Steam-stable silica-based membranes

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Designing steam-stable silica membranes

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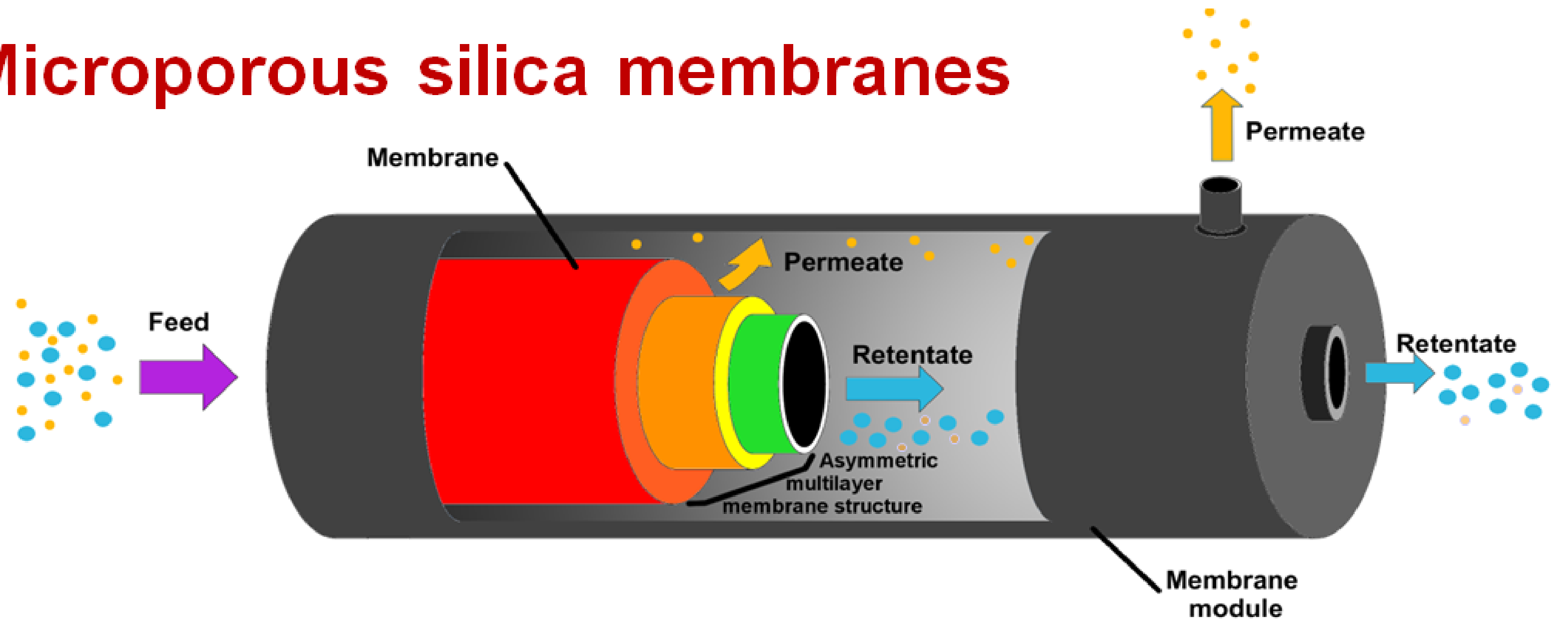
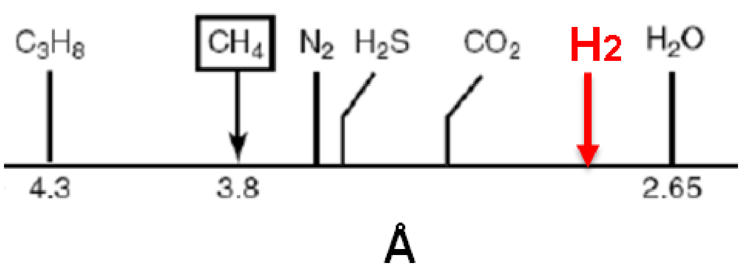
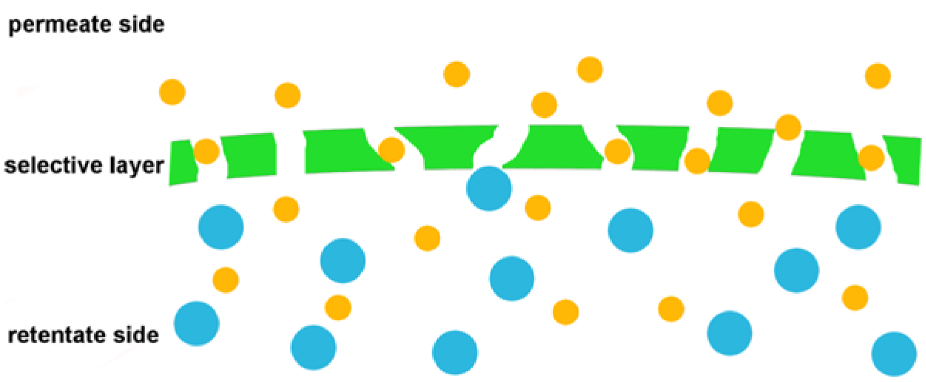
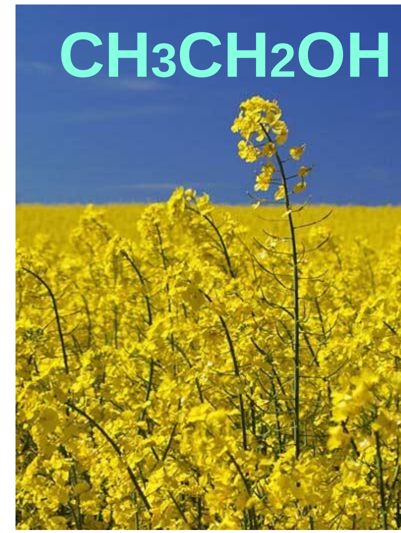
Microporous silica membranes



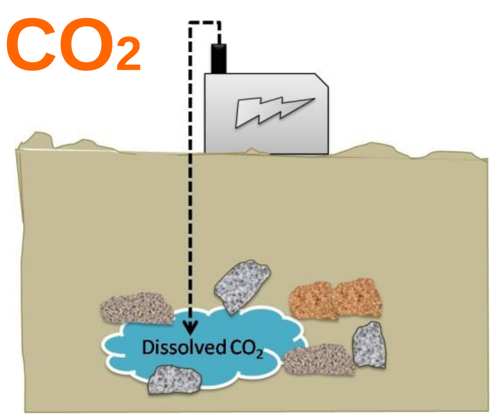




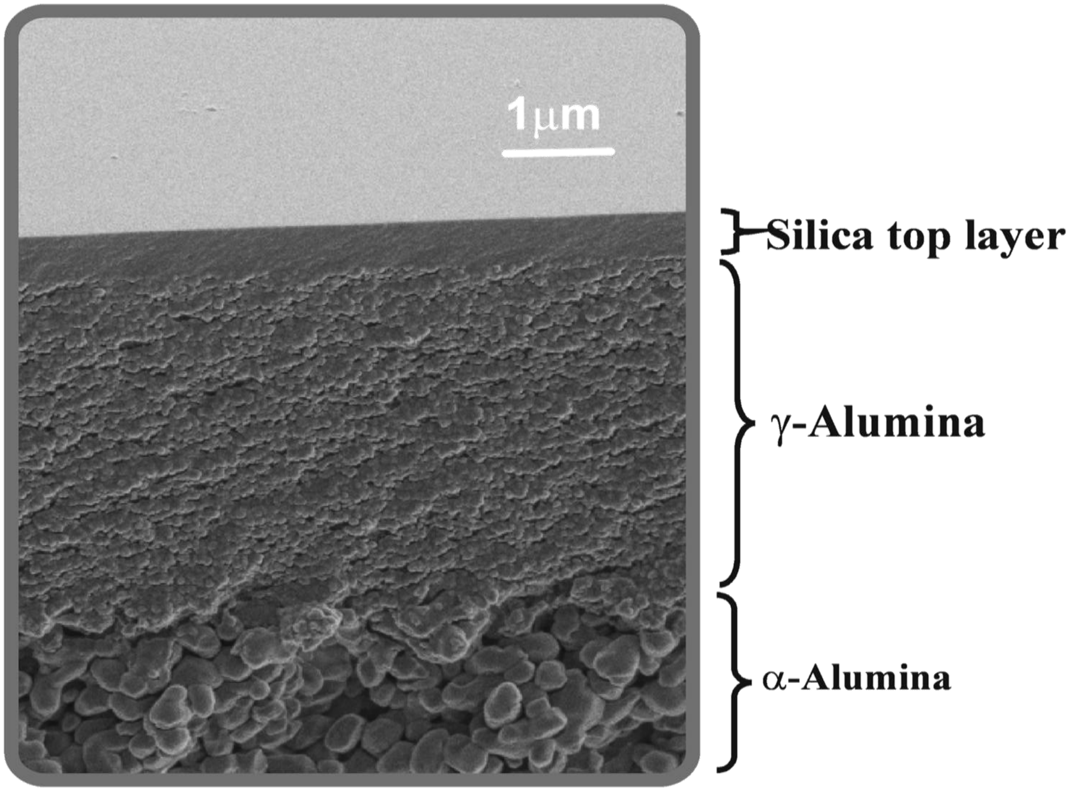
Upcoming technology platforms for green fuel production require the development of advanced molecular separation systems for recovering liquid biofuels, biomethane and hydrogen.

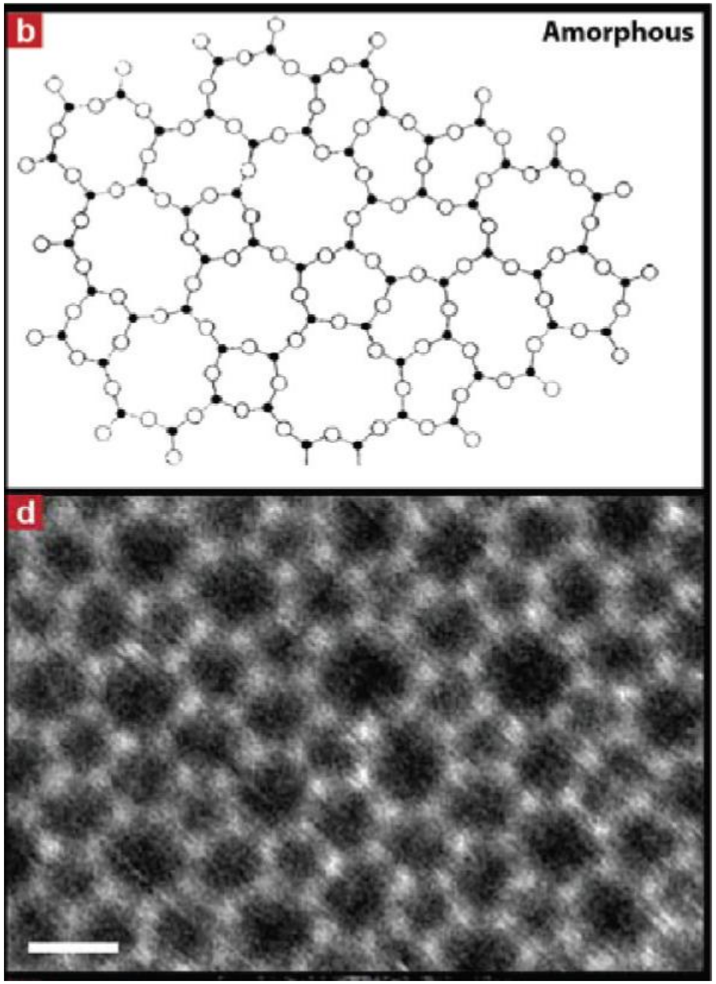


Gas separation	Pervaporation
• H_2 purification • CO_2 sequestration • Biogas upgrading	• Alcohol dehydration • Separation of organic solvents



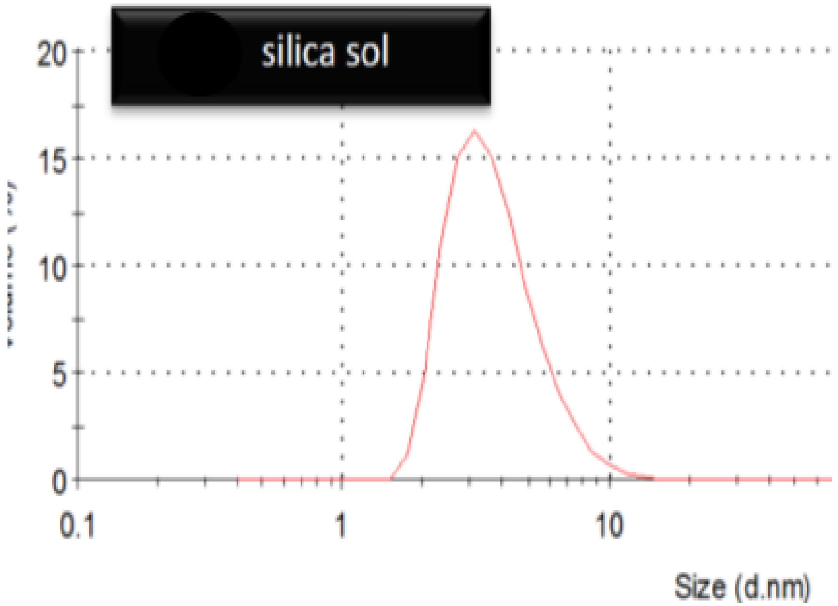
Ultramicroporous silica membranes



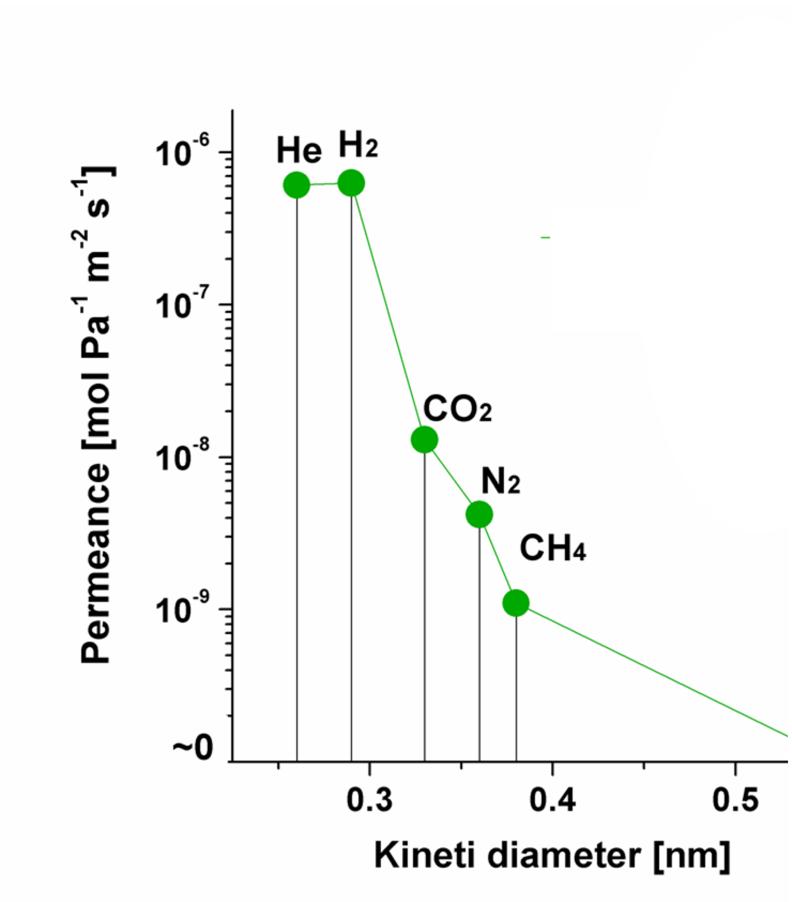


Nano Lett. 2012, 12, 1081−1086

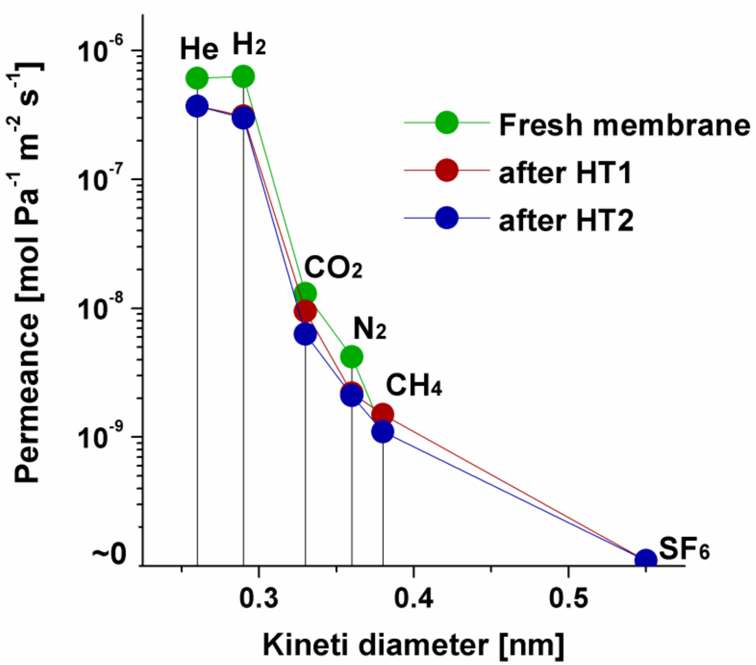
Sol-gel

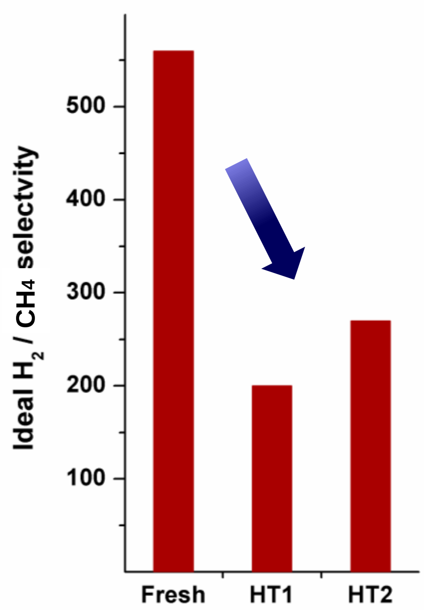


Sol-gel


Permeance [mol Pa⁻¹ m⁻² s⁻¹]
10⁻⁶
10⁻⁷
10⁻⁸
10⁻⁹
~0
He
H2
CO2
N2
CH4
0.3
0.4
0.5
Kineti diameter [nm]

Silica membranes

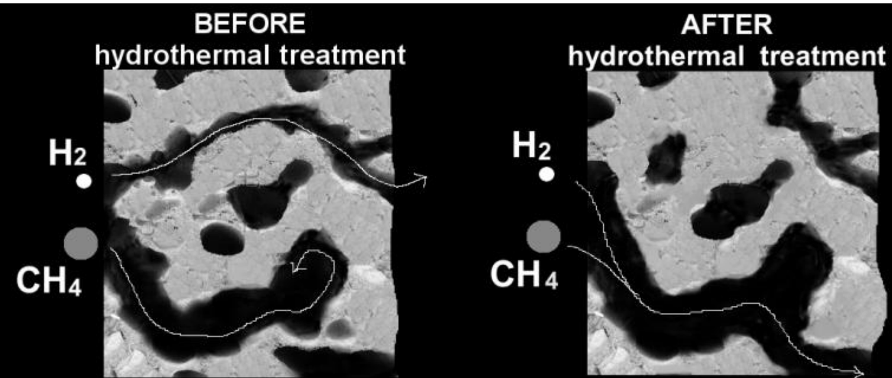




Hydrothermal treatment

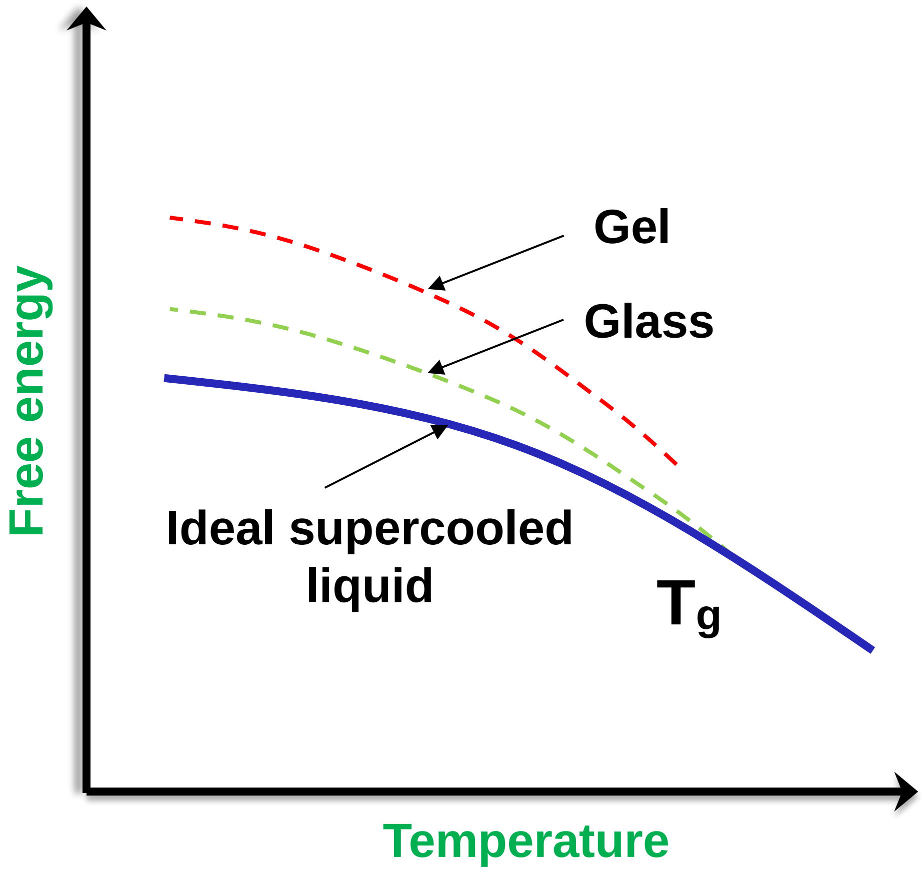
HT1: steam exposure (P_{H2O} = 0.56 bar) at 150 °C for 70 h;

HT2: steam exposure (P_{H2O} = 0.56 bar) at 200 °C for 70 h.



V. Boffa et al. *J. Membrane Sci.* 319 (2008) 256–263

Nature of sol-gel derived silica membranes

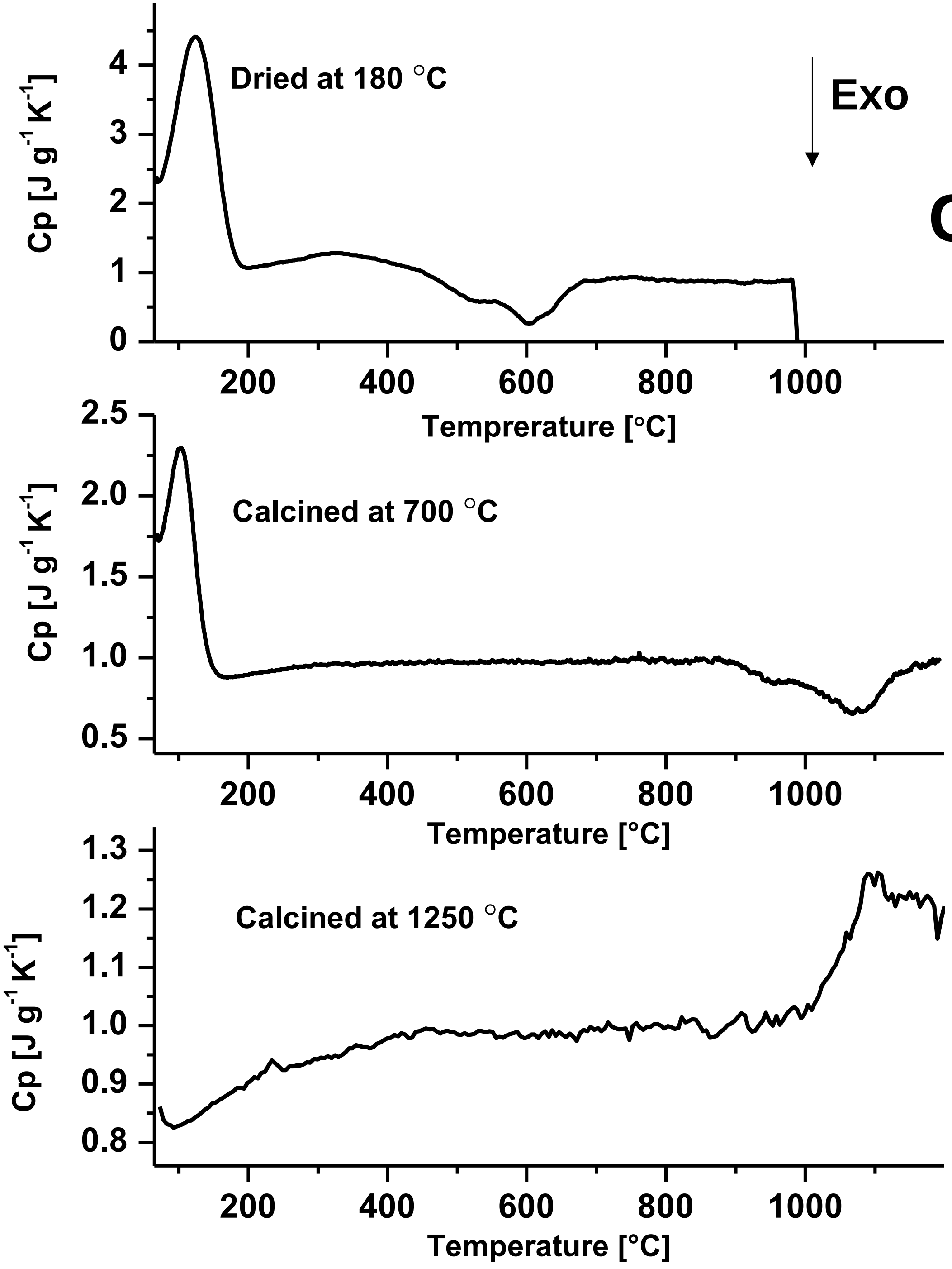


High free energy:

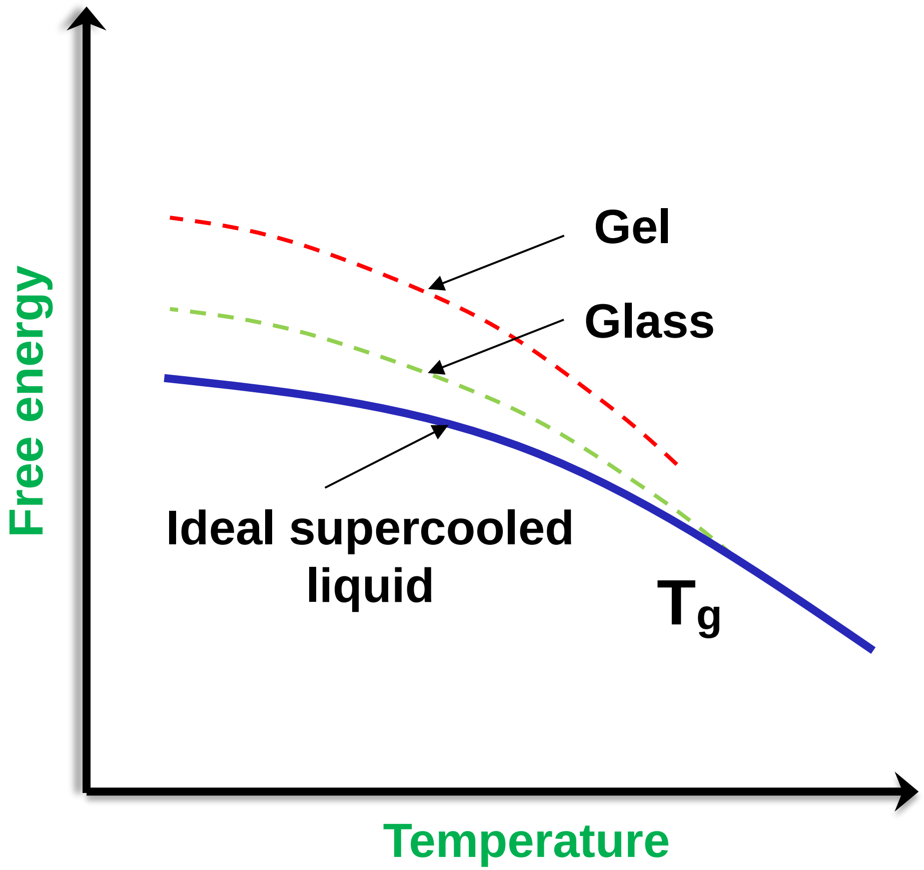
- Reduced cross linking
- High surface area
- High pore volume
- Strained SI-O-Si bonds

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

Calorimetric analysis



Nature of sol-gel derived silica membranes



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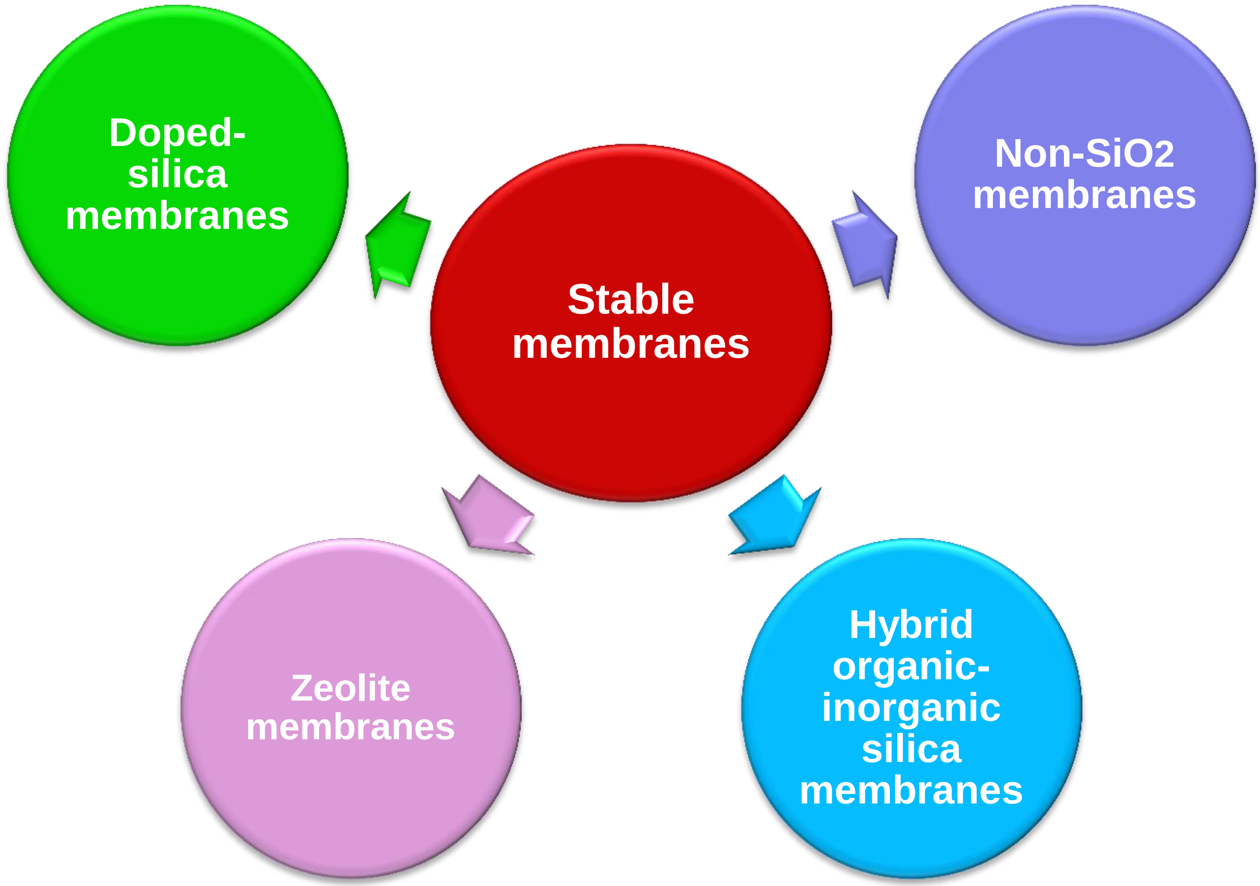
After C. J. Brinker, G. W. Scherer *J. Non-Cryst. Sol.* 1985, *70*, 301-322.

Fabrication of hydrothermally stable microporous membranes

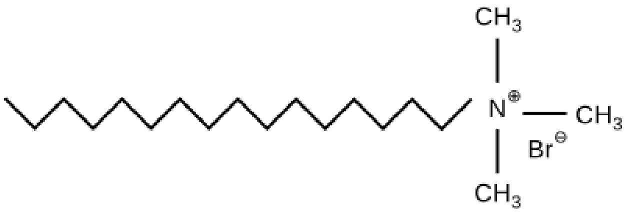
Strategies:



Doping			Support		Deposition			
Modifier	Precursor	M/Si molar ratio	Geometry	Material	Method	Calcination T [°C]	H_2 Permeance $\times 10^9$ [mol Pa^{-1} m^{-2} s^{-1}]	Hydrothermal stability
Reference silica membrane								
Pure silica		0	disk	α-Al_2O_3/γ-Al_2O_3	Sol-gel	400-600	1700	
modified membranes								
Al_2O_3	Al(O-*sec*Bu)$_3$	0.02-0.065	tube	α-Al_2O_3/γ-Al_2O_3	CVD	600	100-160	+
TiO_2	Ti(O-*i*Pr)$_4$	0.03-0.2	tube	α-Al_2O_3/γ-Al_2O_3	CVD	500-700	200-700	+
ZrO_2	Zr(O-*n*Bu)$_4$	0.11-1	tube	α-Al_2O_3/γ-Al_2O_3	Sol-gel	570	40-300	+
Nb_2O_5	Nb(O-*n*Bu)$_5$;	0.33	disk	α-Al_2O_3/γ-Al_2O_3	Sol-gel	500	37	+
NiO/Ni	$Ni(NO_3)_2 \cdot 6H_2O$	0.25-1	tube	α-Al_2O_3/SiO_2-ZrO_2	Sol-gel	550-650	188	+
Co_xO_y	$Co(NO_3)_2 \cdot 6H_2O$	0.25	tube	α-Al_2O_3/γ-Al_2O_3	Sol-gel	600	6-10	+
C	HTAB		disk	α-Al_2O_3/γ-Al_2O_3	Sol-gel	500	48	+

V. Boffa, 2012, Fabrication of ultramicroporous silica membranes for pervaporation and gas-separation, in Molecules at Work (B. Pignataro ed.) Wiley-VCH, 177-205.

Synthesis of mesoporous *MxOy*-silica powders



Synthesis of *MxOy*-silica sols

↓

Addition of CTAB as pore tailoring agent

↓

Drying and calcination at 450 °C

→ Characterization

↓

Hydrothermal treatment

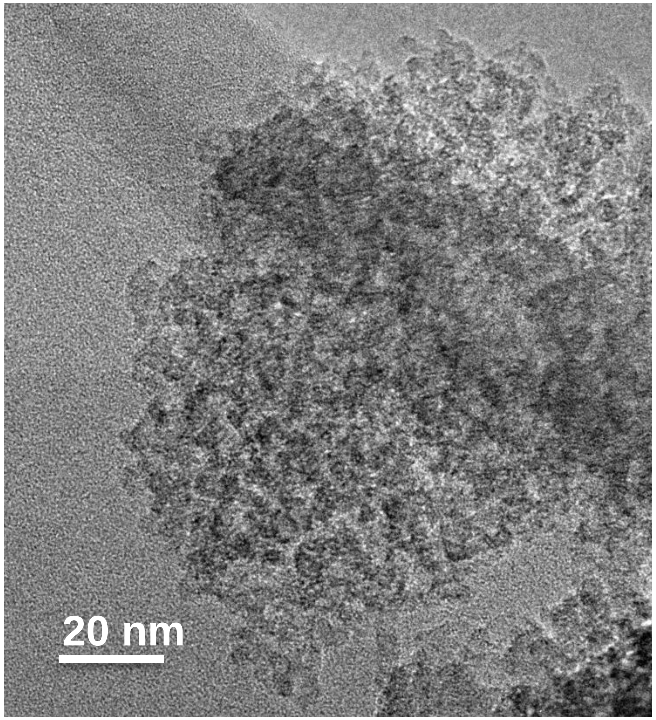
In autoclave
at 120 °C
for 48 h

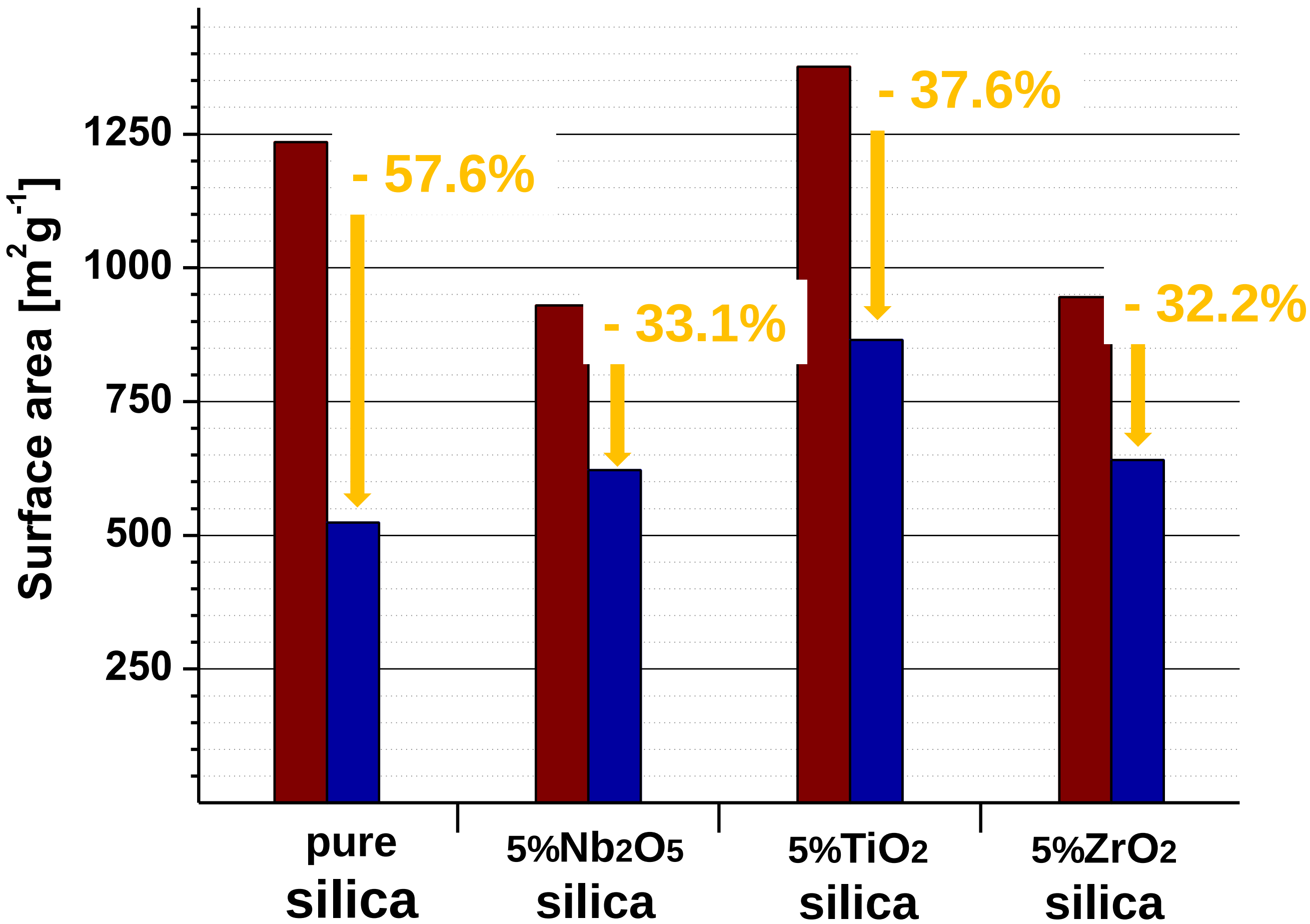
↓

Drying

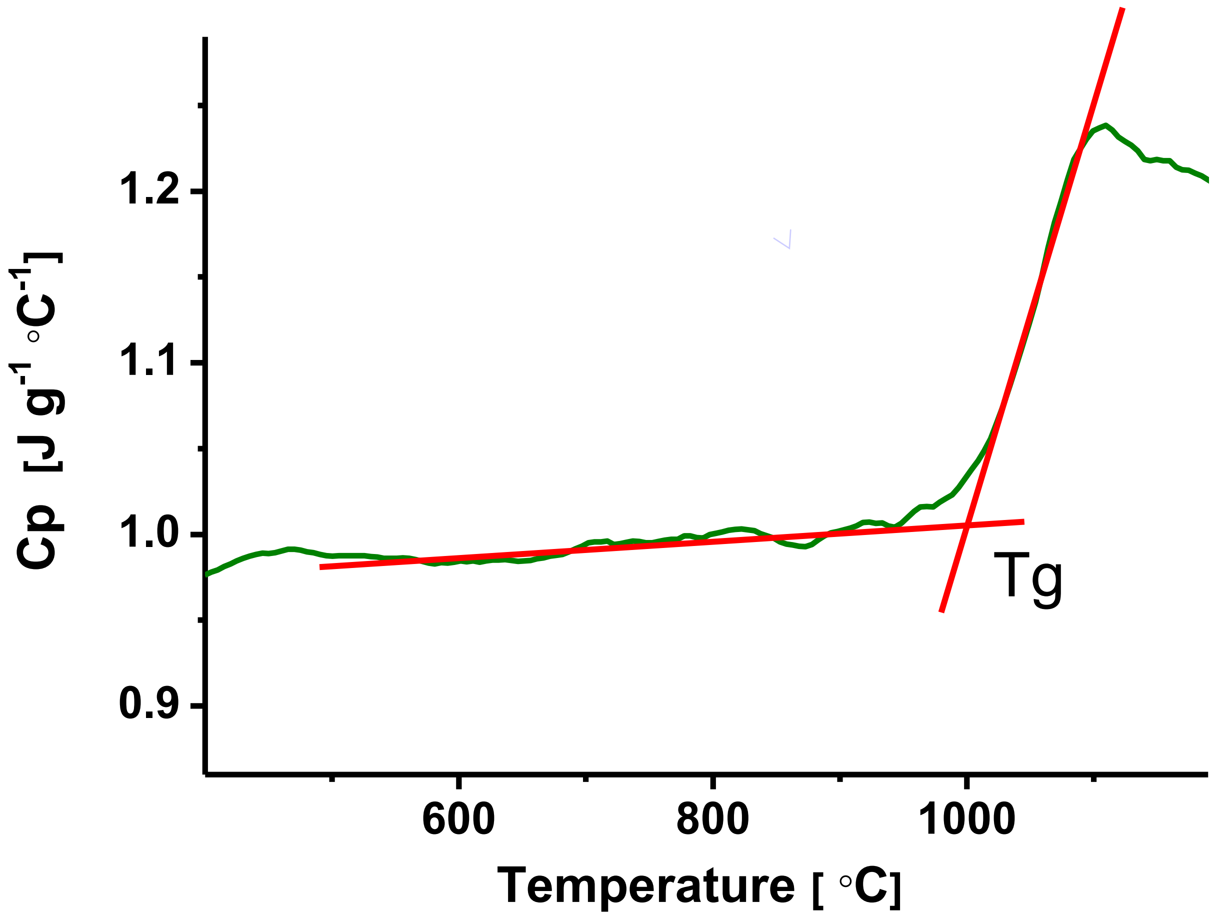
→ Characterization

comparison

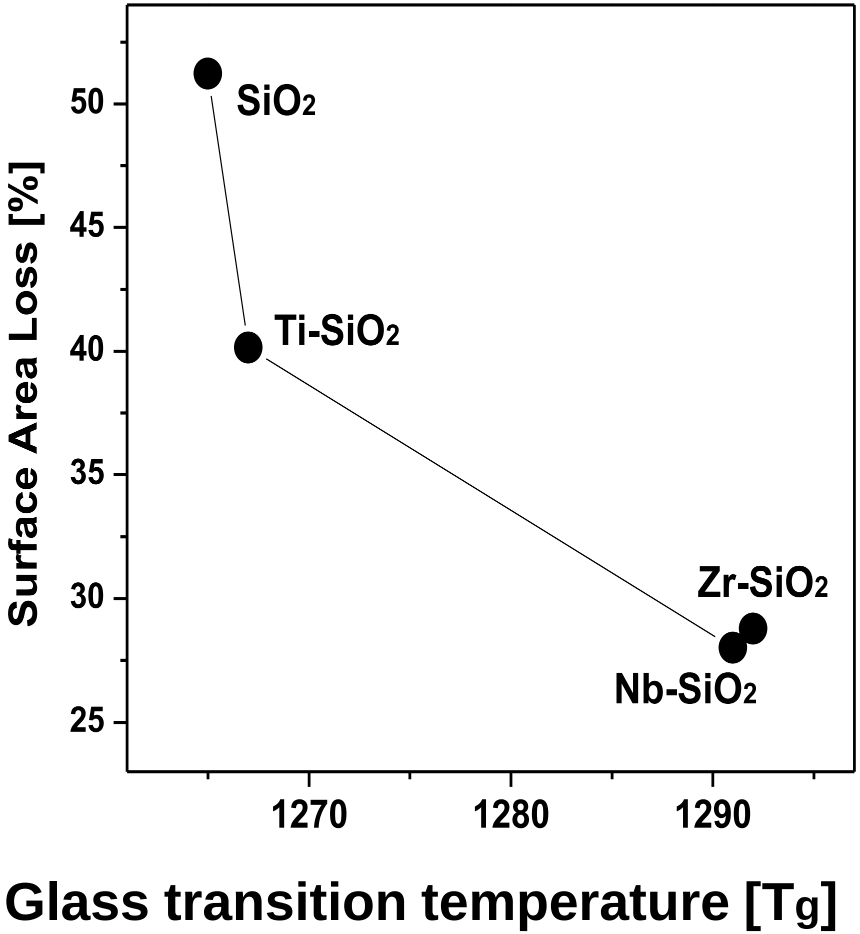




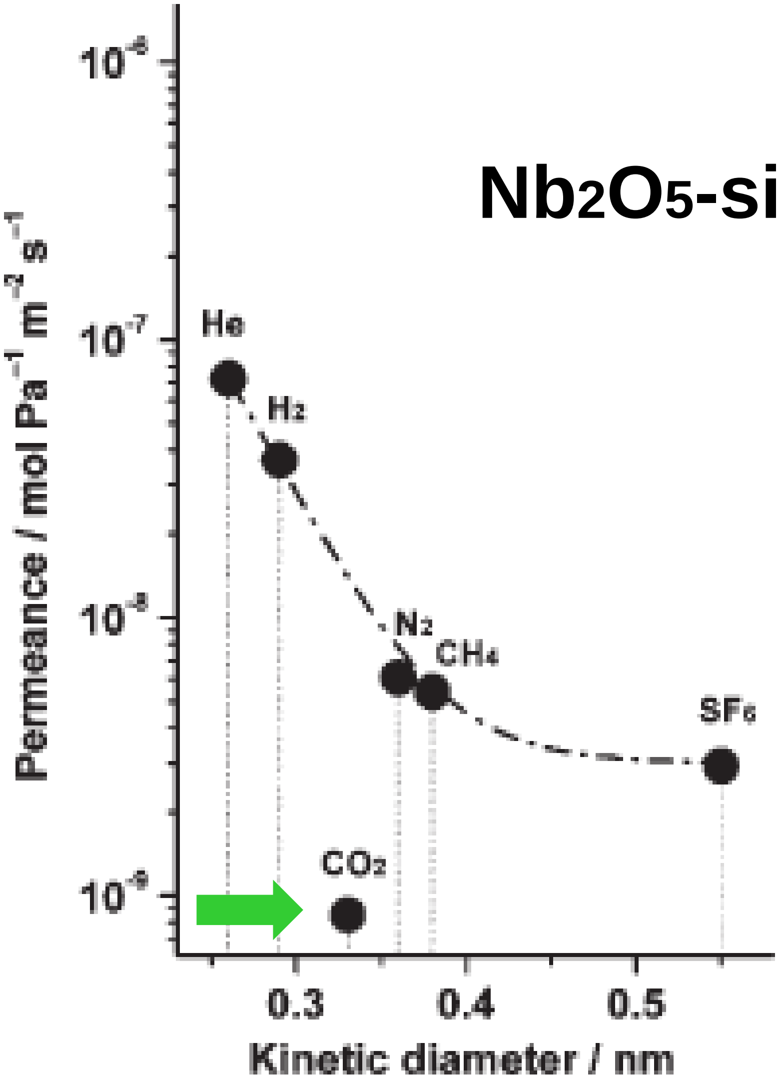
- TiO_2 doping is suitable to stabilize silica membranes for applications, which require high membrane permeability.
- ZrO_2 and Nb_2O_5-doped silica layers can be used where membrane stability is more important than membrane permeability.


1.2
1.1
1.0
0.9
Cp [J g-1 ◦C-1]
600
800
1000
Temperature [◦C]
Tg

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.



Nb_2O_5-silica membrane



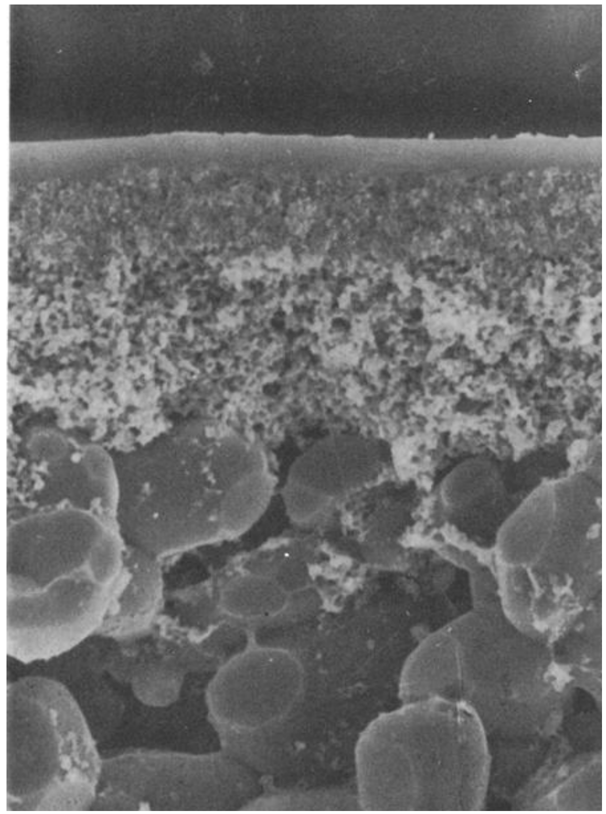
This membrane is not a simple sieve,

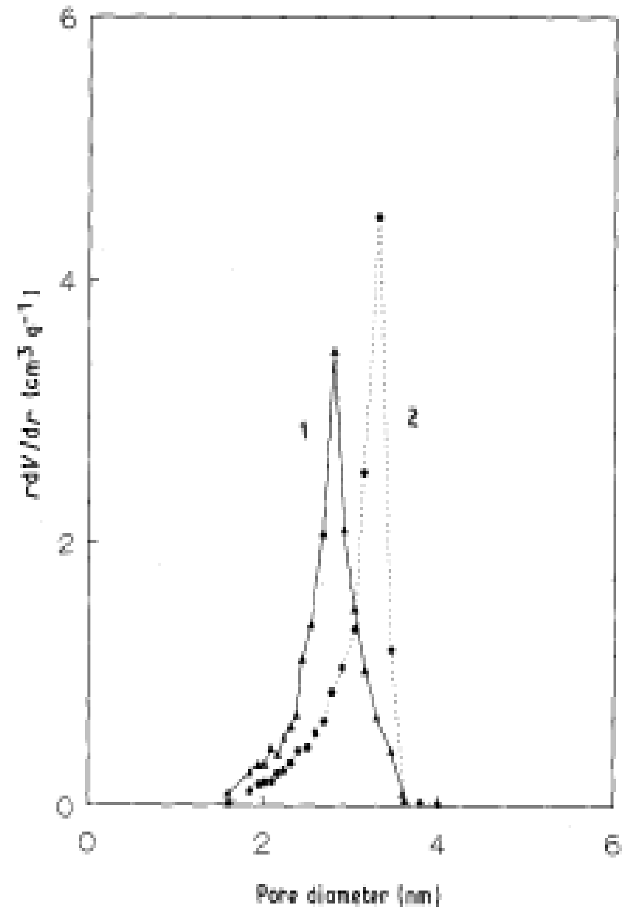
it can separate molecules also on the basis of their chemical properties

V. Boffa et al. 2008, ChemSusChem, 1, 437.

Inorganic nanoporous membranes

1) Uhlhorn et al. 1992 "Synthesis of ceramic membranes", J. Meter. Sci. 27 (527).





Defect free-membranes

Sol-gel science and technology

1980

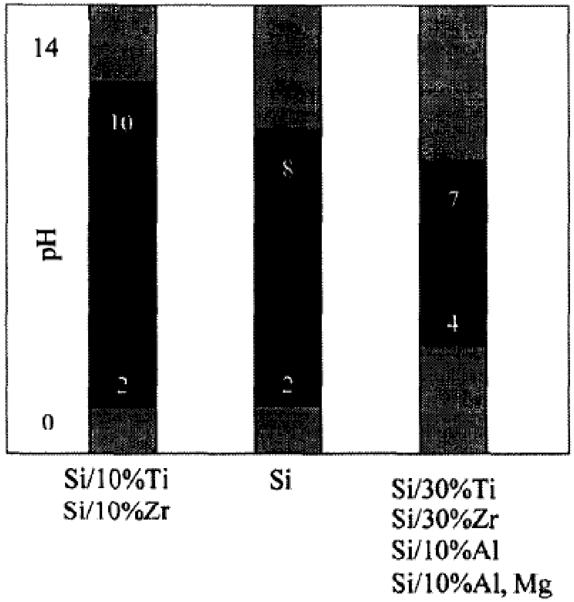
1990

2000

2010

Inorganic nanoporous membranes

Doped materials

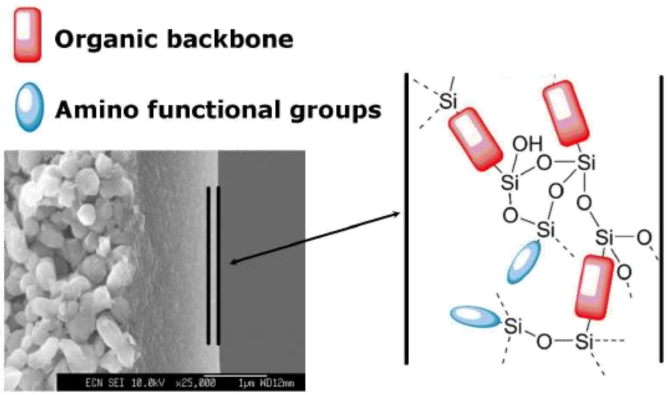


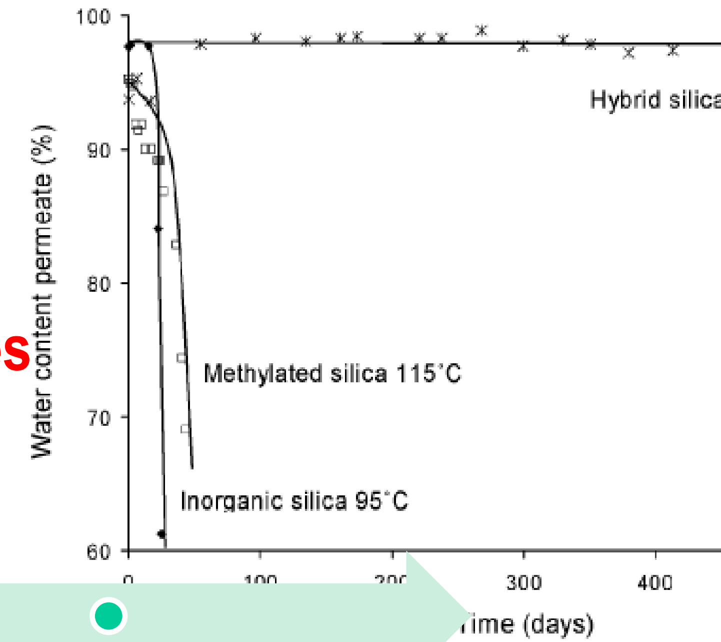
1. J. Sekulic et al. 2002 Microporous silica and doped silica membrane for alcohol dehydration by pervaporation, Desalination 148 (19).

2. T. Van Gestel et. al. 2006 ZrO_2 and TiO_2 membranes for nanofiltration and pervaporation, J. Membrane Sci. 284 (128).

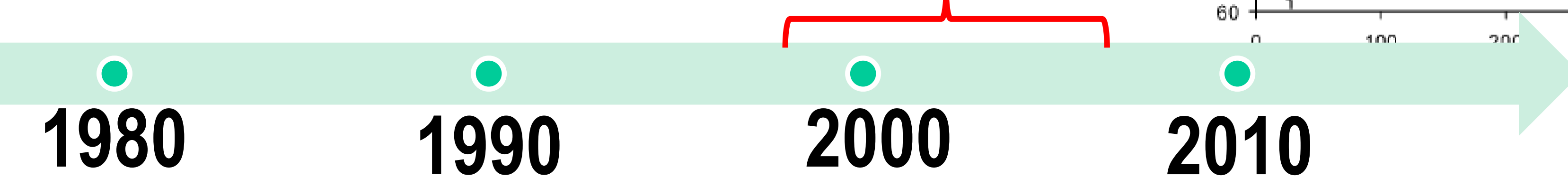
3. H. L. Castricum et al. 2008 Hybrid ceramic nanosieves: stabilizing nanopores with organic links, Chem. Comm. (1103).

Hybrid materials





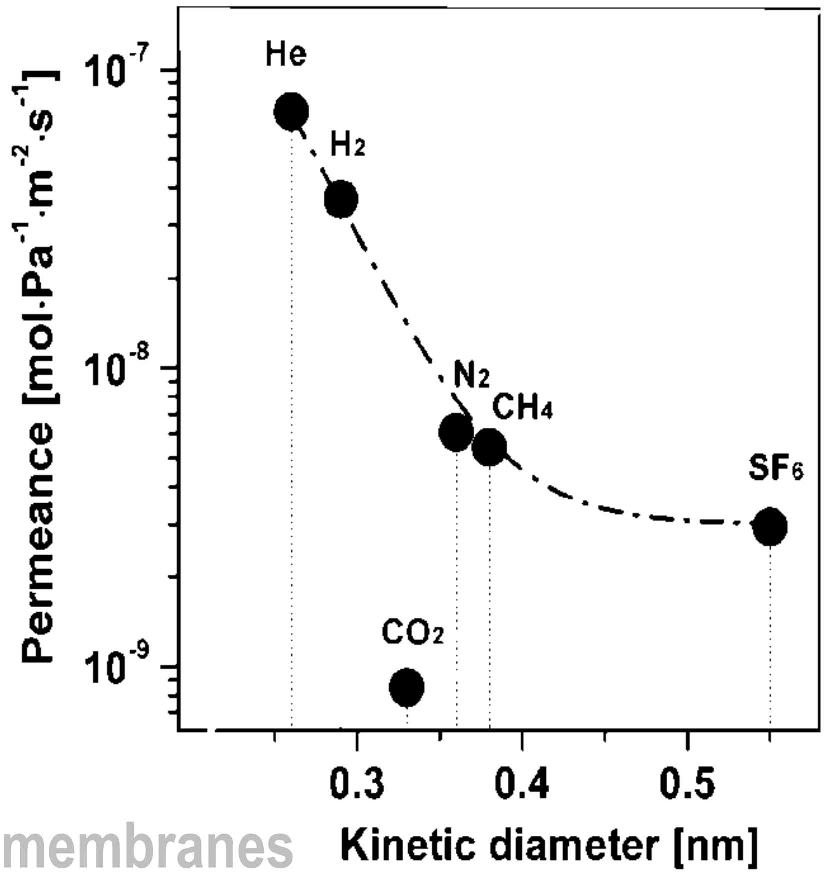
Stable membranes

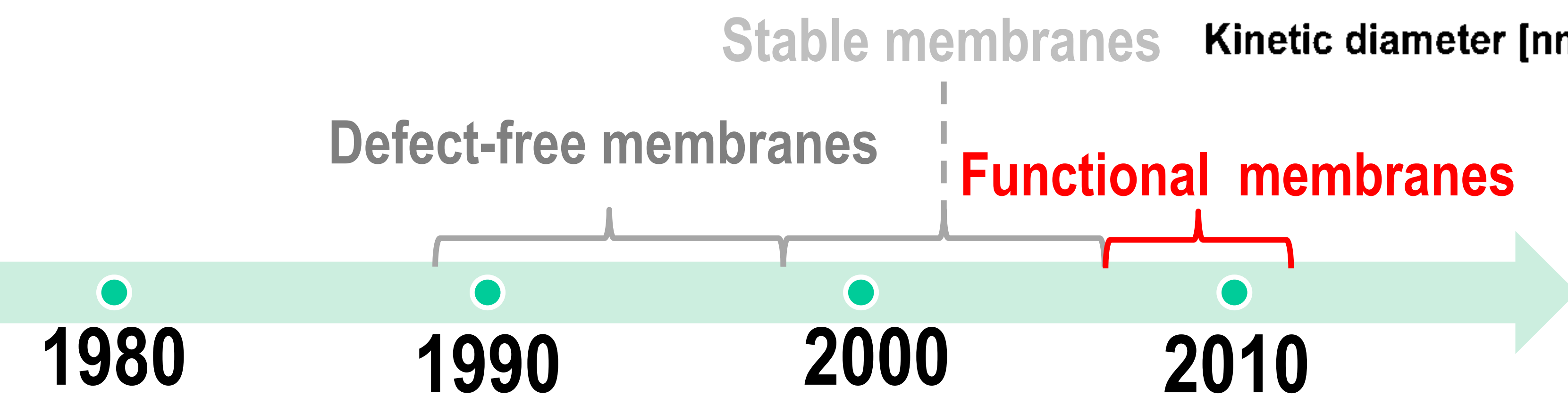


Inorganic nanoporous membranes

Doped materials

V. Boffa et al. 2008 Microporous niobia–silica membrane with very low CO_2, ChemSusChem 1 (437).





Conclusions

“Fabrication and application of inorganic membranes relies on the development of new functional and ultrastable materials”

Acknowledgements

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- **Dr. Giuliana Magnacca**

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