# Characterization of microporous silica-based membranes by calorimetric analysis

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# Characterization of silica membranes by calorimetric analysis

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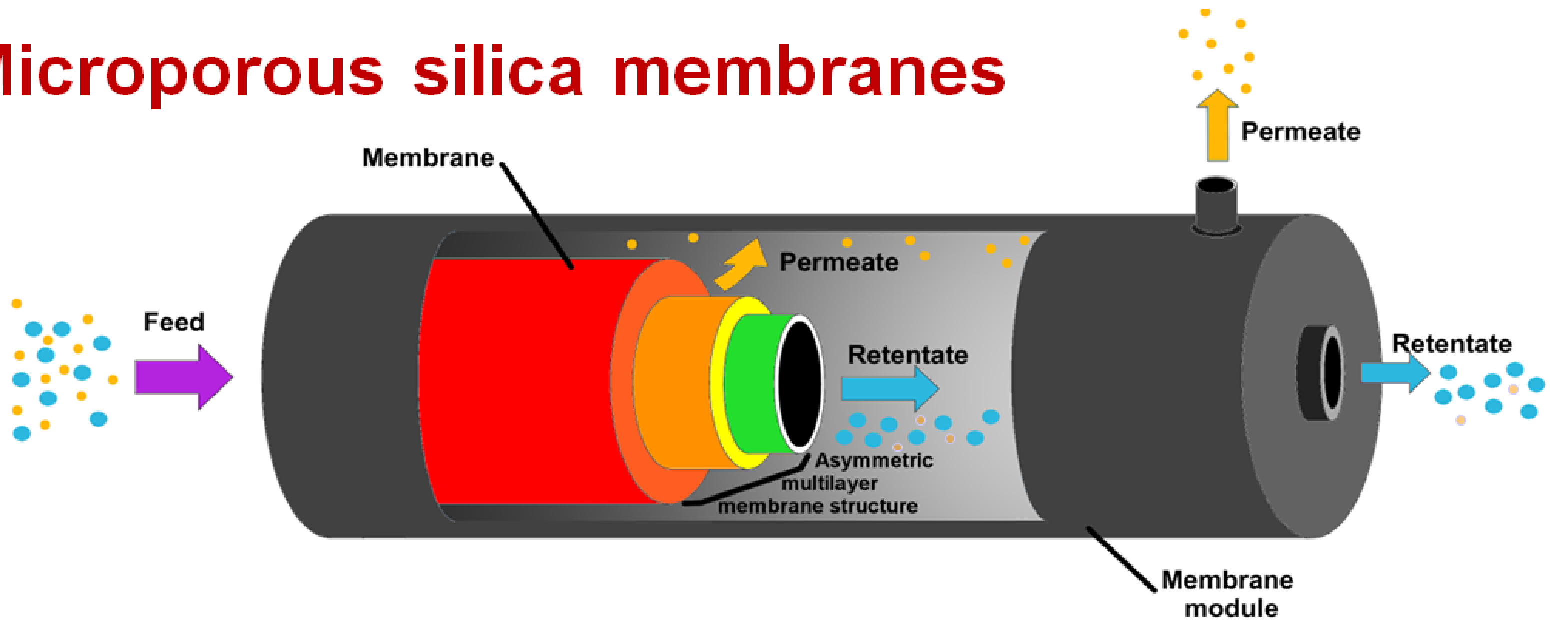
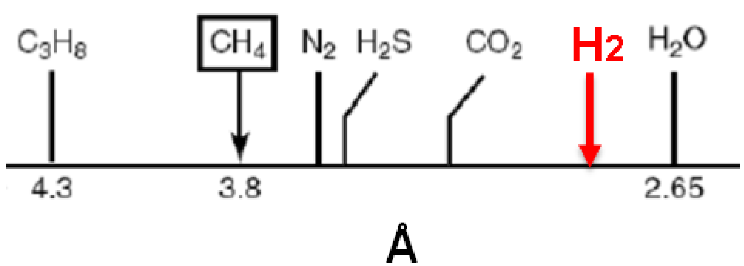
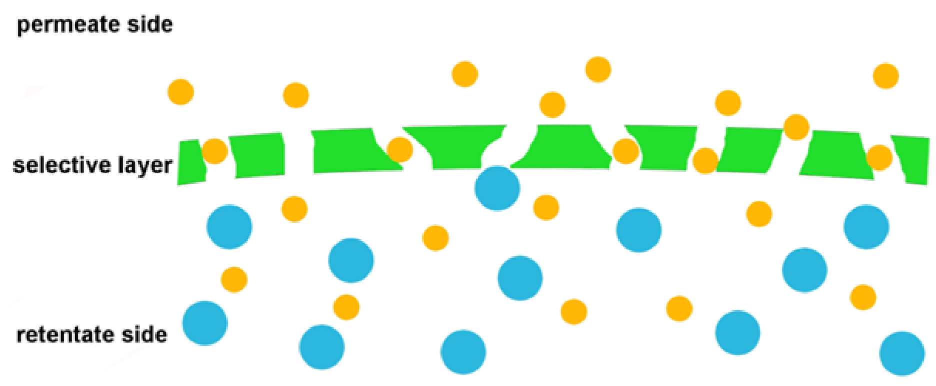
## Section of Chemistry

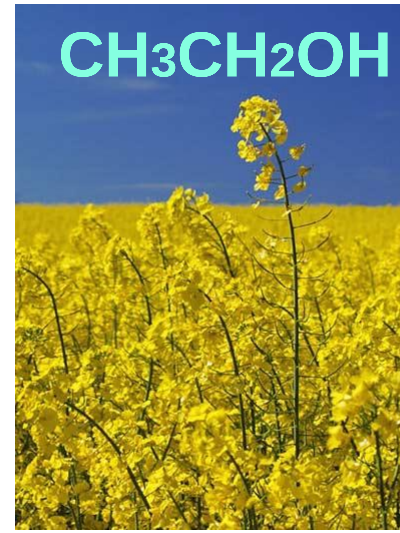
# Microporous silica membranes



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

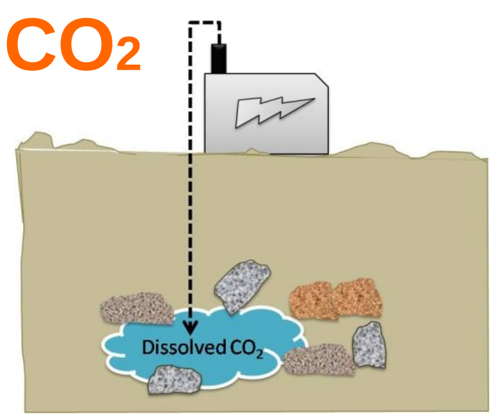



**Gas separation**

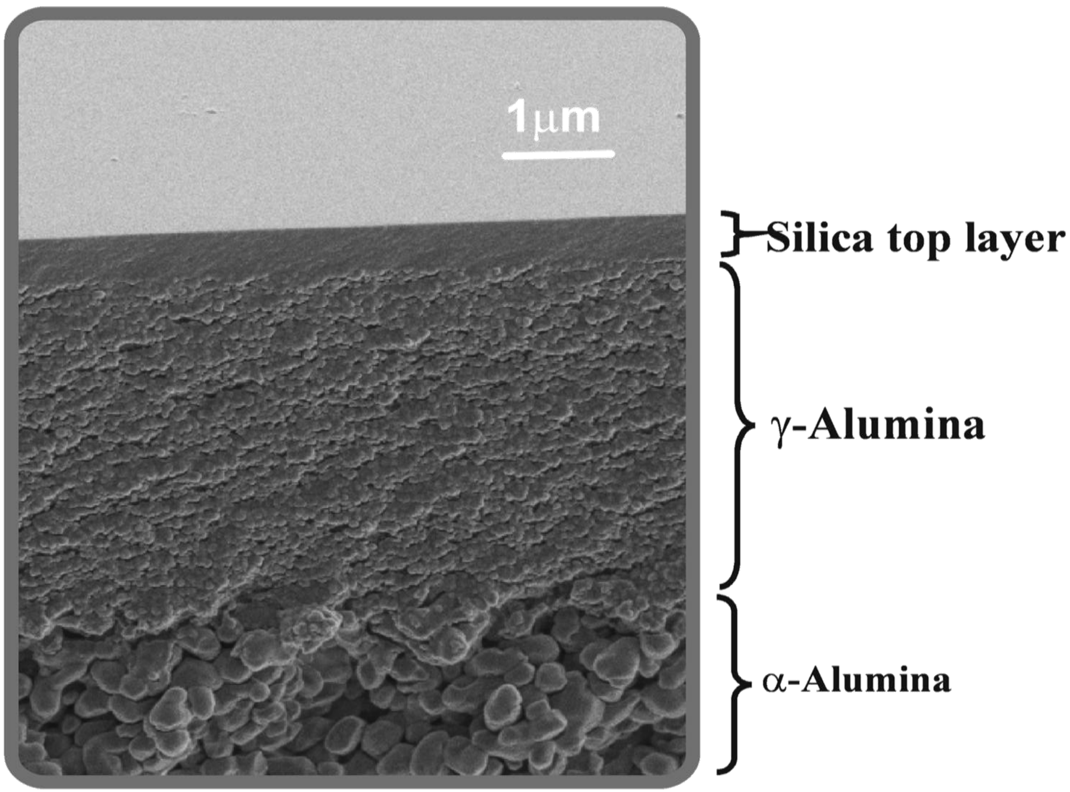
- $H_2$ purification
- $CO_2$ sequestration
- Biogas upgrading

**Pervaporation**

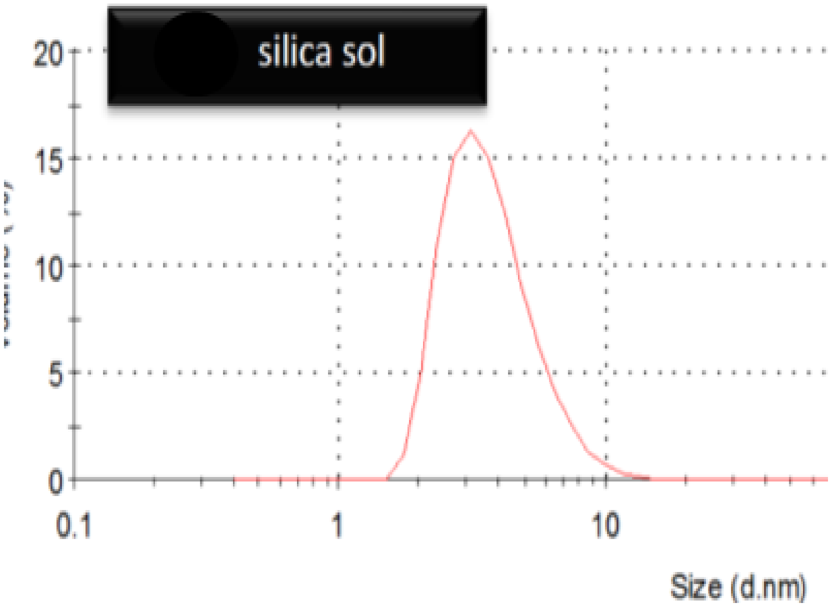
- Alcohol dehydration
- Separation of organic solvents




# Ultramicroporous silica membranes

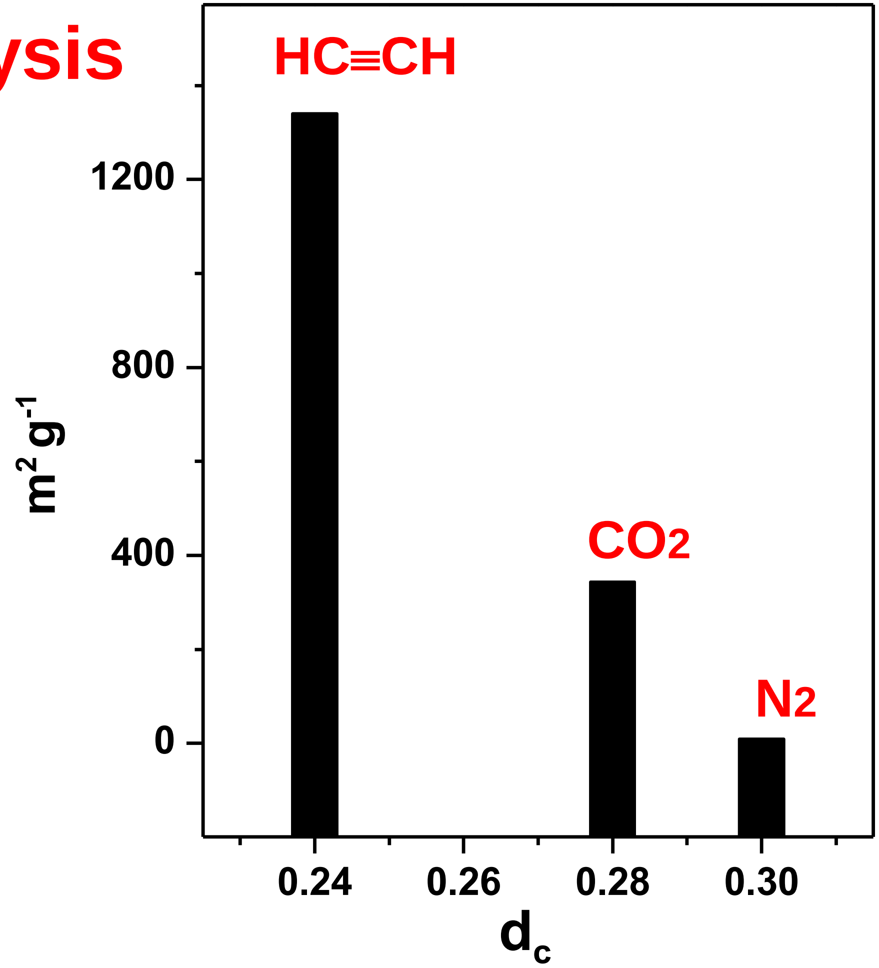


# Sol-gel

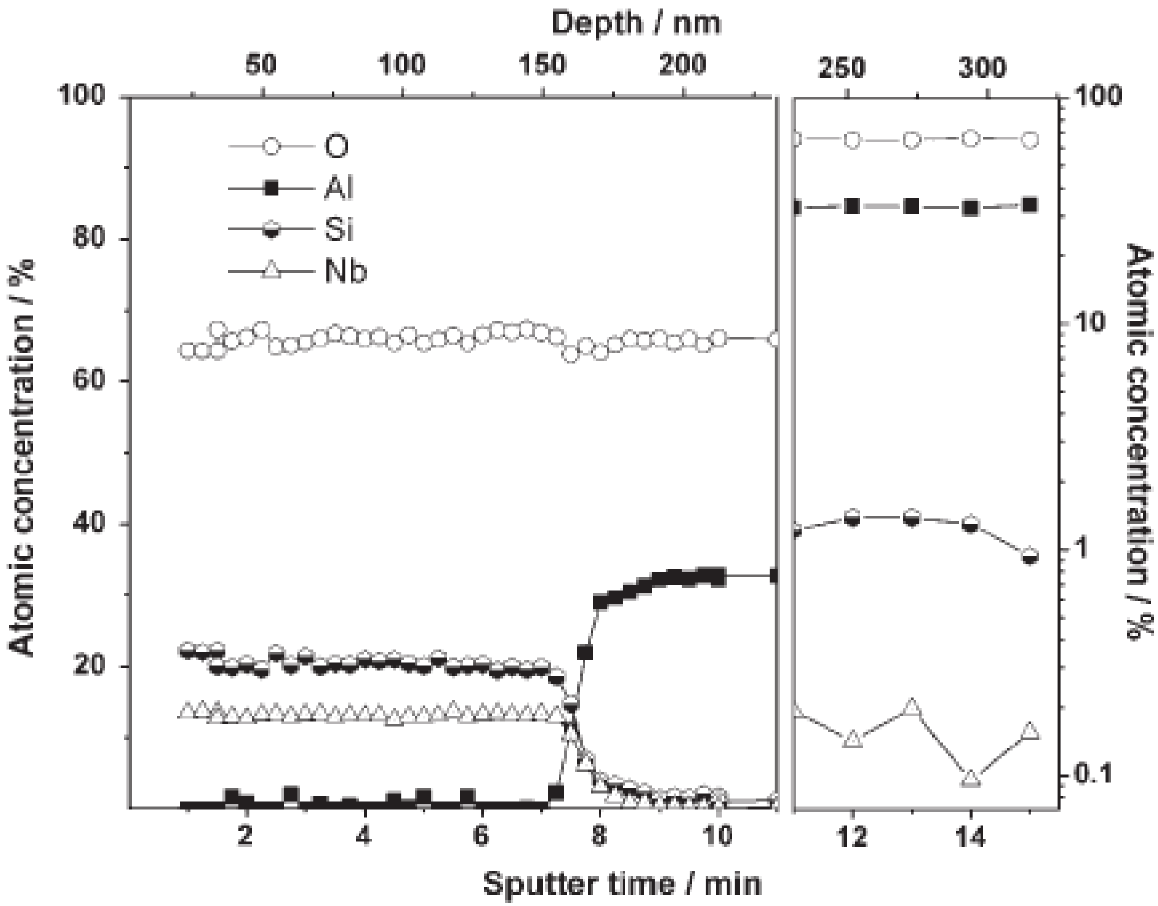



# Nitrogen sorption analysis on powder samples

- **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. Castricum et al. (2007) J. Mater. Chem., 17, 1509–1517.**




**Theoretical**

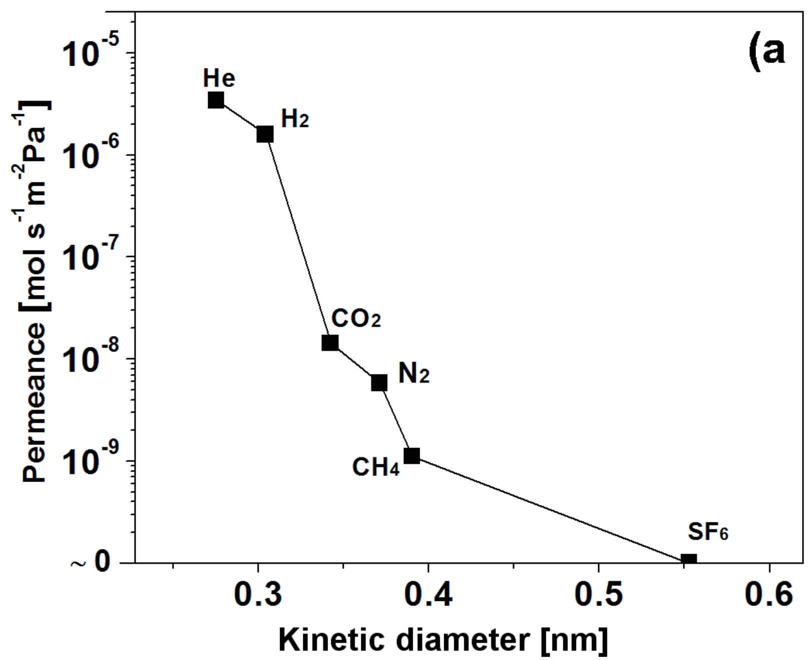
**Si:Nb = 3**

**Measured**

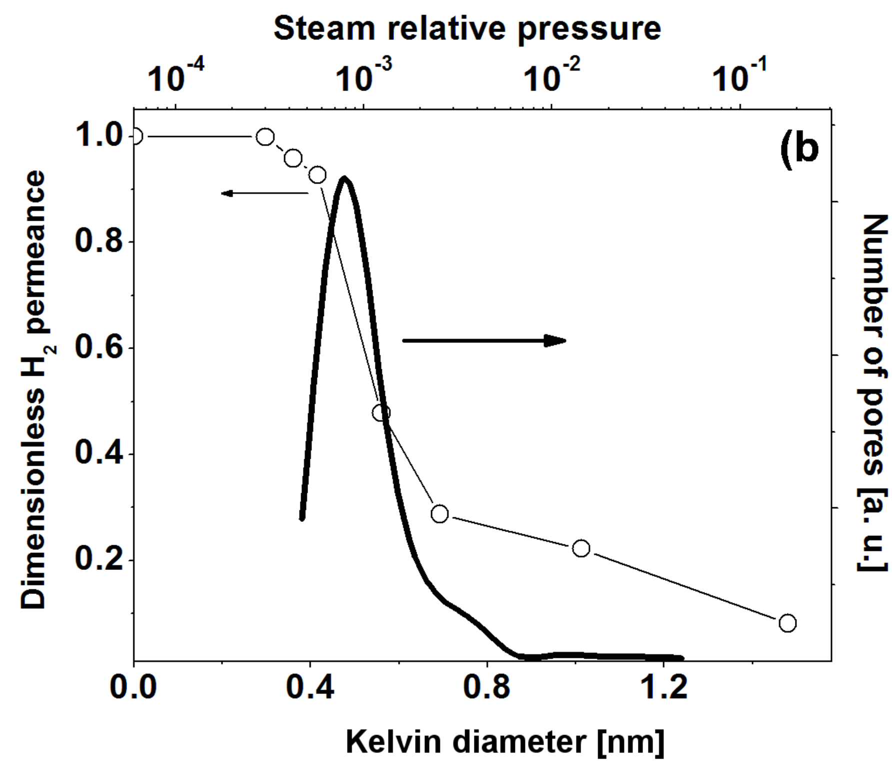
**Si:Nb = 1.5**

**V. Boffa et al. ChemSusChem 2008, 1, 437 – 443**

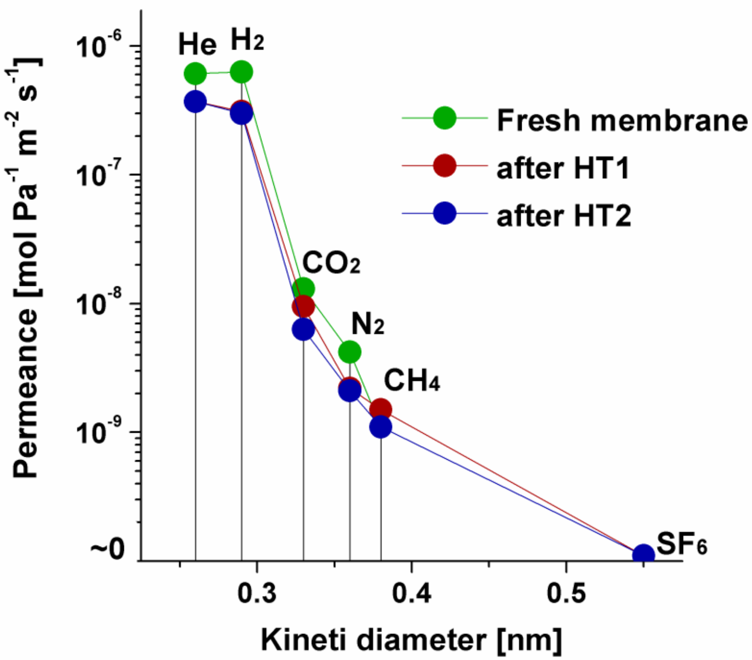
## Single-gas permeation experiments

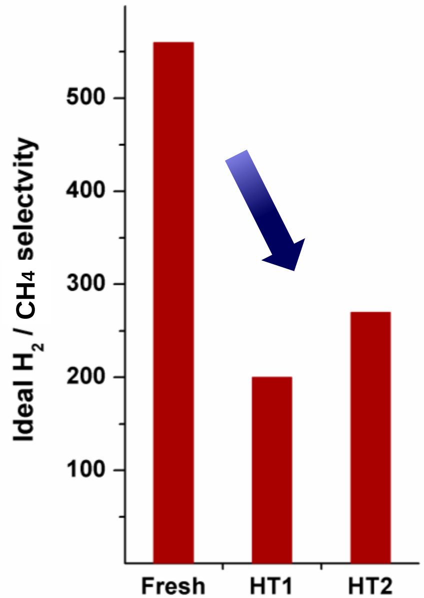



## He-permporometry




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

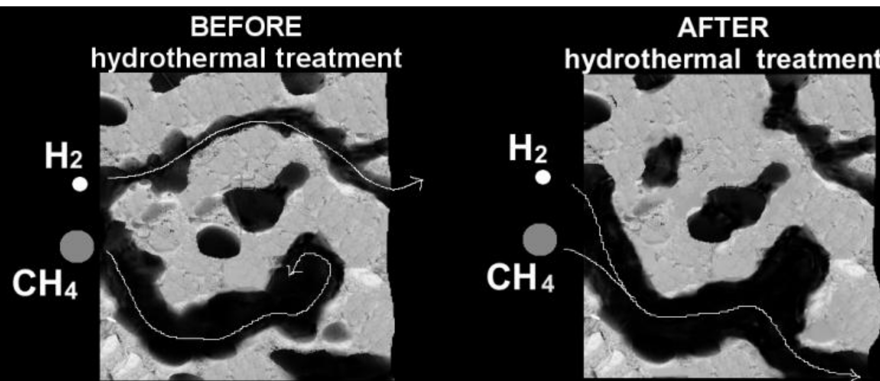



## Hydrothermal treatment

**HT1:** steam exposure ($P_{H_2O}$ = 0.56 bar) at 150 °C for 70 h;

**HT2:** steam exposure ($P_{H_2O}$ = 0.56 bar) at 200 °C for 70 h.

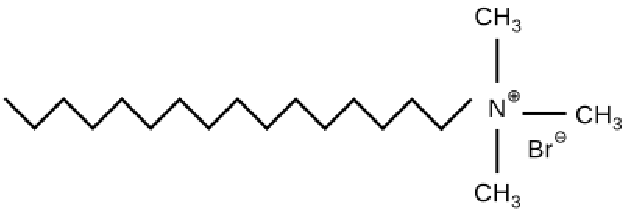



V. Boffa et al. *J. Membrane Sci.* 319 (2008) 256–263

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

↓

**Hydrothermal treatment**

In autoclave at 120 °C for 48 h

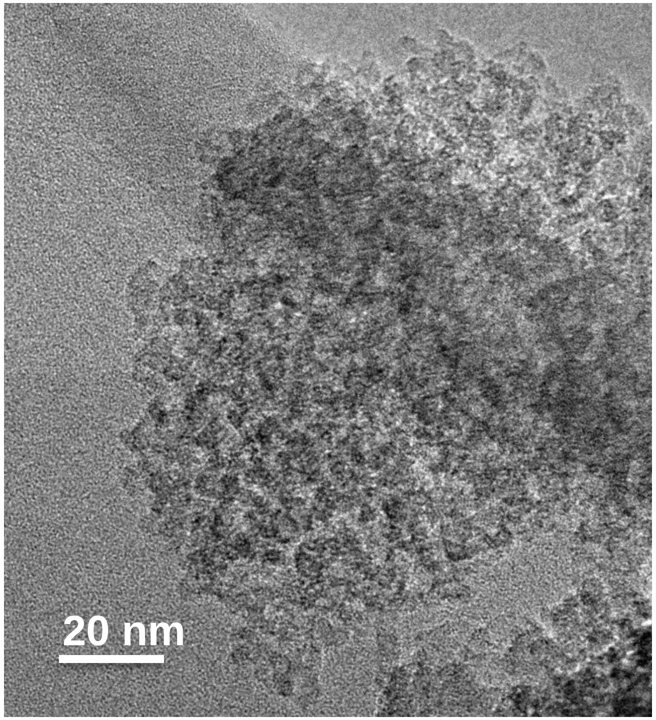
↓

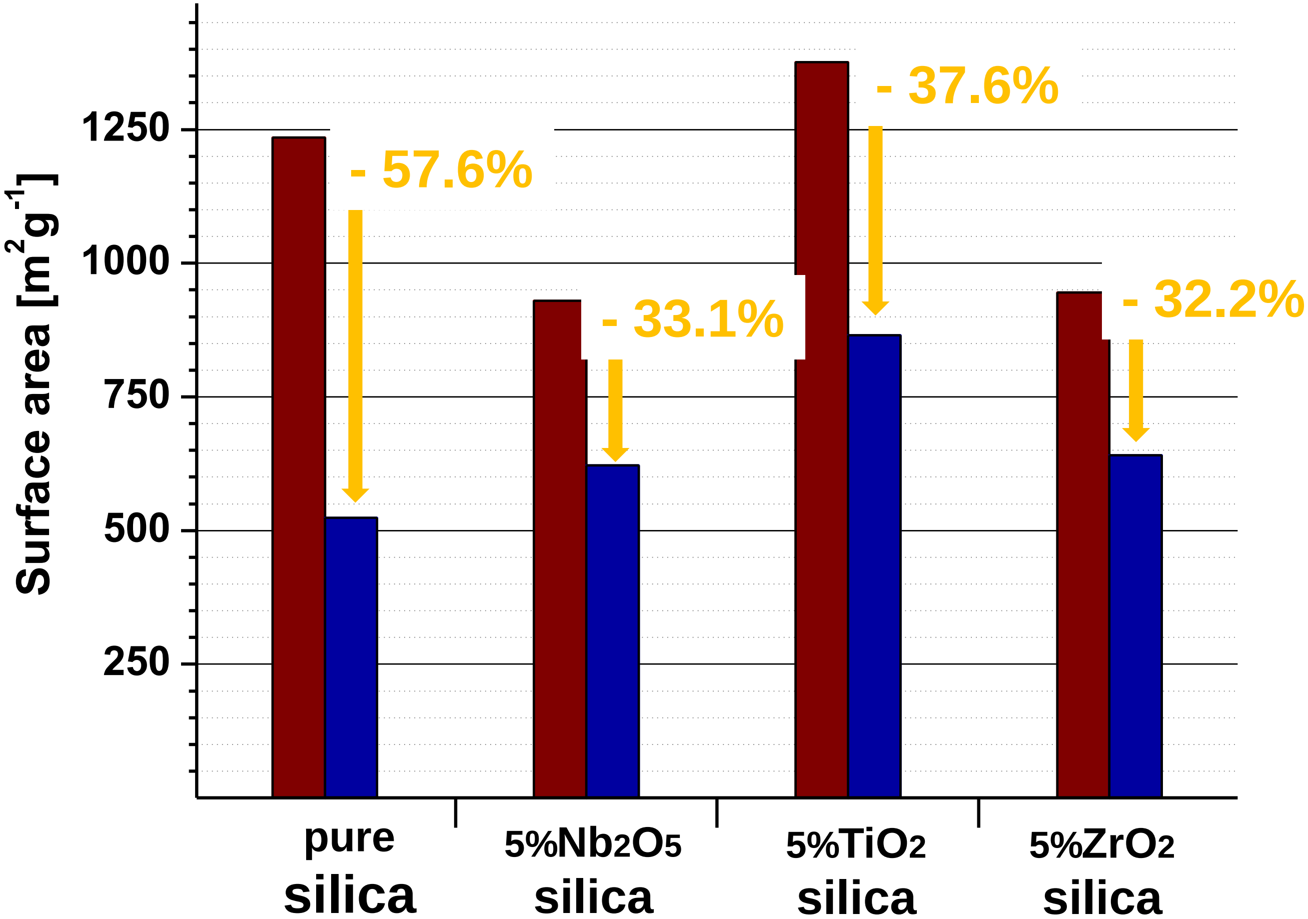
**Drying**

Characterization

comparison

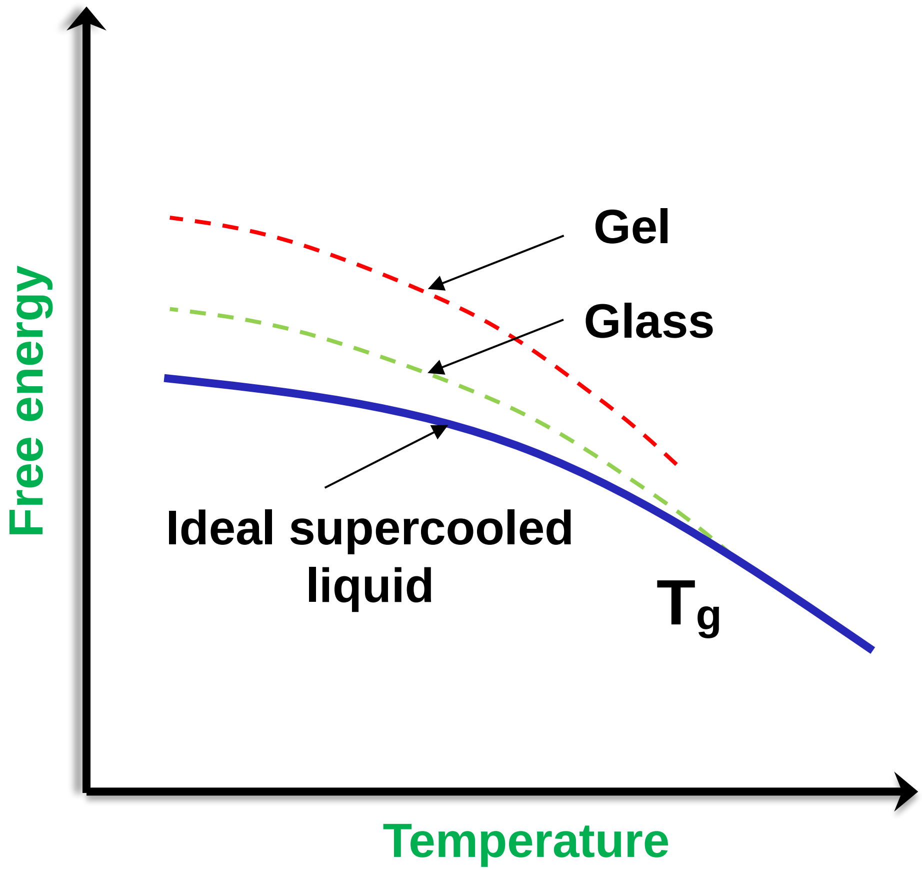
Characterization






- $TiO_2$ 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.

# Nature of sol-gel derived silica membranes

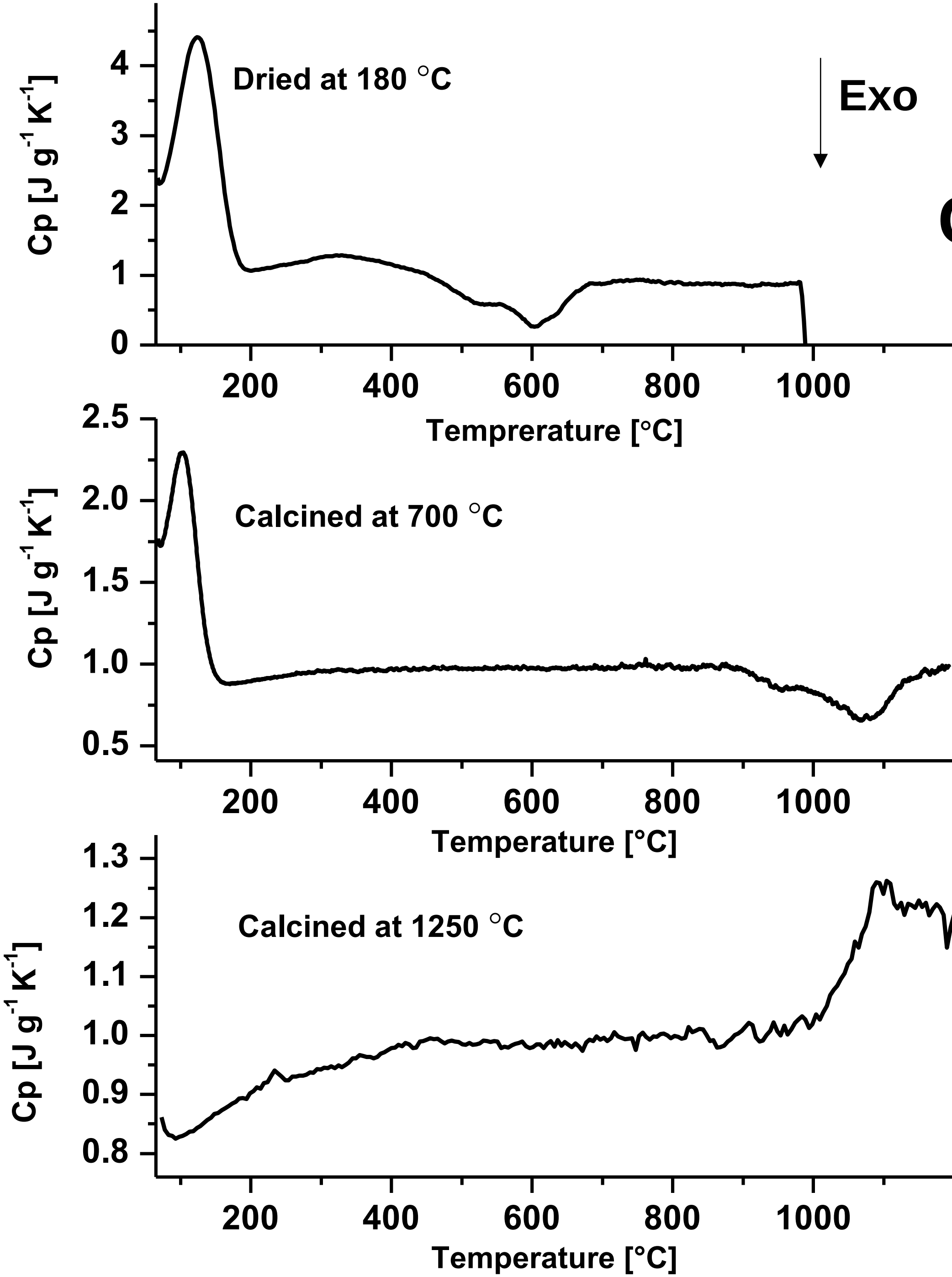



## High free energy:

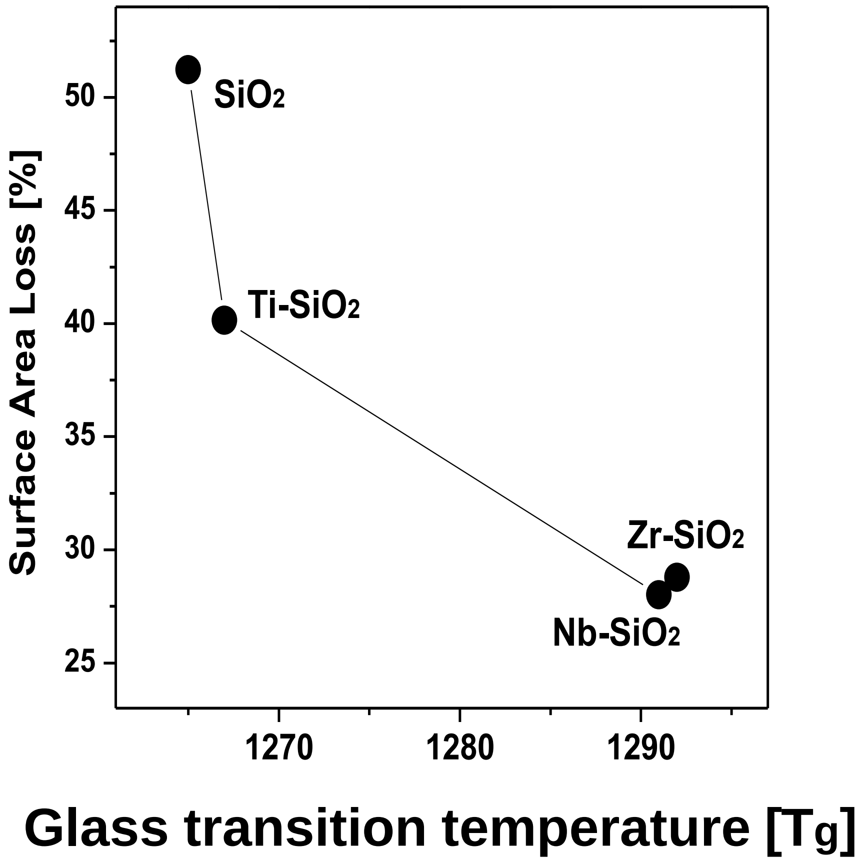
- Reduced cross linking
- High surface area
- High pore volume
- Strained SI-O-Si bonds

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

# Calorimetric analysis



**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.**



# 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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