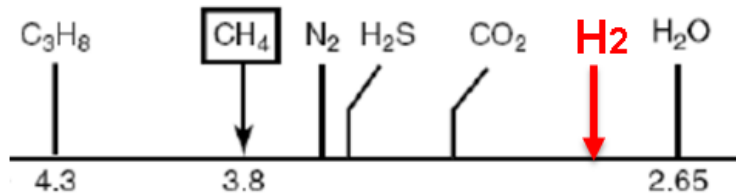
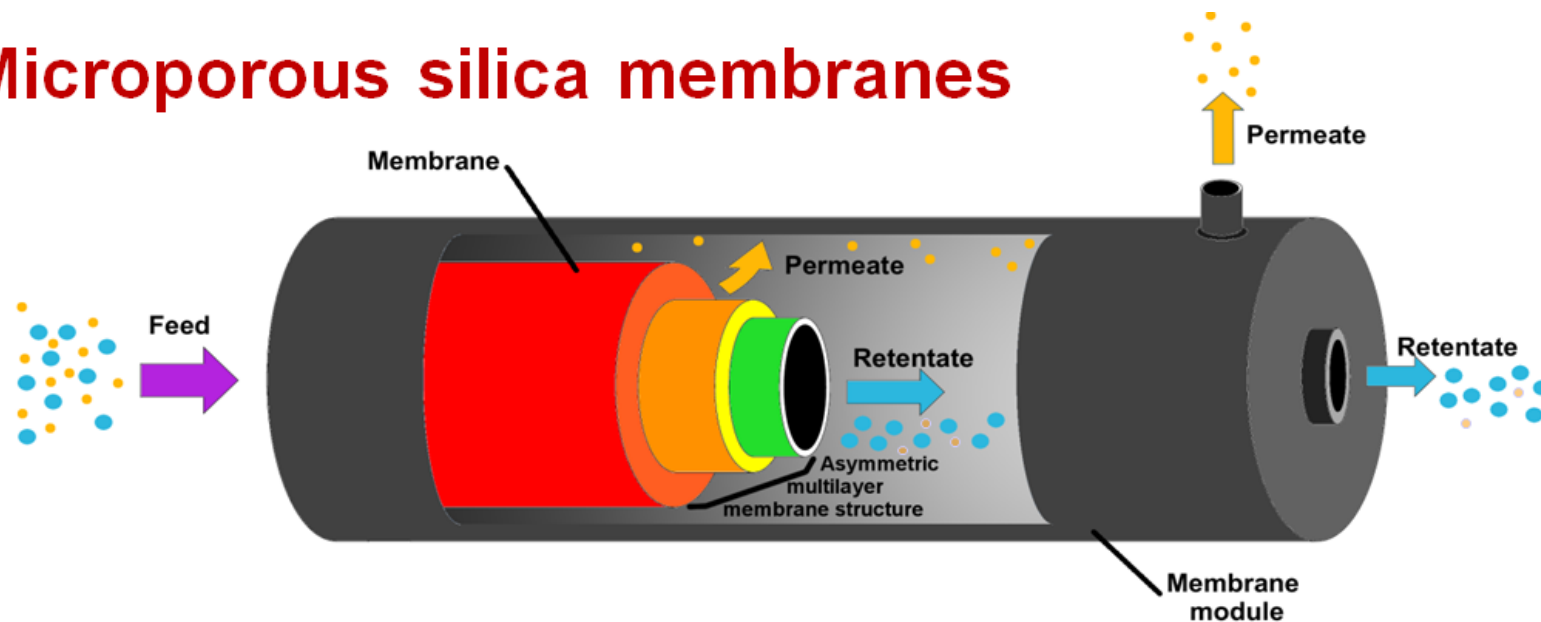
**vb@bio.aau.dk**

# Aalborg University

## Section of Chemistry



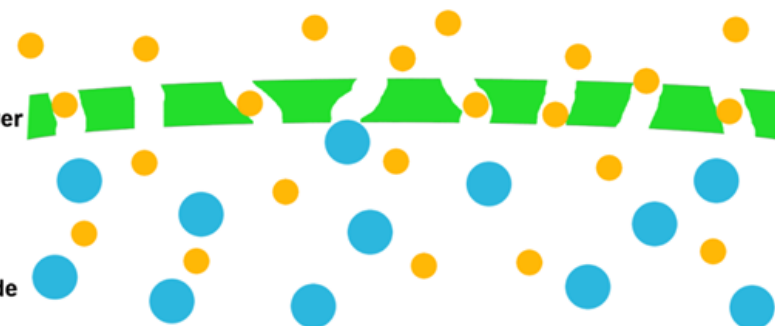
## Microporous silica membranes



permeate side

selective layer

retentate side



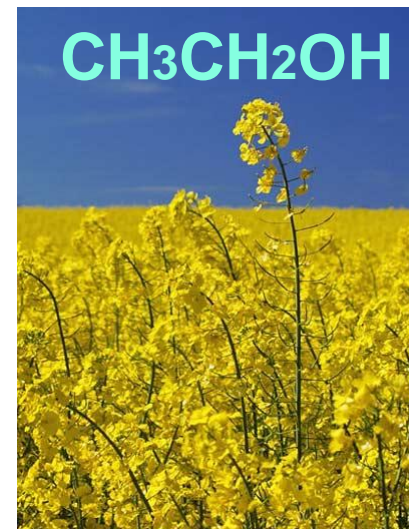
Upcoming technology platforms for green fuel production require the development of advanced molecular separation systems for recovering liquid biofuels, biomethane and hydrogen.

## Gas separation

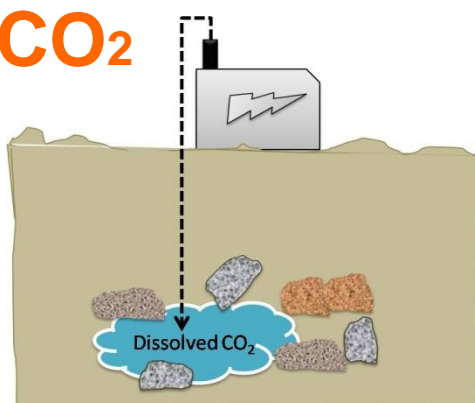
- H<sub>2</sub> purification
- CO<sub>2</sub> sequestration
- Biogas upgrading

## Pervaporation

- Alcohol dehydration
- Separation of organic solvents

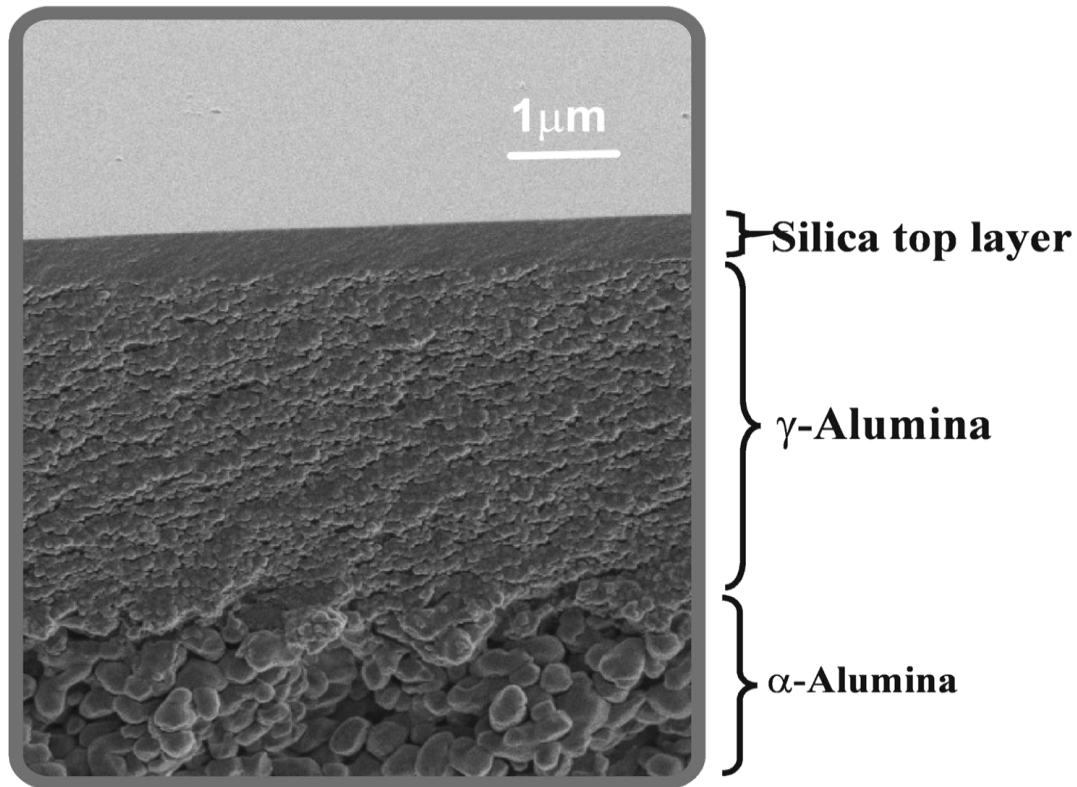


CO<sub>2</sub>

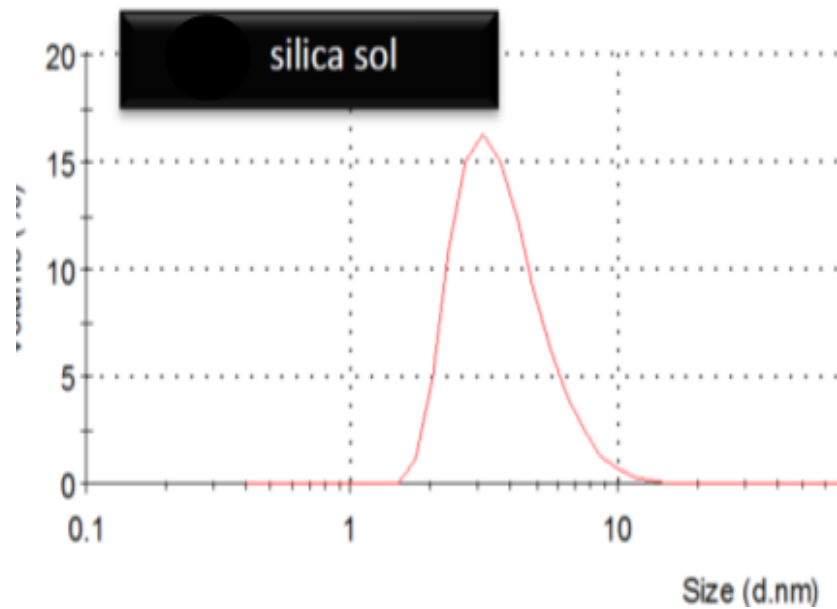




# Ultramicroporous silica membranes

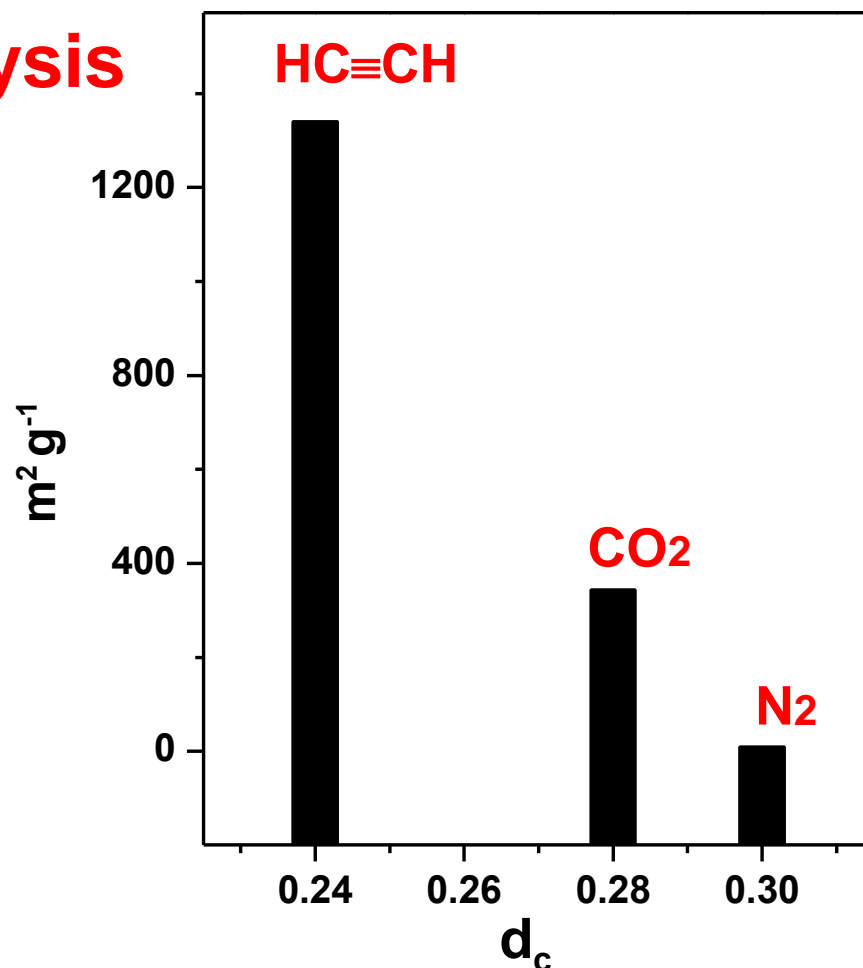


## Sol-gel



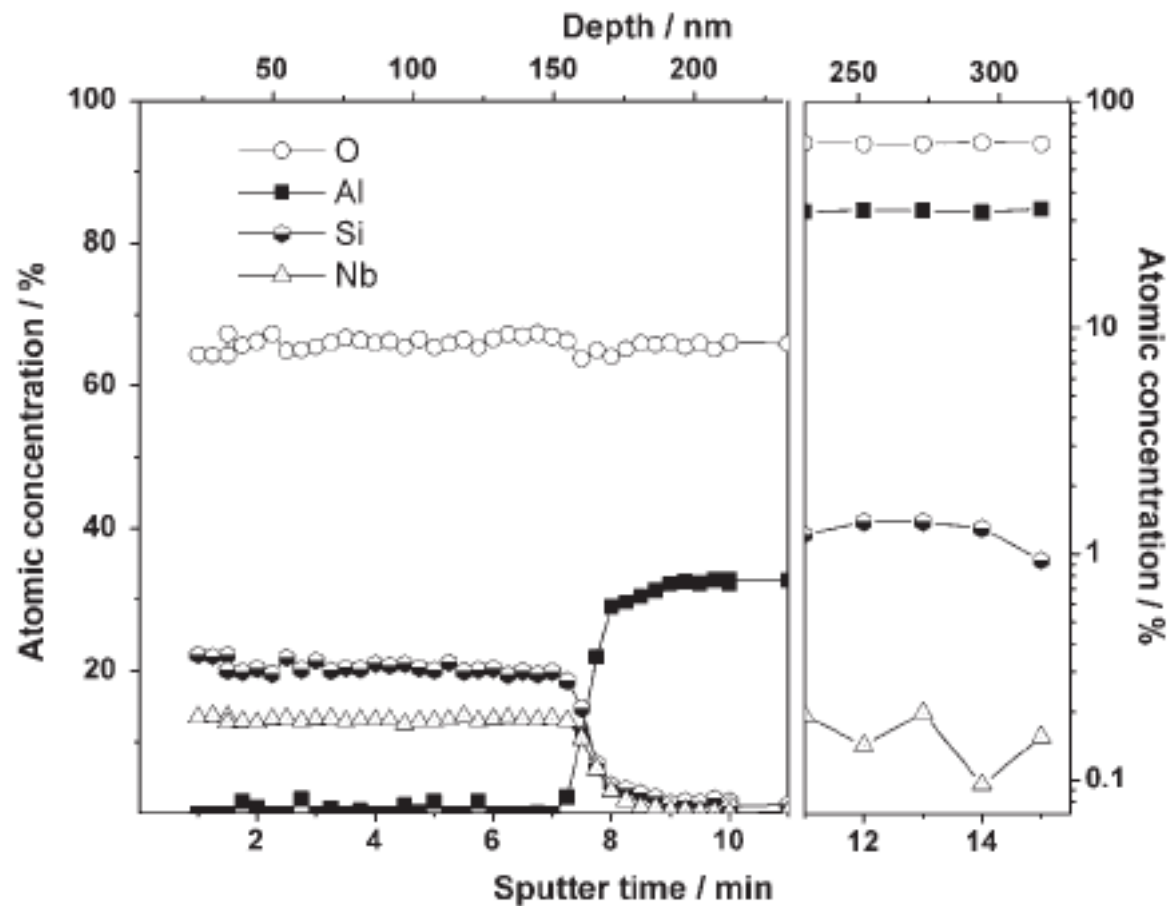
## Nitrogen sorption analysis on powder samples

- Detection of all accessible pores of a material, also those with a dead-end, which do not participate to the permeate transport in a membrane.
- Ultramicropores are so small that they cannot be accessed by nitrogen molecules.
- Membranes and powders can have different pore structure.



H. Casticum et al. (2007) J. Mater. Chem., 17, 1509–1517.





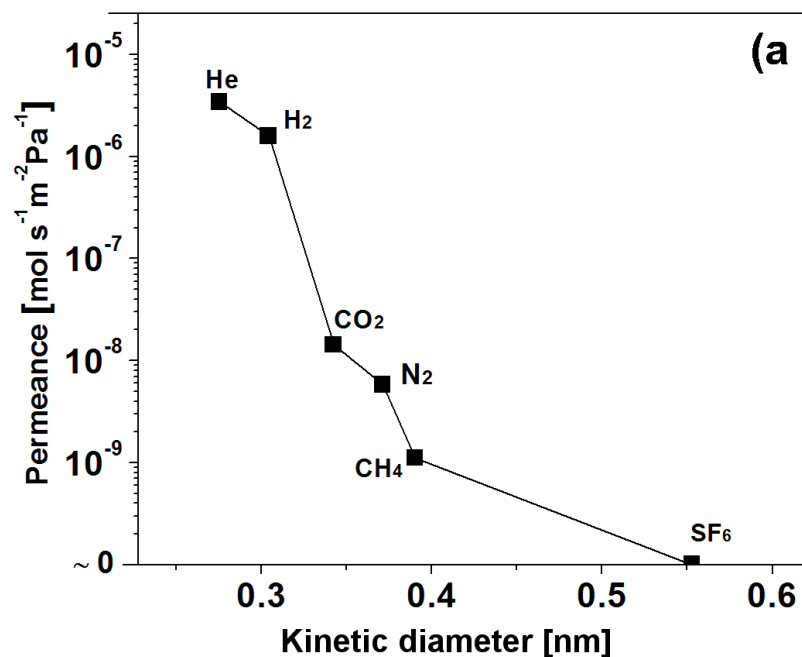
**Theoretical**

**Si:Nb = 3**

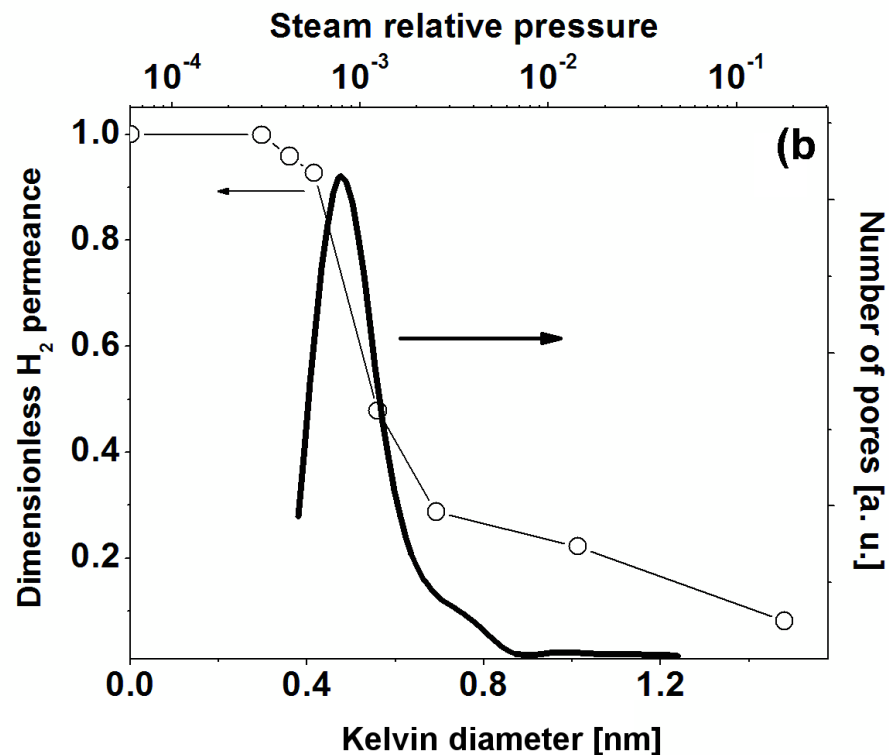
**Measured**

**Si:Nb = 1.5**

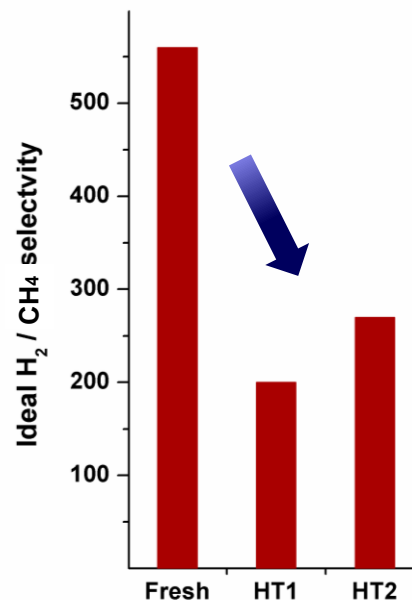
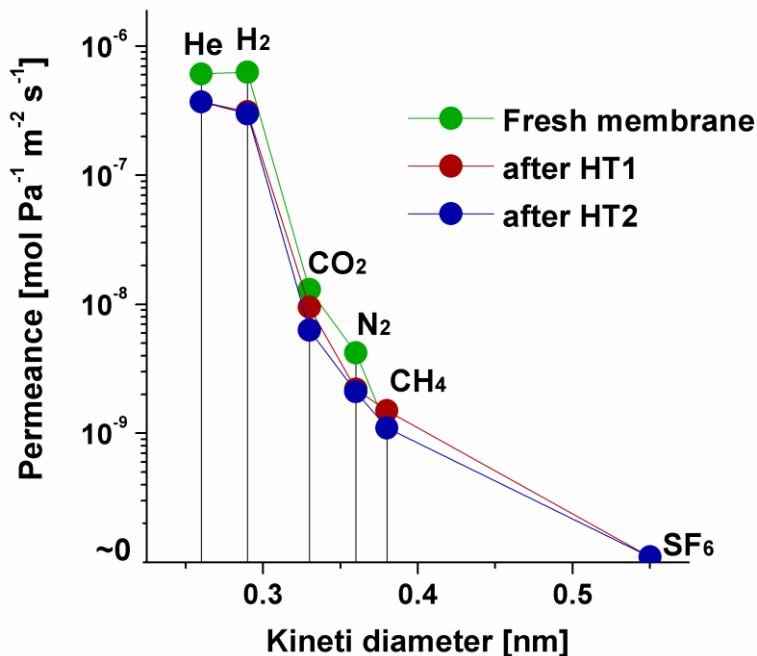
## Single-gas permeation experiments



## He-permporometry



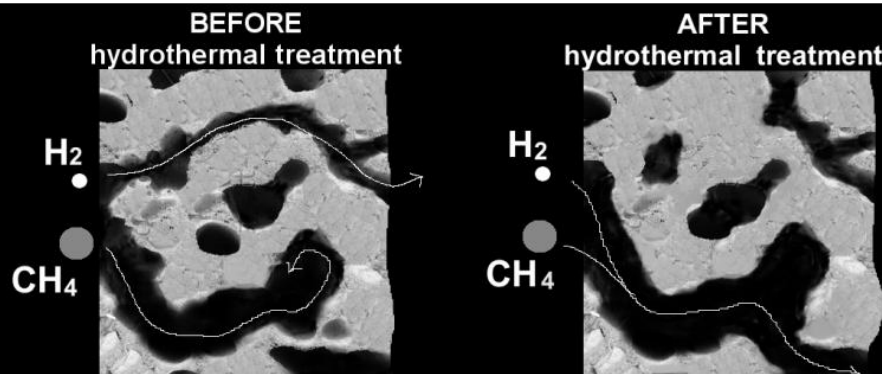
V. Boffa et al. (2008) Hydrothermal stability of microporous silica and niobia-silica membrane, J. Membrane Sci., 319, 256-263.



## Hydrothermal treatment

**HT1:** steam exposure (P<sub>H2O</sub> = 0.56 bar) at 150 °C for 70 h;

**HT2:** steam exposure (P<sub>H2O</sub> = 0.56 bar) at 200 °C for 70 h.

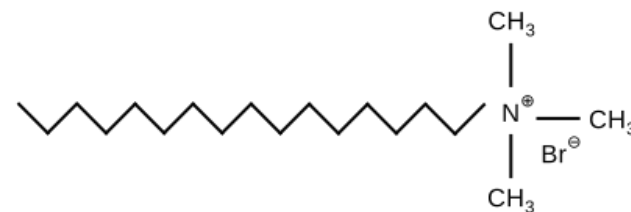


Doping			Support		Deposition		H <sub>2</sub> Permeance × 10 <sup>9</sup> [mol Pa <sup>-1</sup> m <sup>-2</sup> s <sup>-1</sup> ]	Hydrothermal stability
Modifier	Precursor	M/Si molar ratio	Geometry	Material	Method	Calcination T [°C]		
Reference silica membrane								
Pure silica		0	disk	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Sol-gel	400-600	1700	
modified membranes								
Al <sub>2</sub> O <sub>3</sub>	Al(O- <u>sec</u> Bu) <sub>3</sub>	0.02-0.065	tube	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	CVD	600	100-160	+
TiO <sub>2</sub>	Ti(O- <u>i</u> Pr) <sub>4</sub>	0.03-0.2	tube	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	CVD	500-700	200-700	+
ZrO <sub>2</sub>	Zr(O- <u>n</u> Bu) <sub>4</sub>	0.11-1	tube	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Sol-gel	570	40-300	+
Nb <sub>2</sub> O <sub>5</sub>	Nb(O- <u>n</u> Bu) <sub>5</sub> ;	0.33	disk	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Sol-gel	500	37	+
NiO/Ni	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.25-1	tube	α-Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> -ZrO <sub>2</sub>	Sol-gel	550-650	188	+
Co <sub>x</sub> O <sub>y</sub>	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	0.25	tube	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Sol-gel	600	6-10	+
C	HTAB		disk	α-Al <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	Sol-gel	500	48	+

Synthesis of  
MxOy-silica sols

Synthesis of mesoporous  
MxOy-silica powders

Addition of CTAB as  
pore tailoring agent



Drying and calcination  
at 450 °C

Characterization

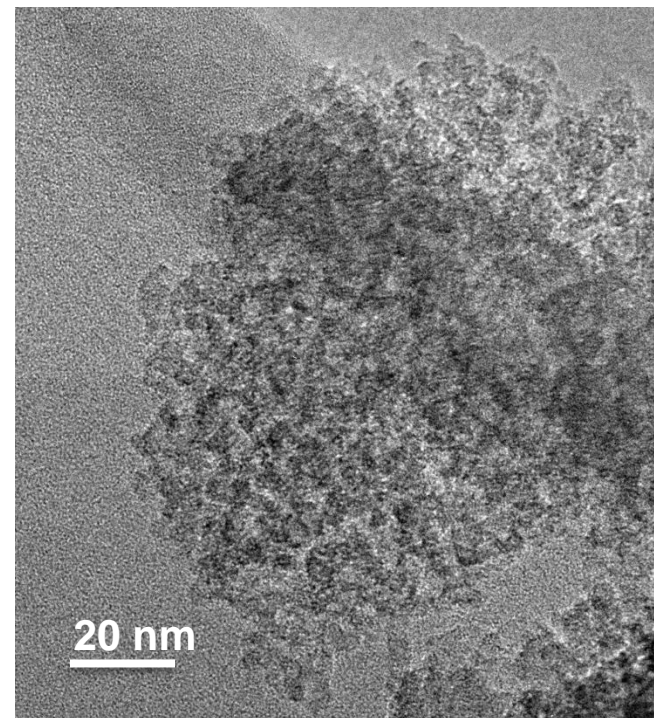
Hydrothermal treatment

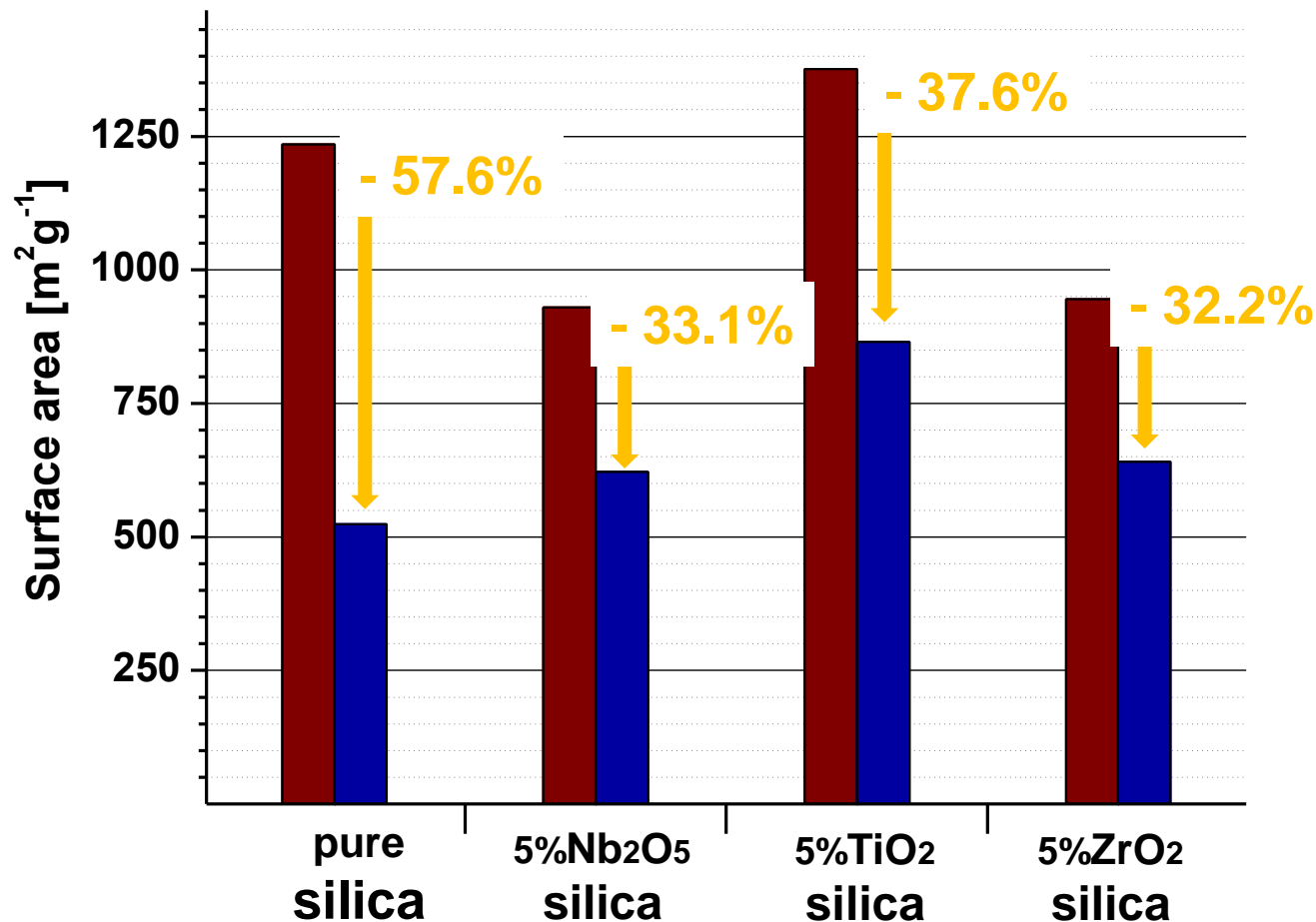
In autoclave  
at 120 °C  
for 48 h

Drying

Characterization

comparison

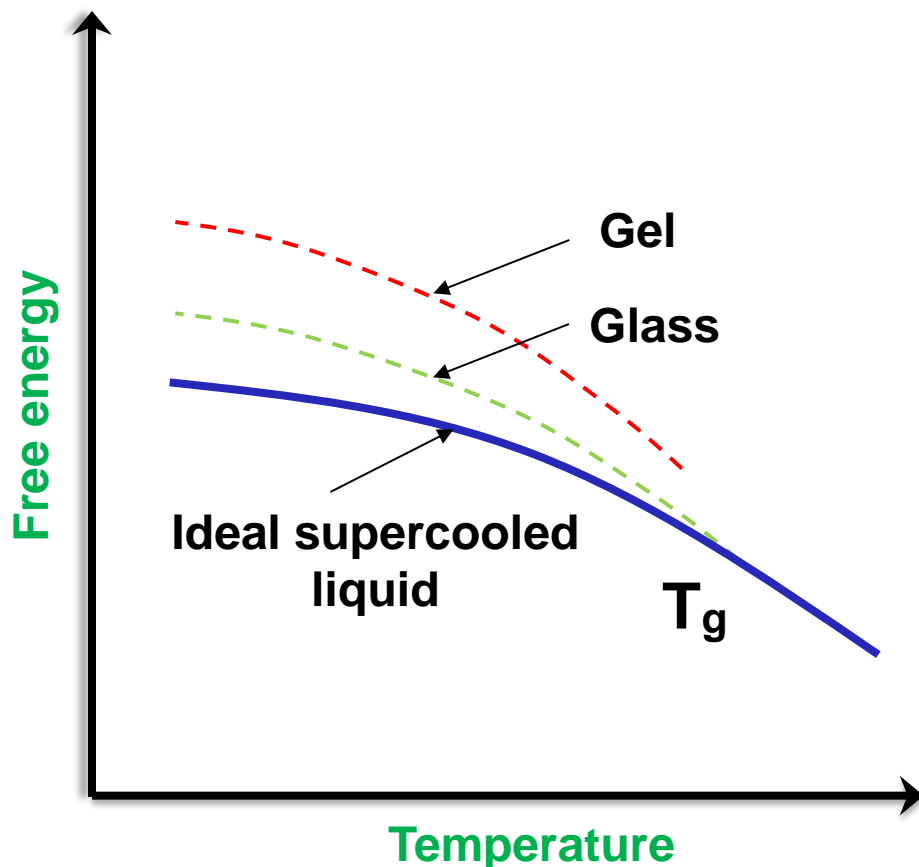




- TiO<sub>2</sub> doping is suitable to stabilize silica membranes for applications, which require high membrane permeability.
- ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>-doped silica layers can be used where membrane stability is more important than membrane permeability.



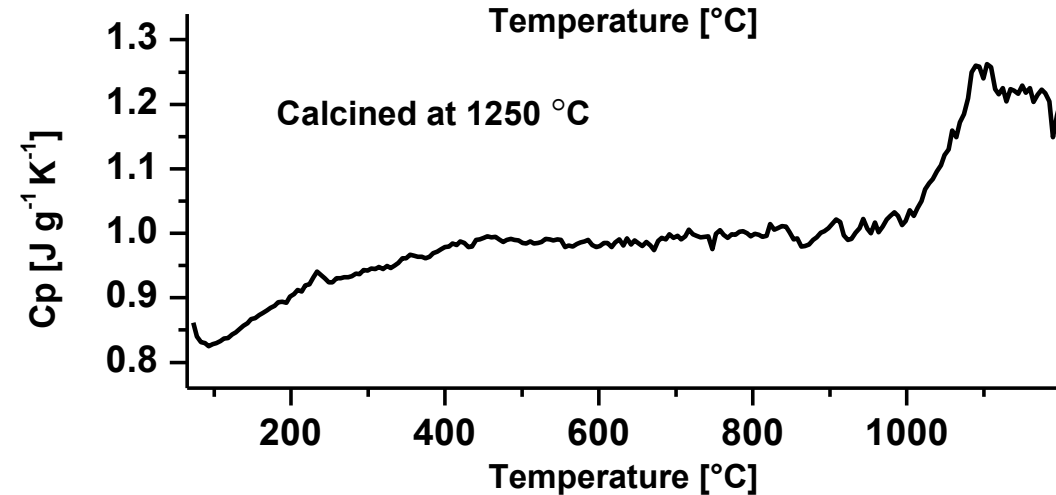
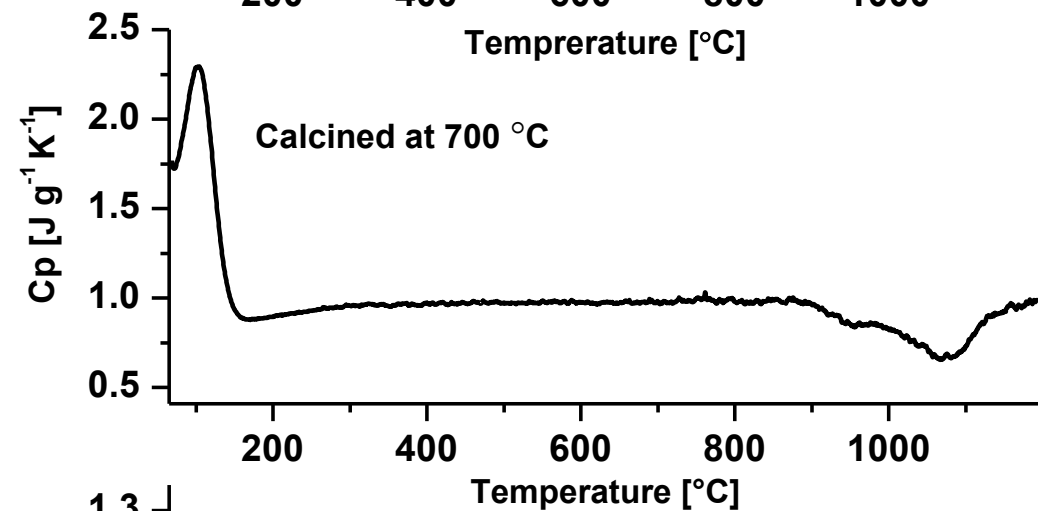
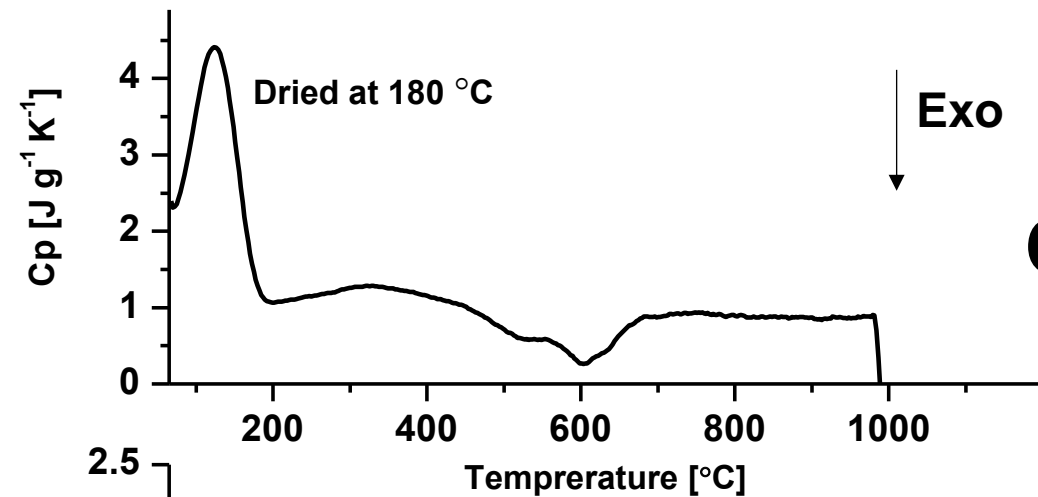
## Nature of sol-gel derived silica membranes



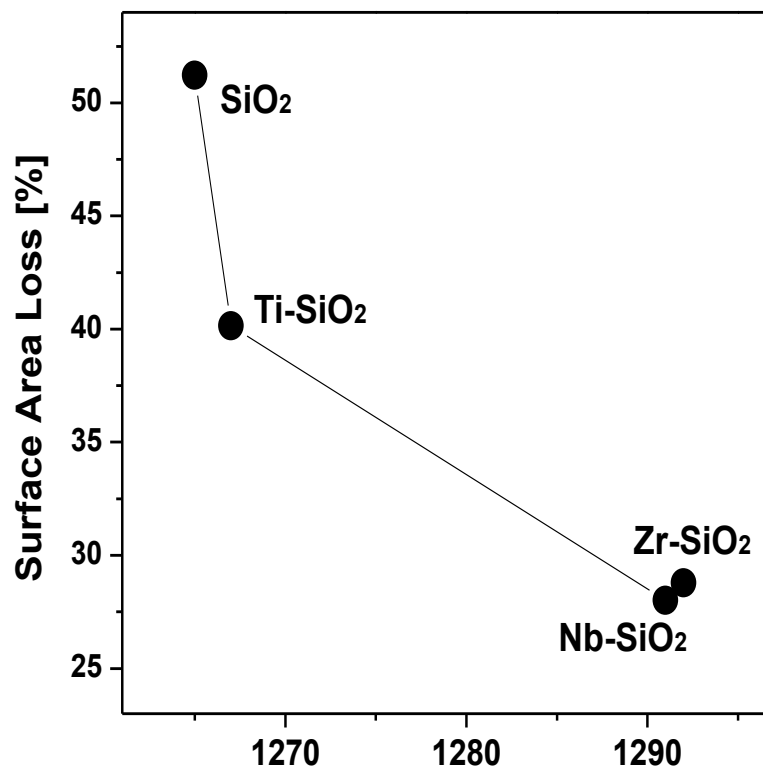
### High free energy:

- Reduced cross linking
- High surface area
- High pore volume
- Strained Si-O-Si bonds

After C. J. Brinker, G. W. Scherer *J. Non-Cryst. Sol.* 1985, 70, 301-322.



Our data indicate that Ti(IV), Zr(IV), and Nb(V) ions act as network formers: they increase  $T_g$  and steam-resistance of porous silica structure, by enhancing its network connectivity.



Glass transition temperature [ $T_g$ ]

## Message of the day

**Calorimetric analysis is a powerful tool for investigating structure and stability of unsupported membranes, and hence for developing basic knowledge for the effective design of sol-gel derived membranes.**

## Acknowledgements

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