Inorganic microporous membranes: fabrication and application

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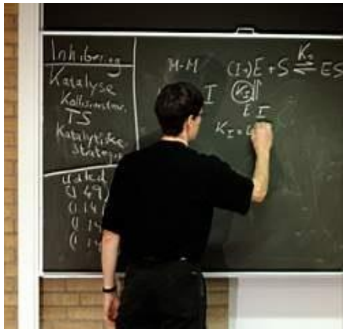
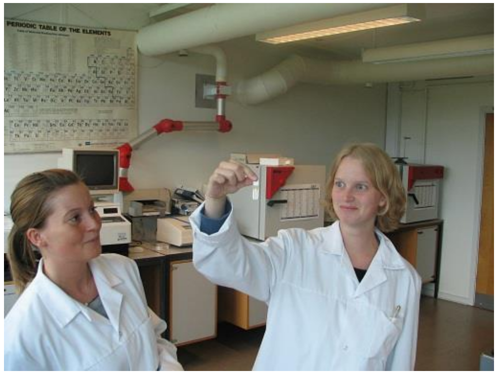
Problem-Based Learning (PBL) Method



- Achieve **knowledge and skills** at a high academic level;
- Learn how to **analyze and**
- **Solve** real-life problems;

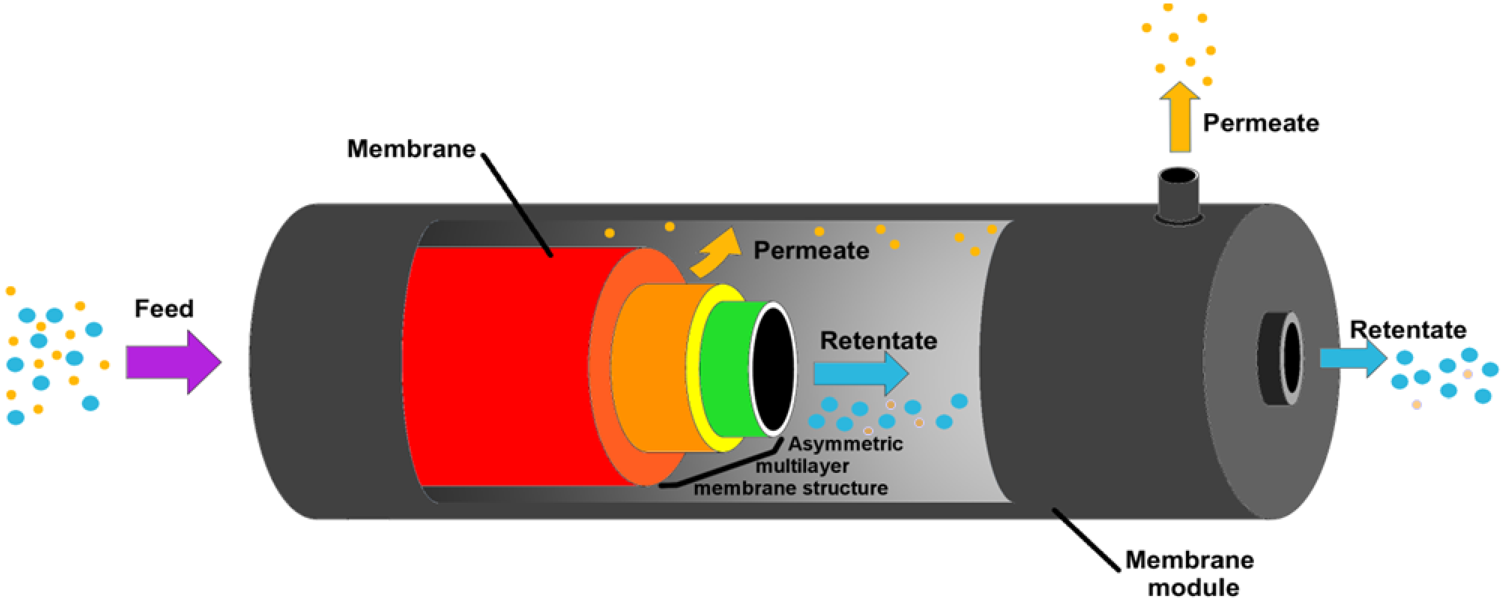
- **Result-oriented** work within a **team**;
- Working with local enterprises.

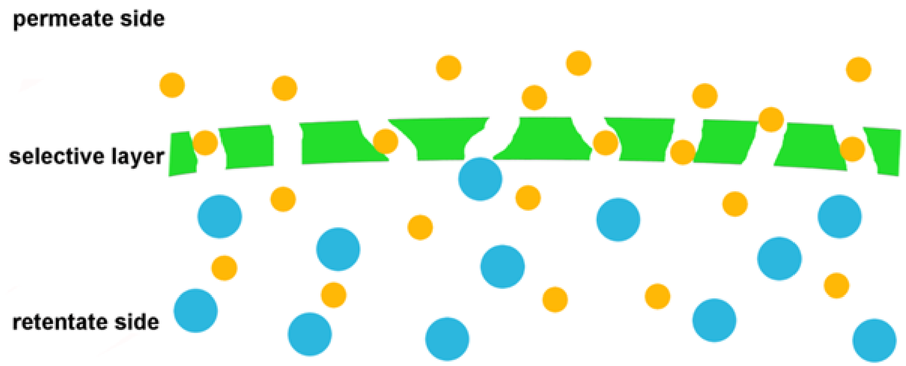


Outline

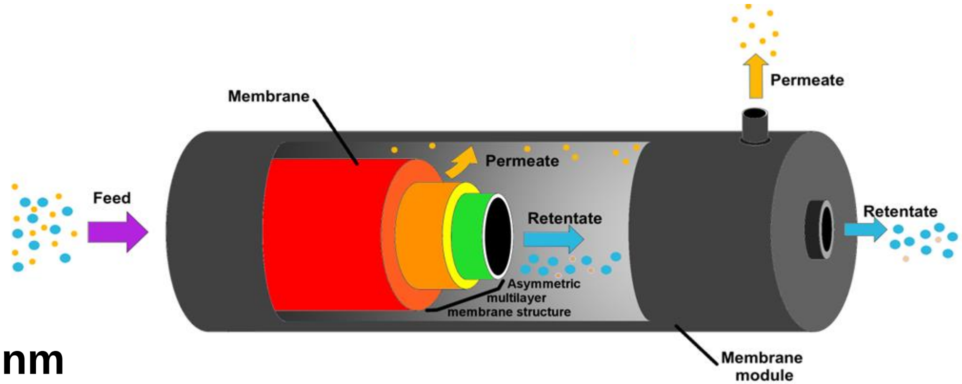
- Introduction
- Gas-selective silica membranes
- Membranes for wastewater tertiary treatment
- Ion-selective silica membranes
- Silicon carbide membranes
- Graphene-based membranes

Introduction





Introduction



Microporous membrane: pores < 2 nm

Gas → membrane	Liquid → membrane → Vapor	Liquid → membrane

Gas separation

- H_2 purification
- CO_2 sequestration
- Biogas upgrading

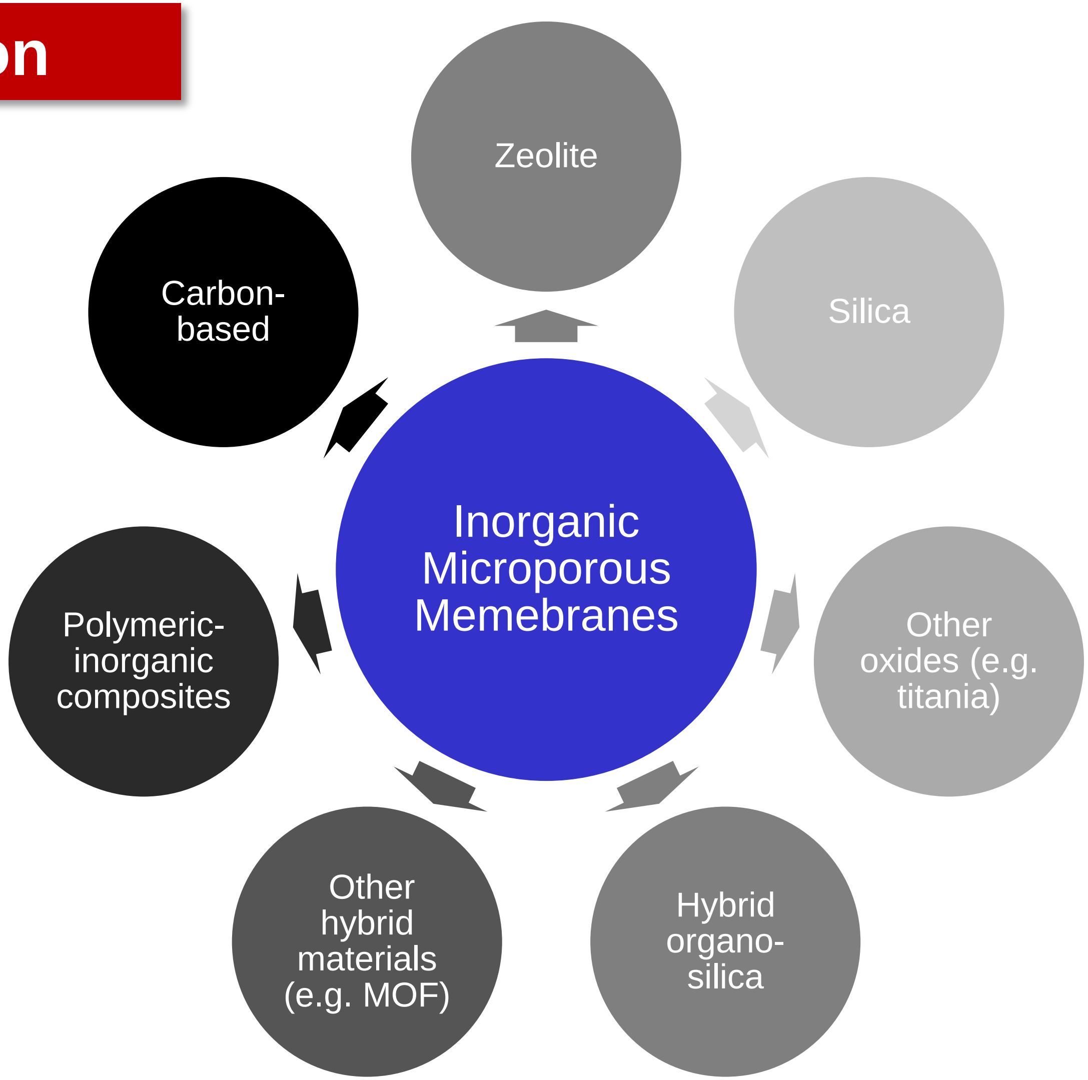
Pervaporation

- Alcohol dehydration
- Separation of organic solvents

Nanofiltration

- Tertiary treatment
- Softening and desalination

Introduction



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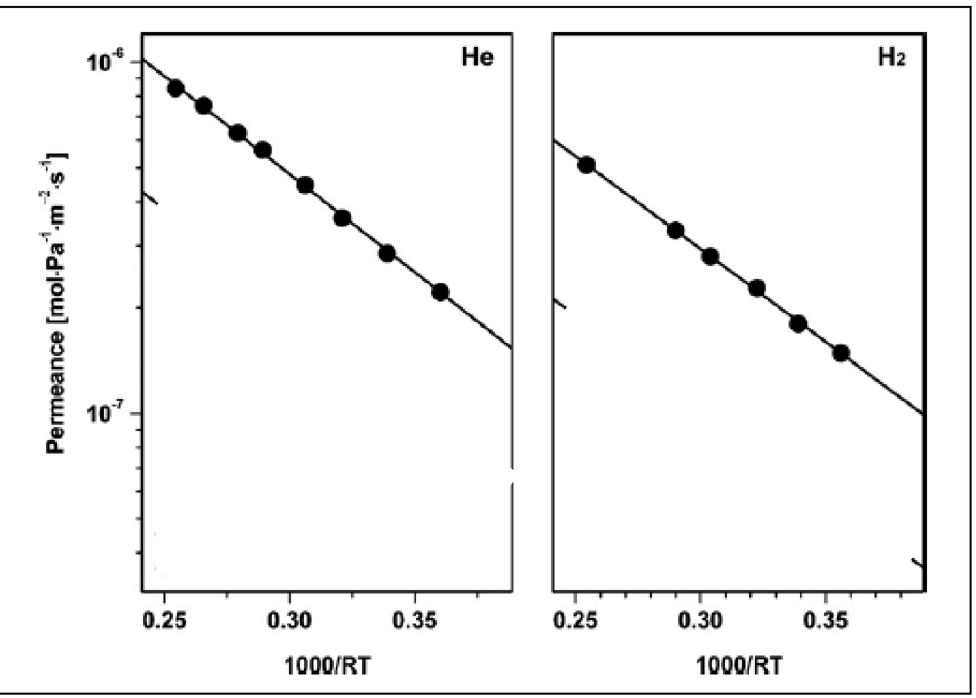
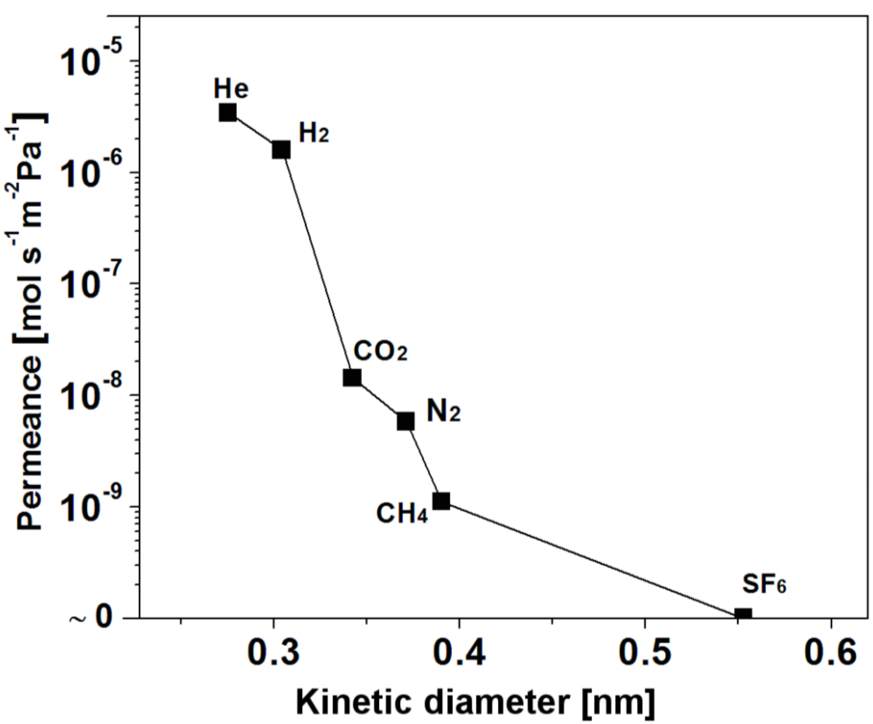
Gas–selective silica membranes

Structure

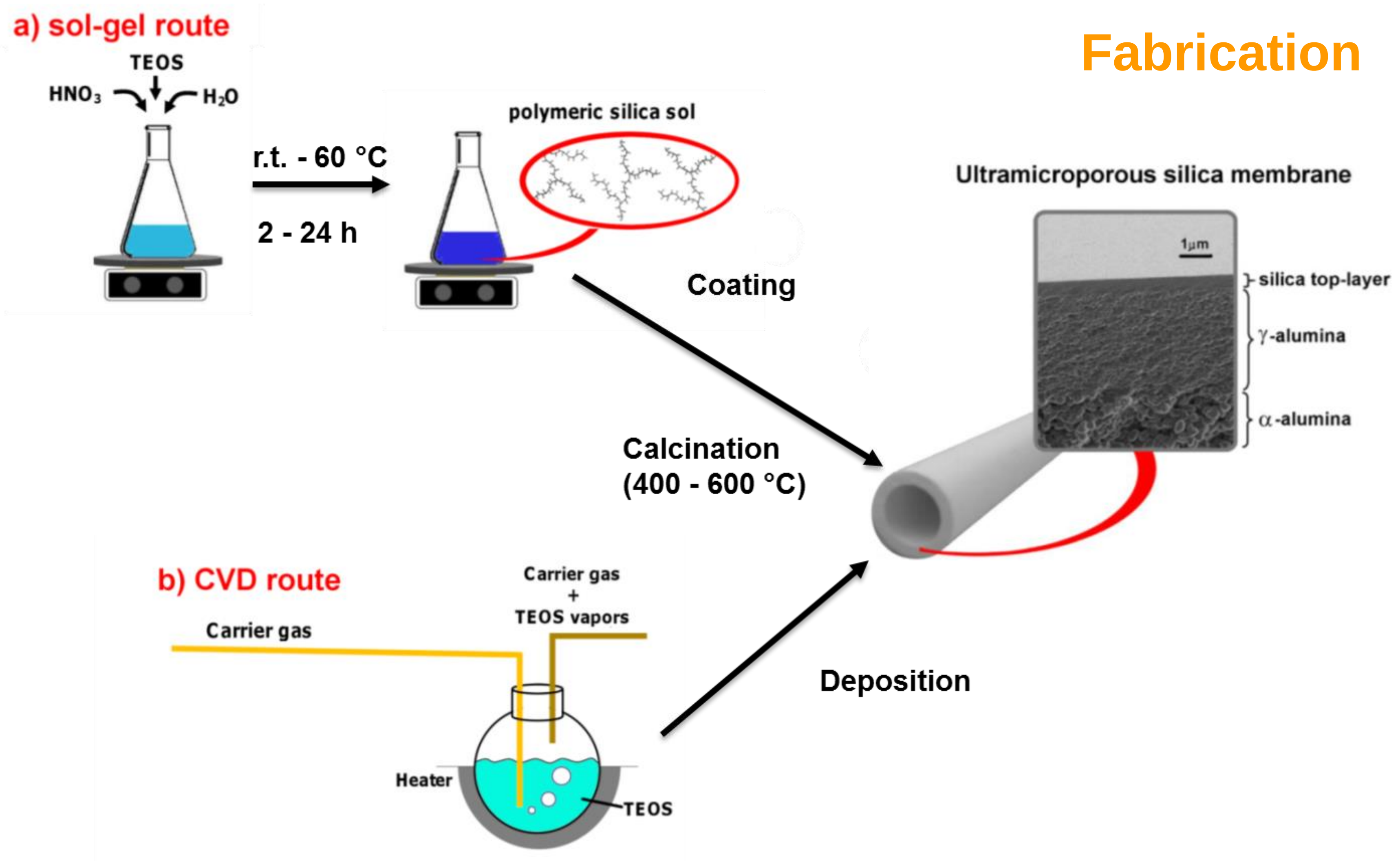


Single-gas permeation measurements



Gas–selective silica membranes

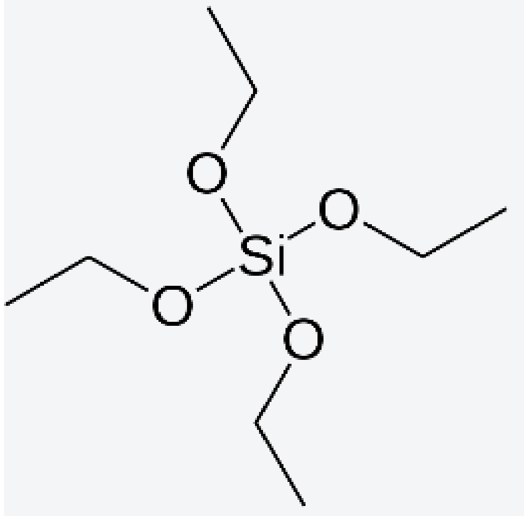
Fabrication



Gas–selective silica membranes

Hydrolysis

$$\equiv Si-OR + H_2O \rightleftharpoons \equiv Si-OH + R-OH$$

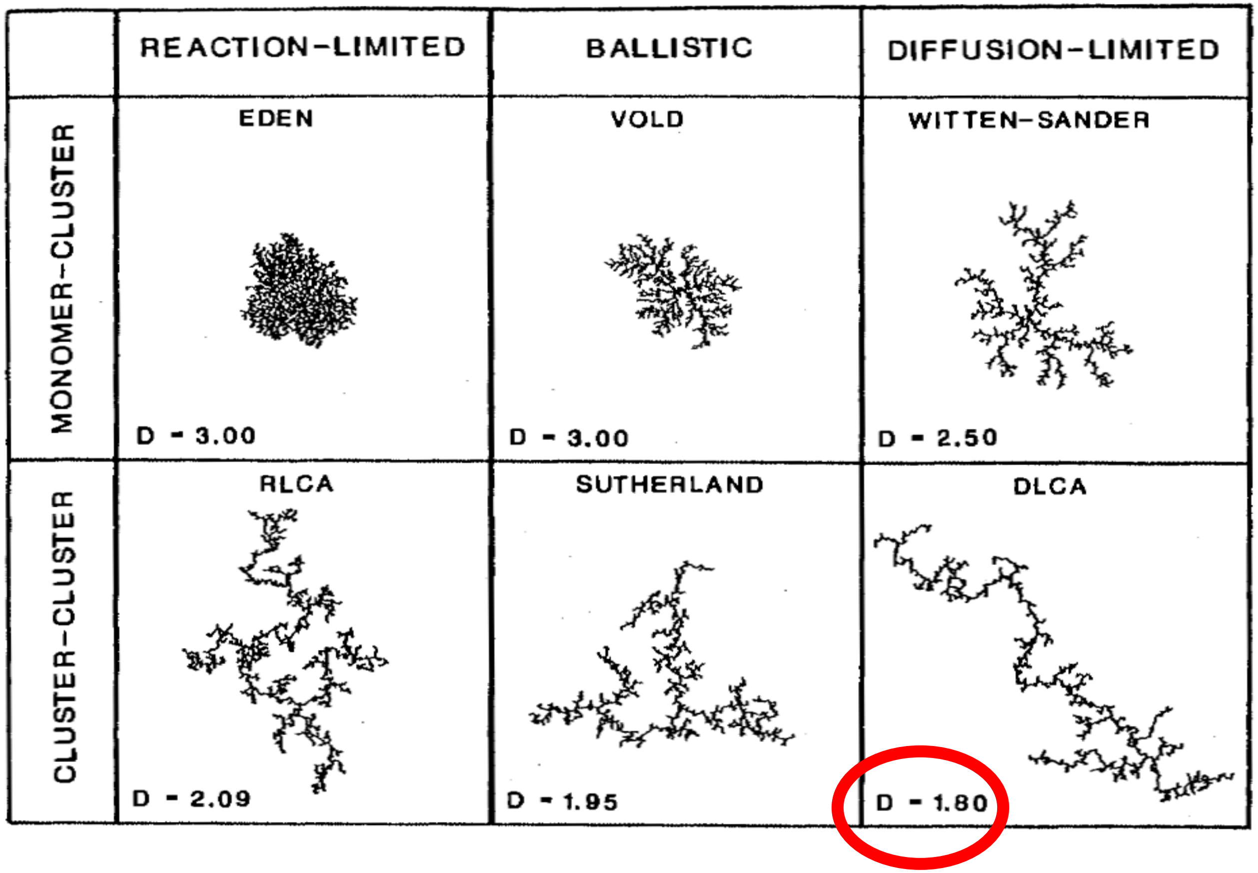


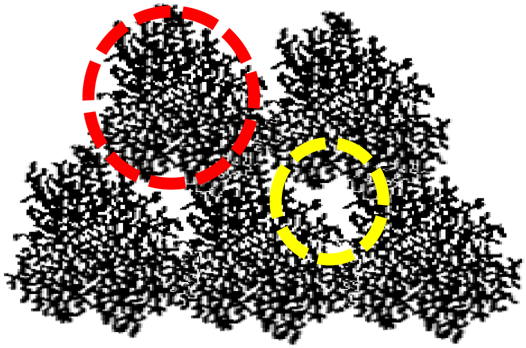
Condensation

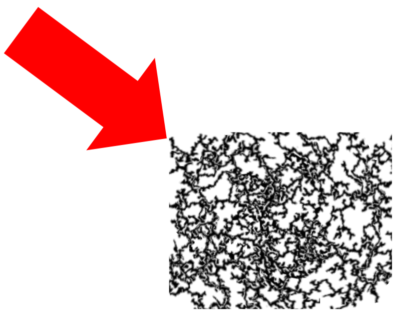
$$\equiv Si-OH + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + H_2O$$

$$\equiv Si-OR + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + R-OH$$

Gas–selective silica membranes







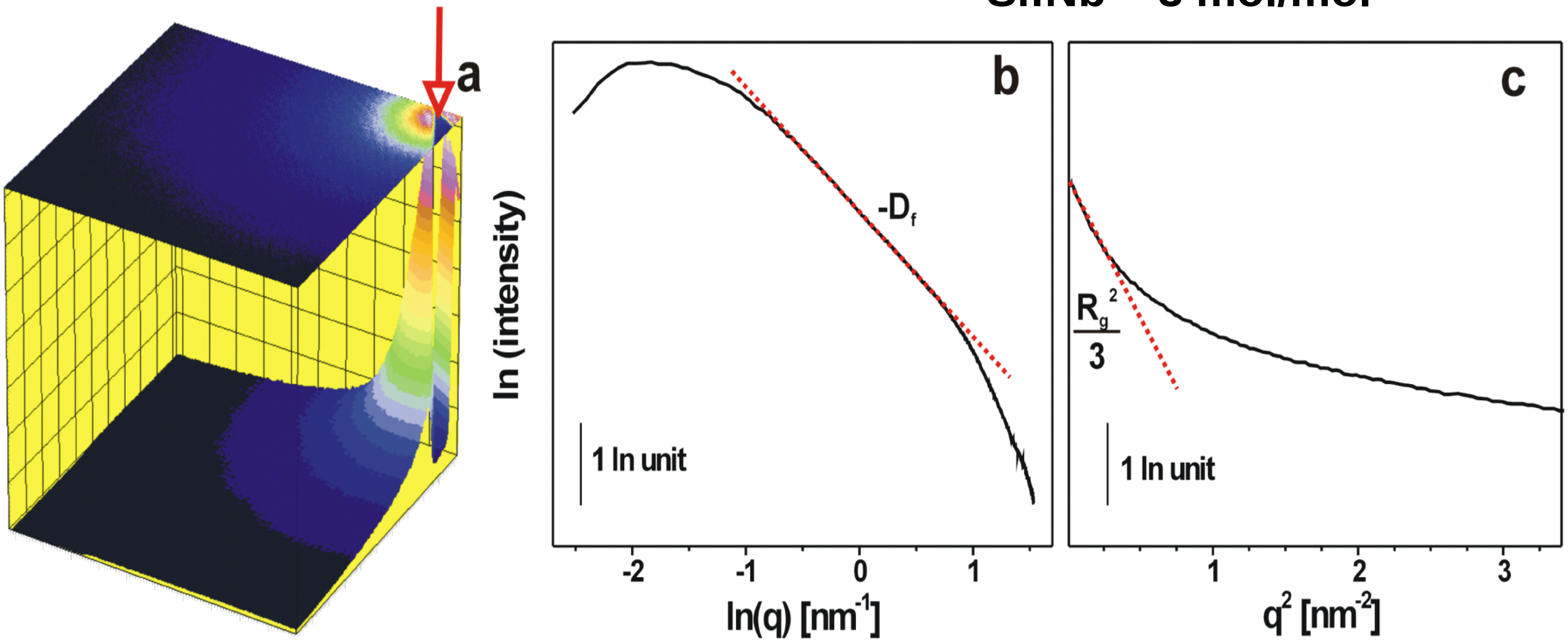
P. Meakin, *Adv. Colloid Interface Sci.* **28**, 249 (1989)

Gas–selective silica membranes

Silica sol evolution during synthesis

Small-angle X-Ray scattering (SAXS)

System: nanoparticles in ethanol
Si:Nb = 3 mol/mol



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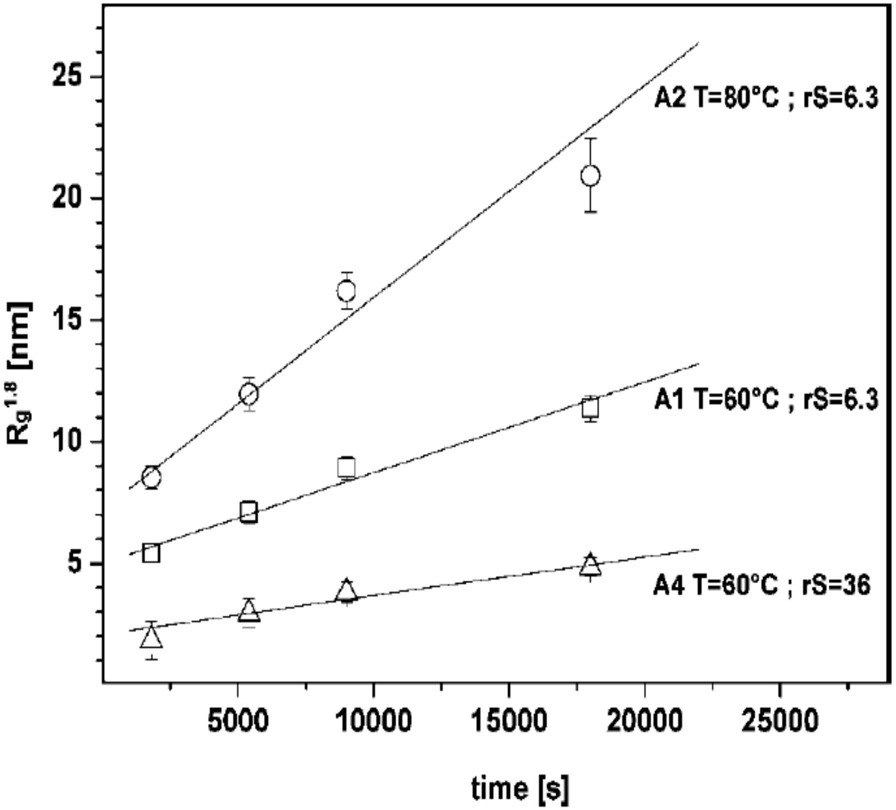
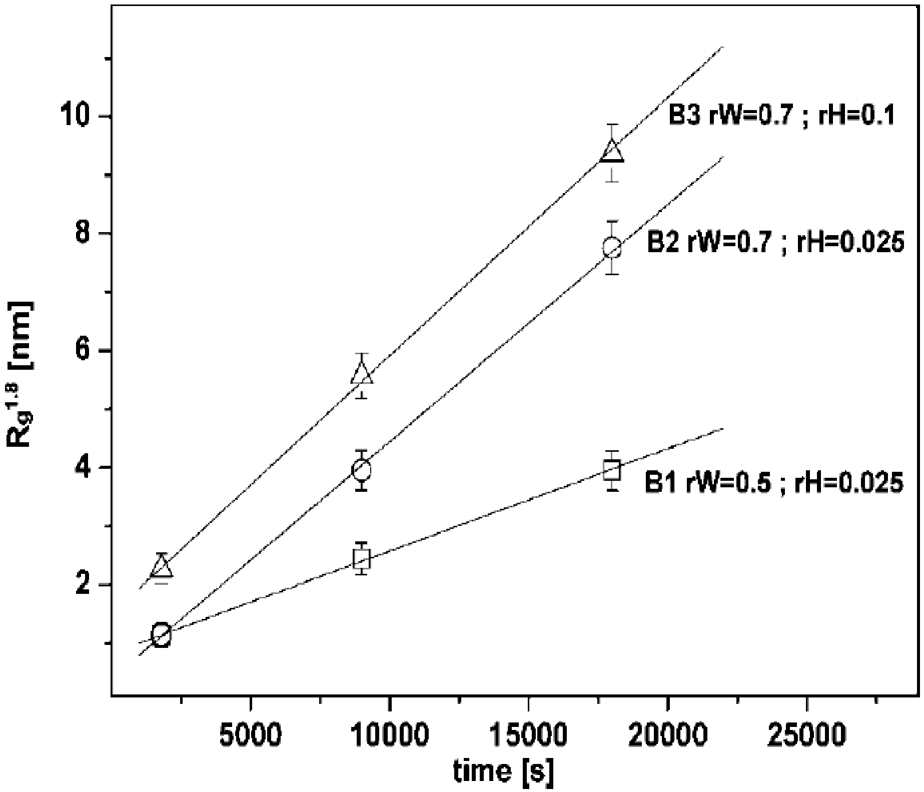
Gas–selective silica membranes

System: nanoparticles in ethanol
Si:Nb = 3 mol/mol

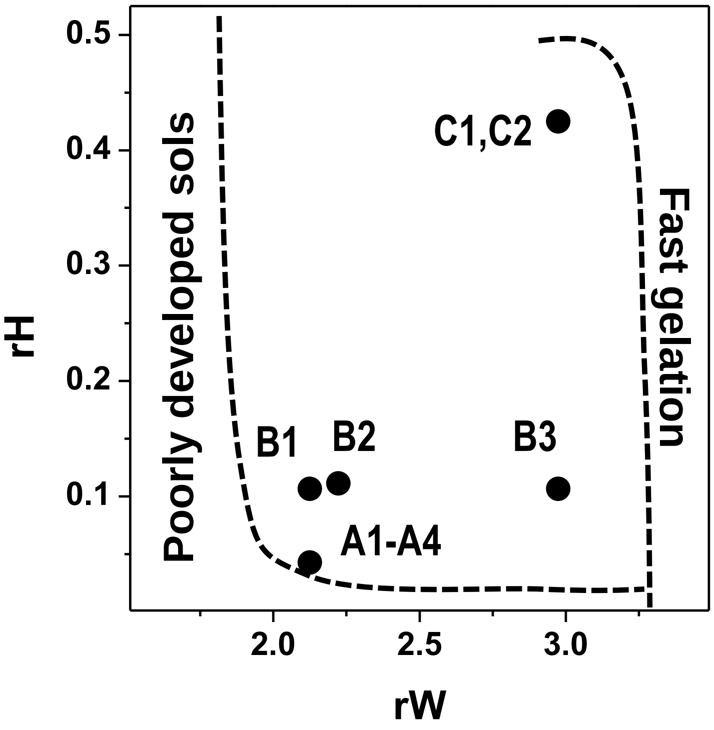


Nb_2O_5-SiO_2 membranes

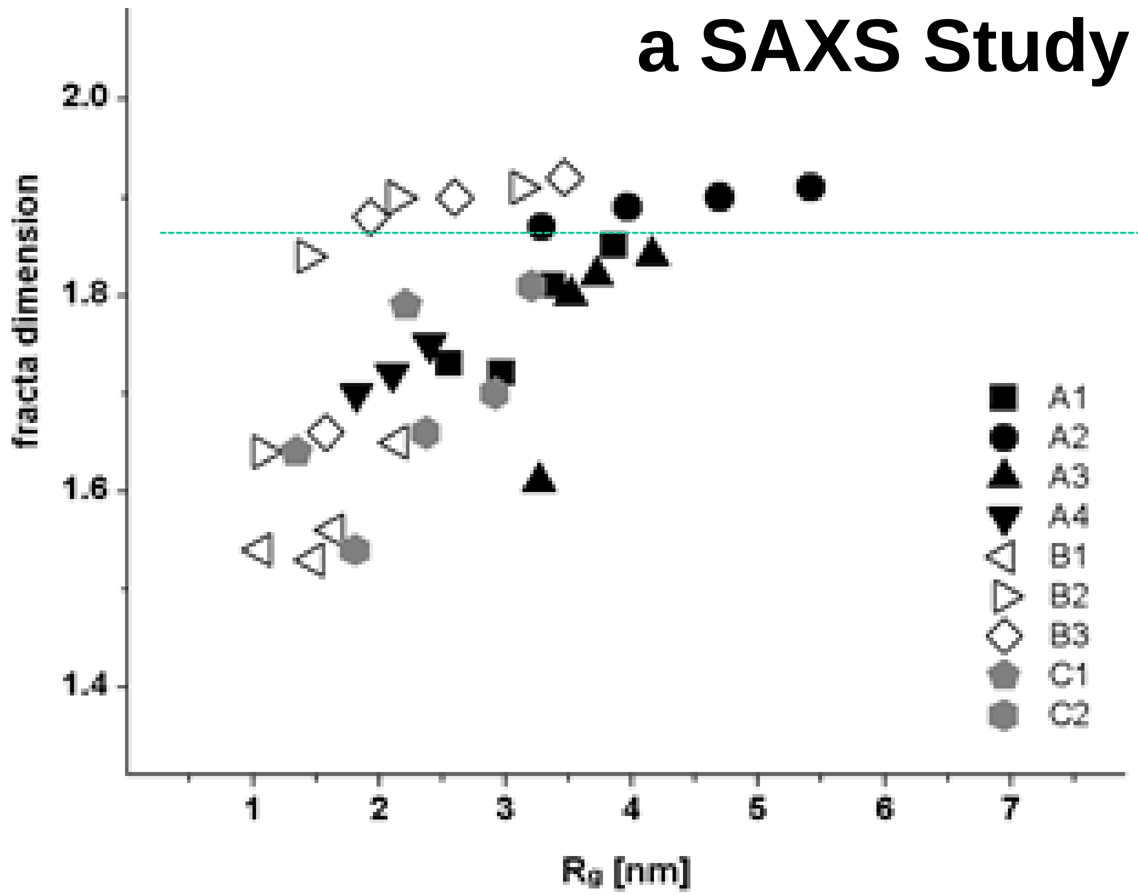


V. Boffa et al Chem. Mater. 21 (2009) 1822-1828.

Gas–selective silica membranes

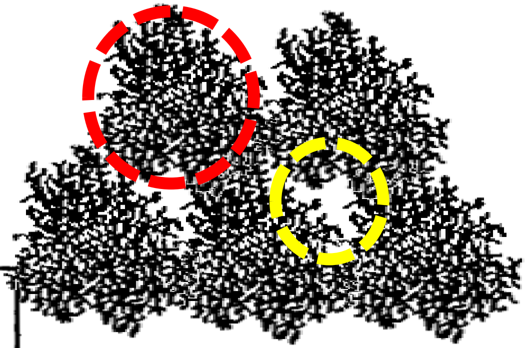


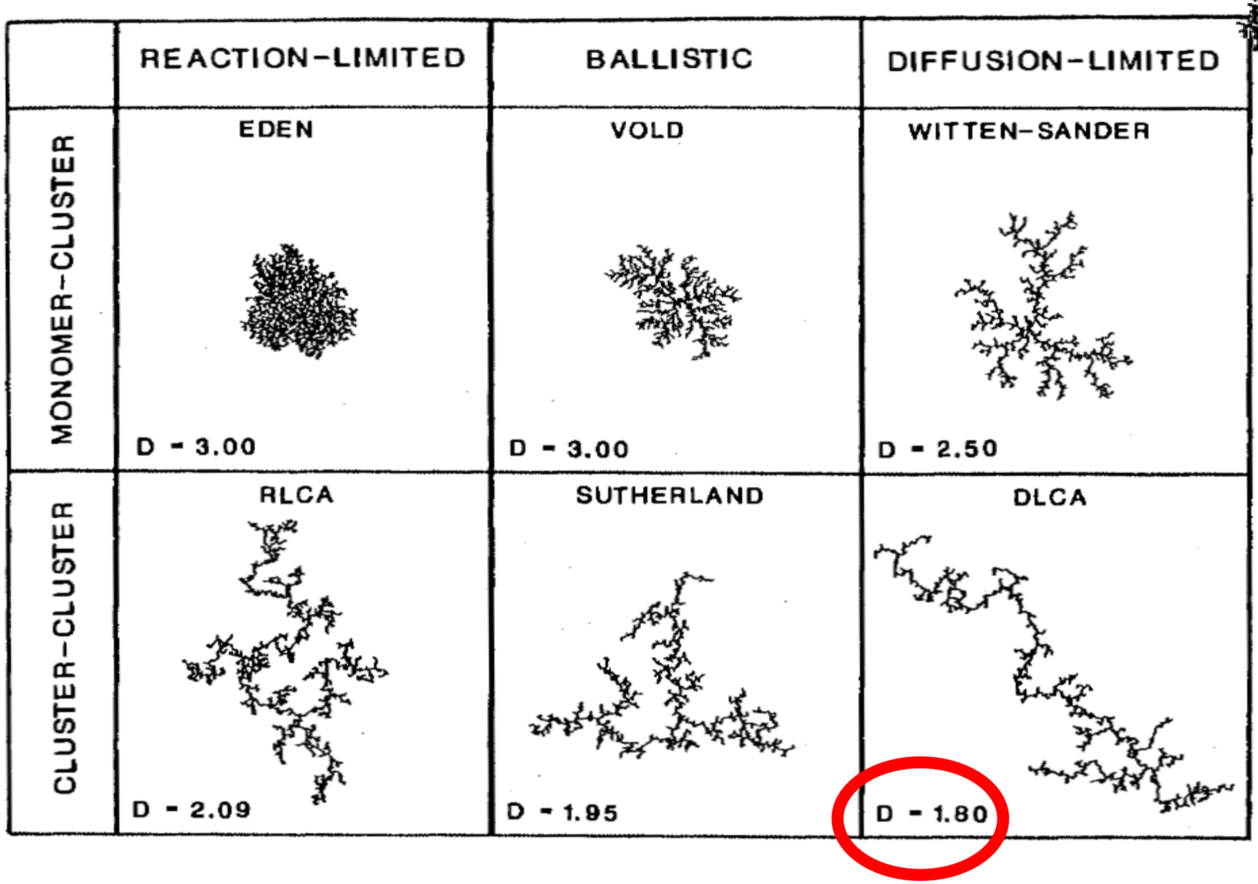
Nb_2O_5-doped SiO_2 sols: a SAXS Study

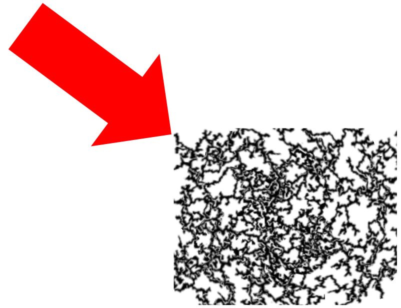


V. Boffa et al Chem. Mater. 21 (2009) 1822-1828.

Gas–selective silica membranes



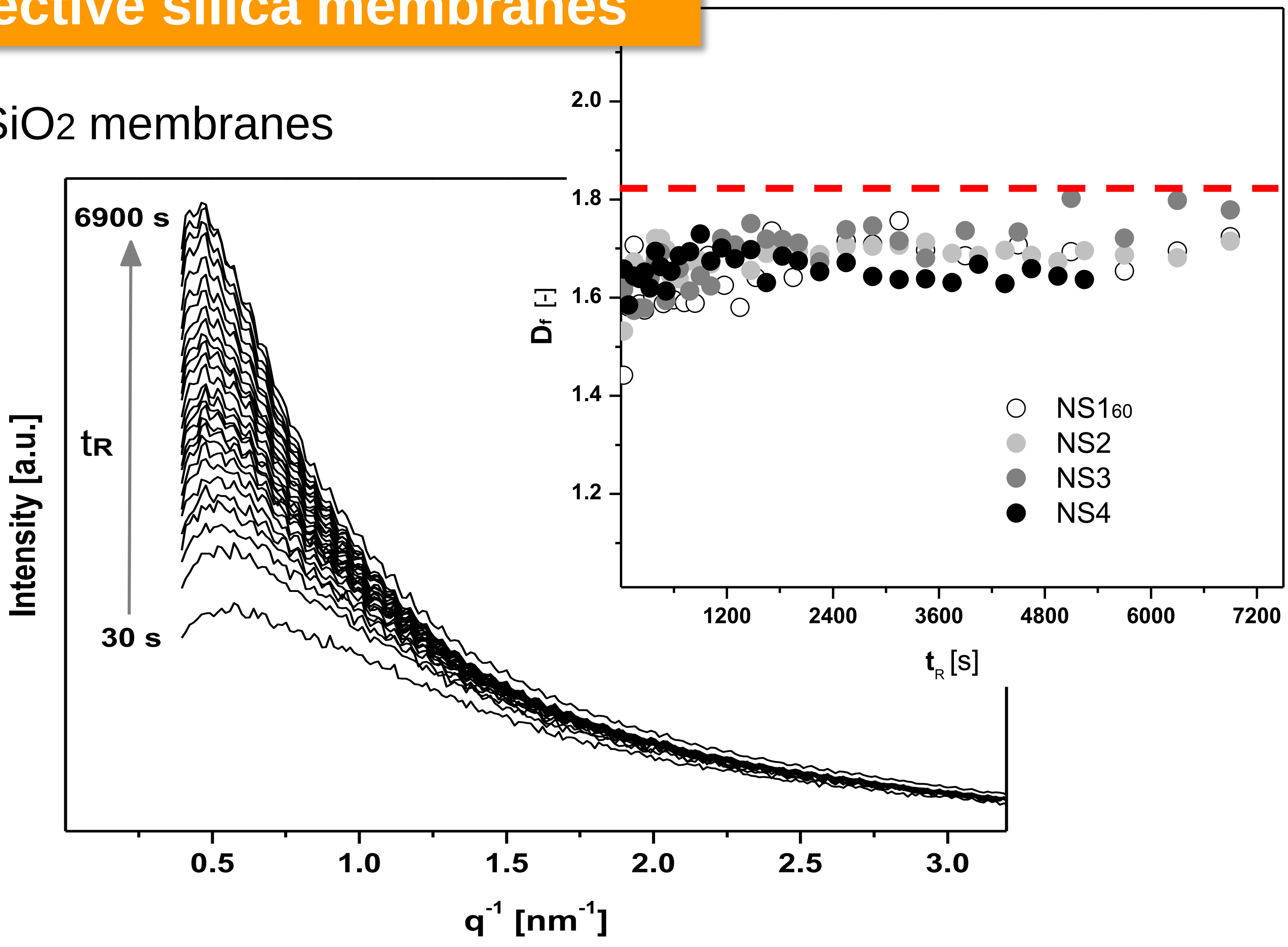




P. Meakin, *Adv. Colloid Interface Sci.* **28**, 249 (1989)

Gas–selective silica membranes

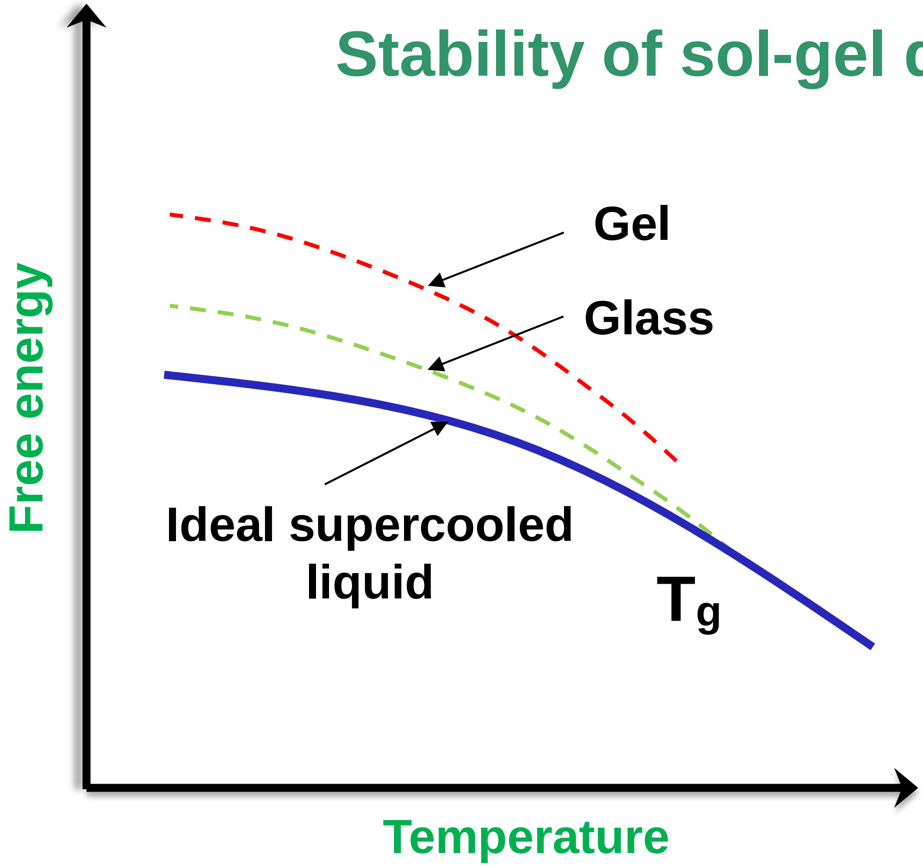
Niobia-SiO2 membranes



V. Boffa et al., in preparation

Gas–selective silica membranes

Stability of sol-gel derived silica membranes

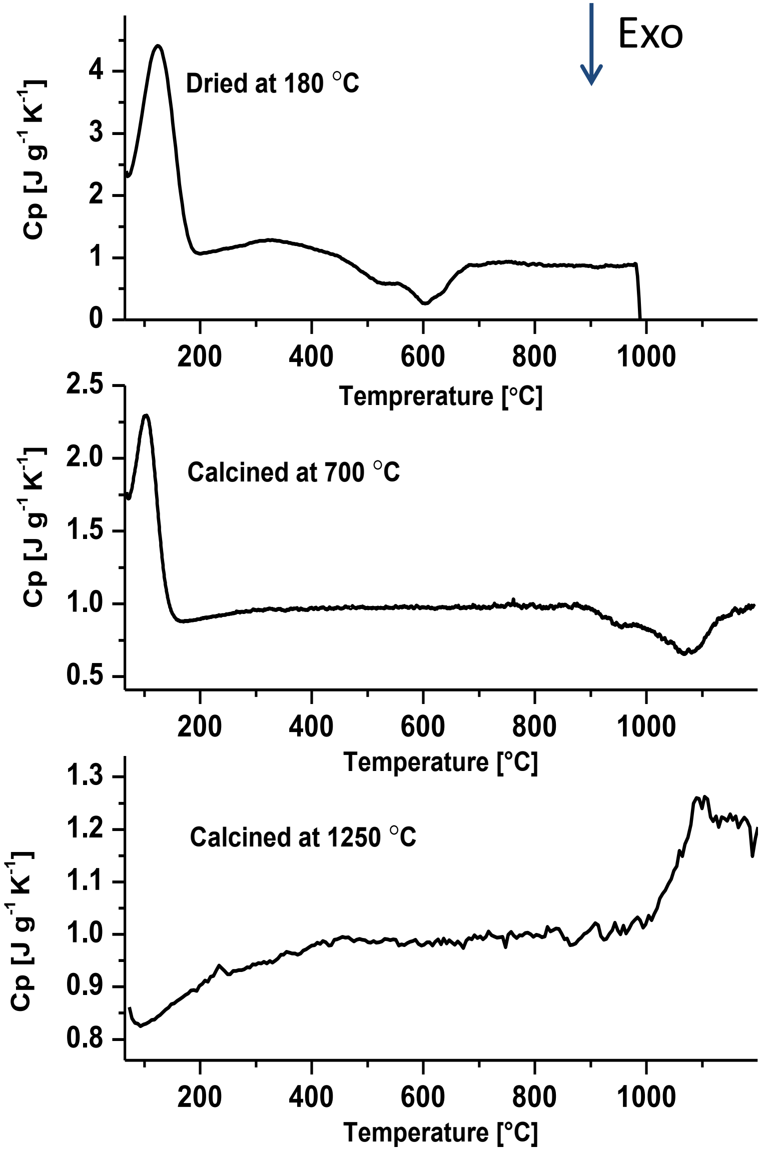


High free energy:

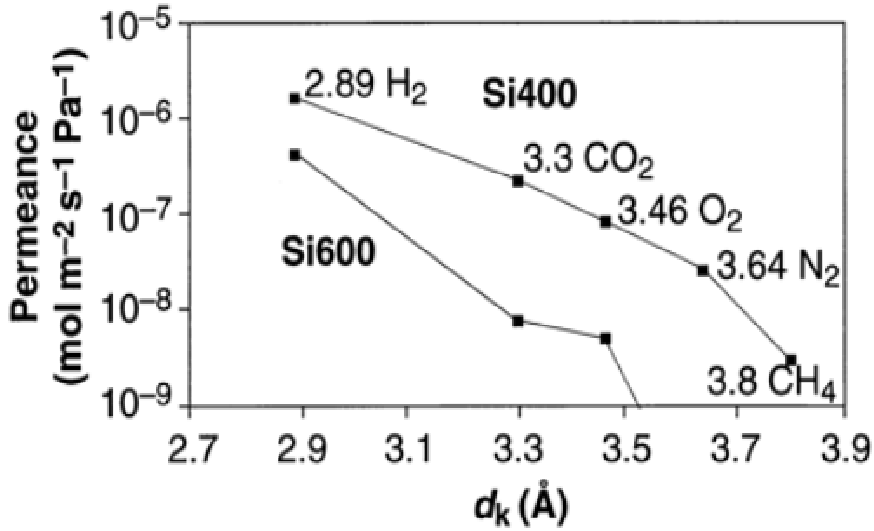
- Reduced cross linking
- High surface area
- High pore volume
- Strained SI-O-Si bonds

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

Calorimetric analysis



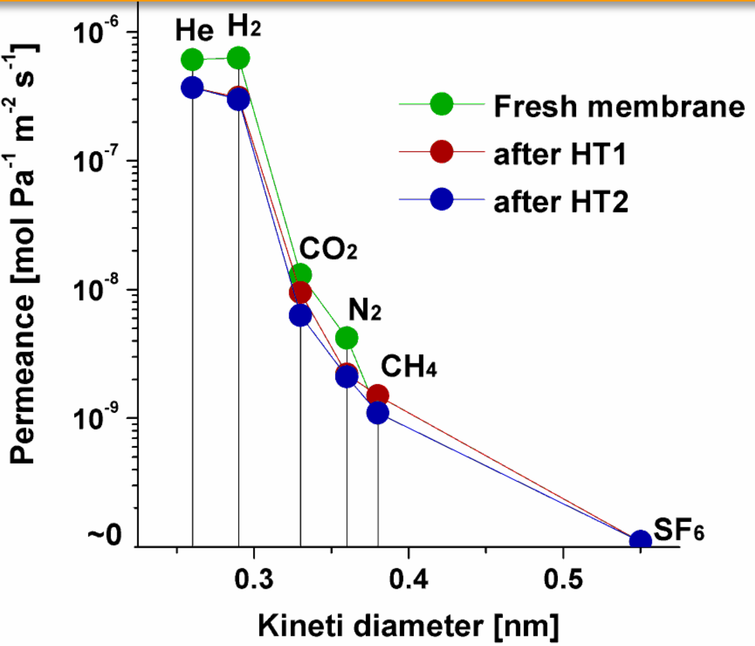
Single-gas permeation

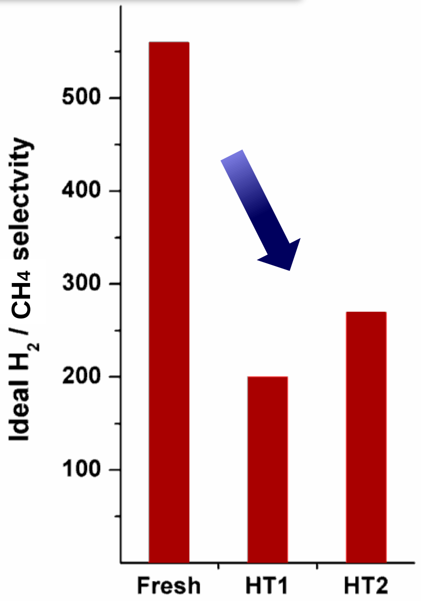


R.M. De Vos et al. Science 1998 (279) 5357

V. Boffa et al. In preparation

Gas–selective silica membranes

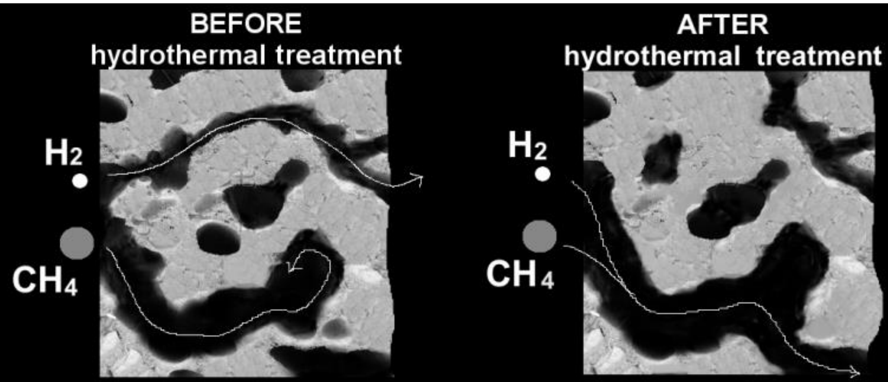




Hydrothermal treatment

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

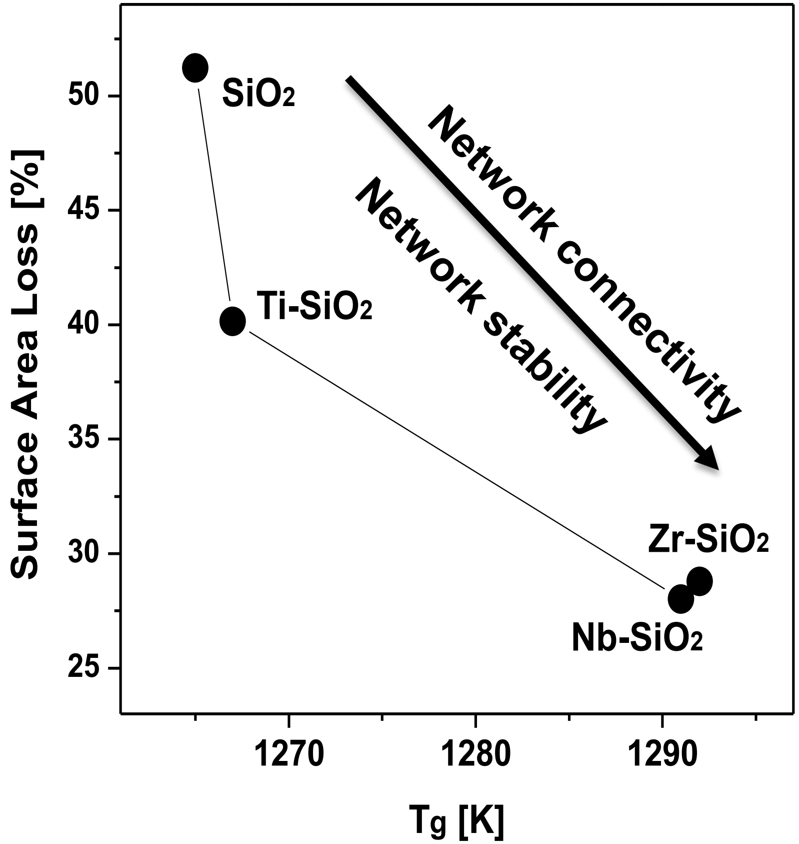
HT2: steam exposure (P_{H2O} = 0.56 bar) at 200 °C for 70 h.



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

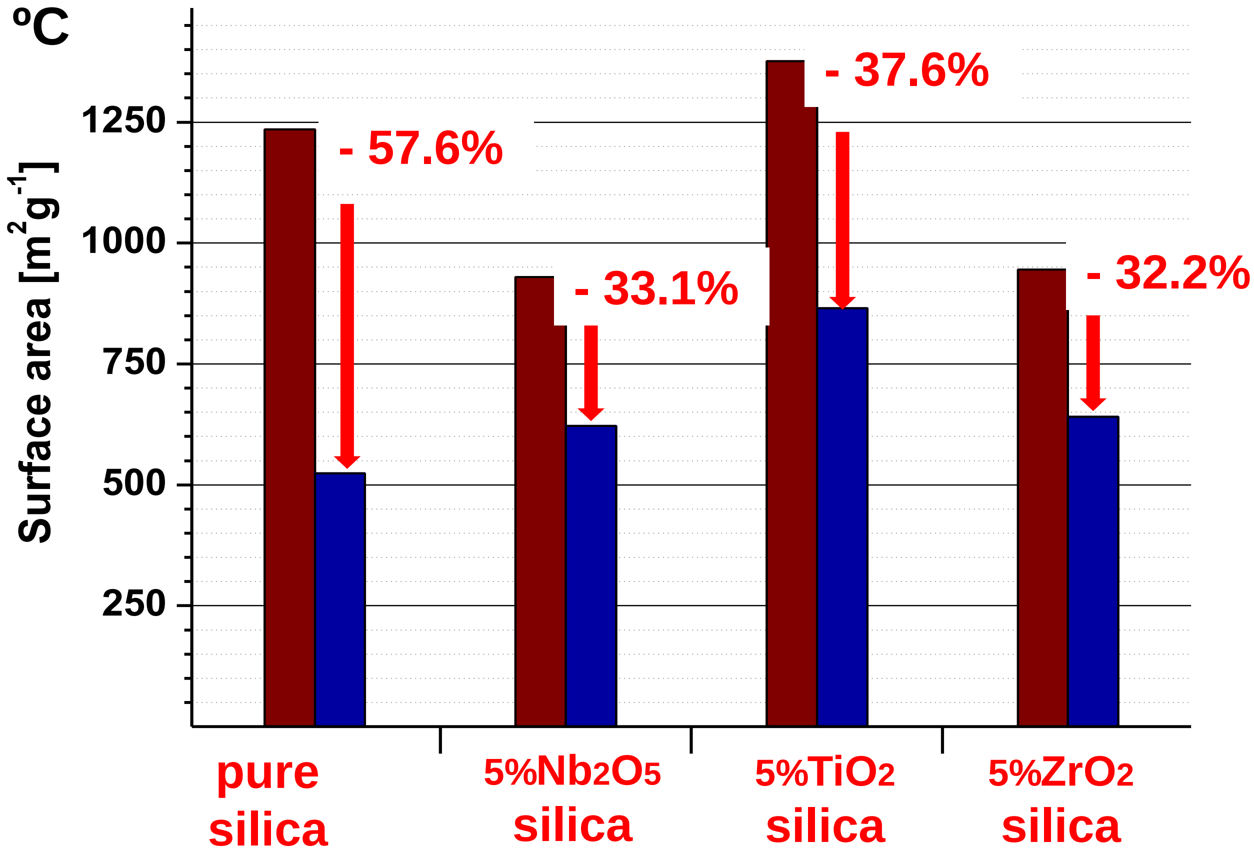
Gas–selective silica membranes

Stabilization by doping



Glass transition temperature [K]

1 day at 120 ºC in steam

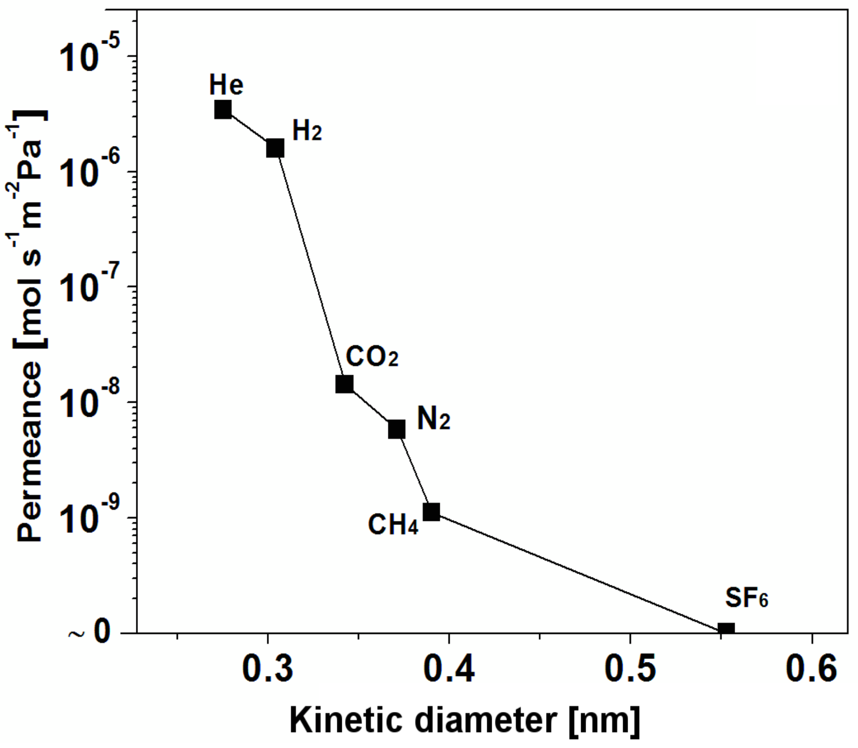


- TiO_2 doping: high membrane permeability.
- ZrO_2 and Nb_2O_5-doped: if stability is more important than permeability.

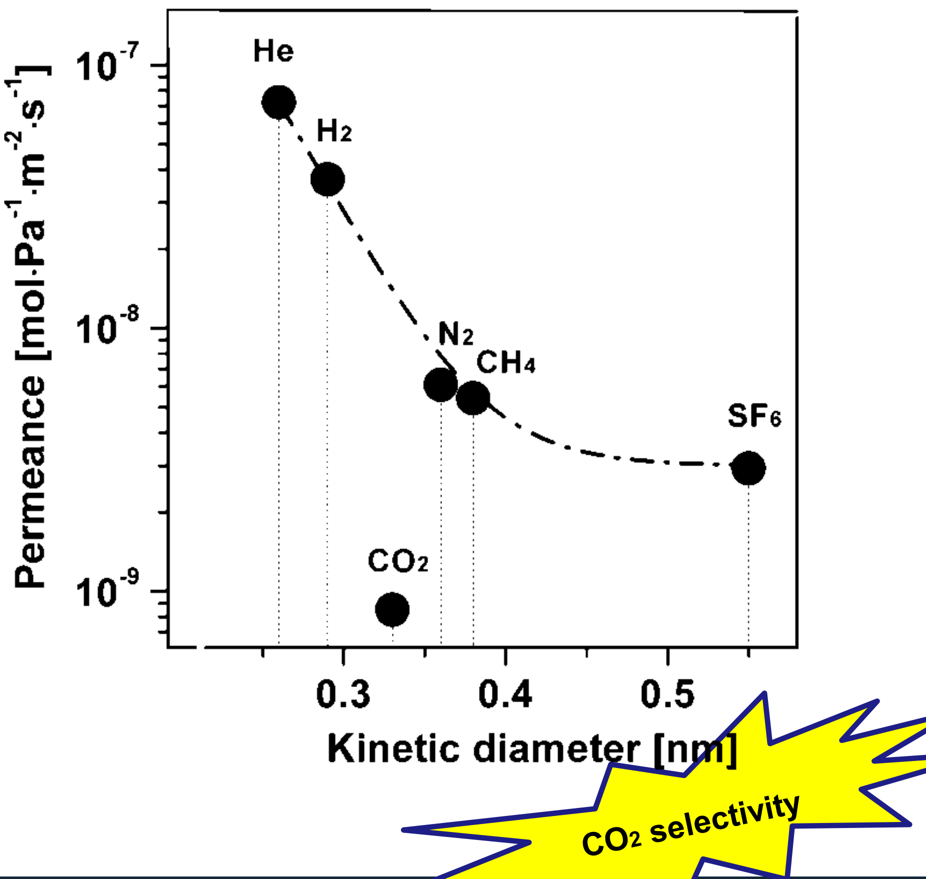
Gas–selective silica membranes

Functional membranes

Pure silica



Nb_2O_5-silica (Nb:Si = 1:2)

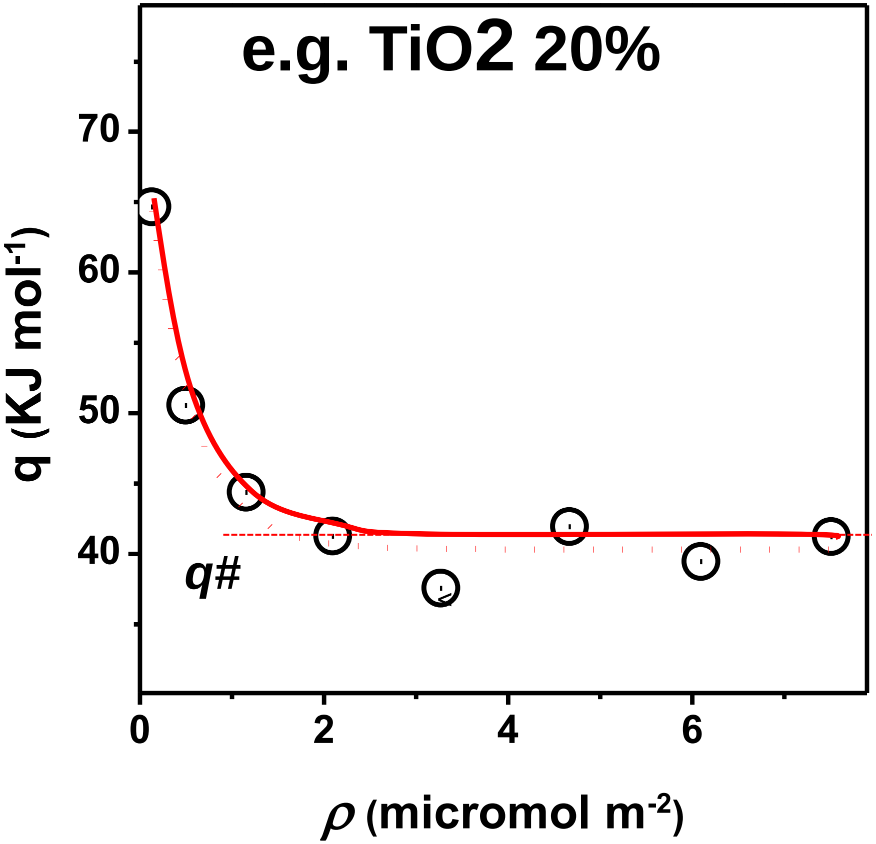


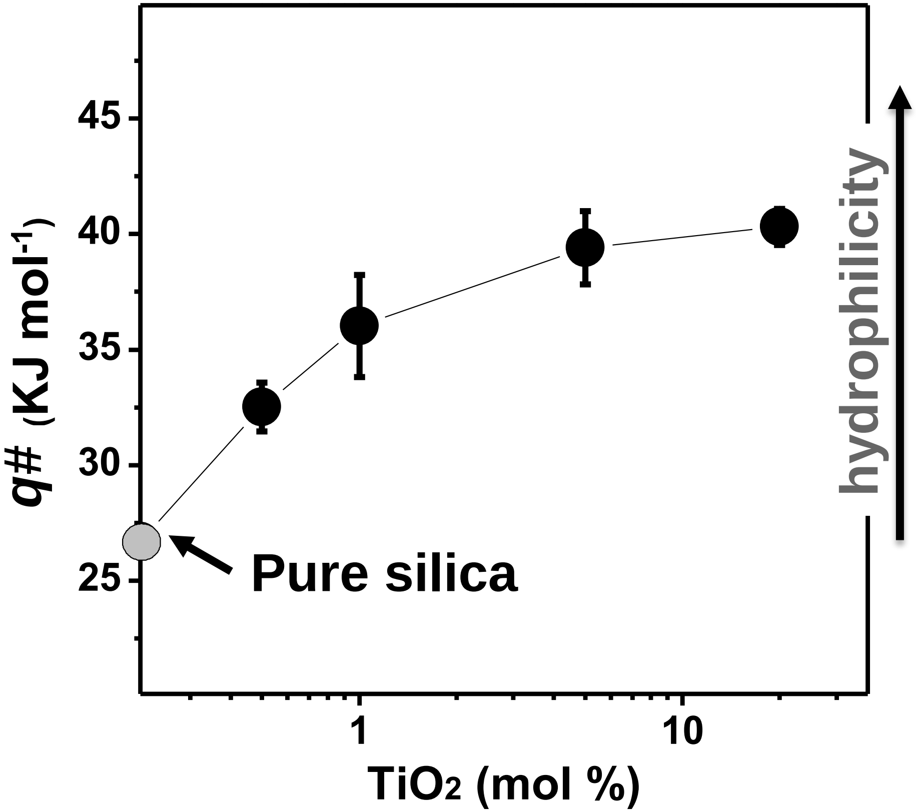
V. Boffa et al. ChemSusChem 2008 (1) 437

Functional membranes

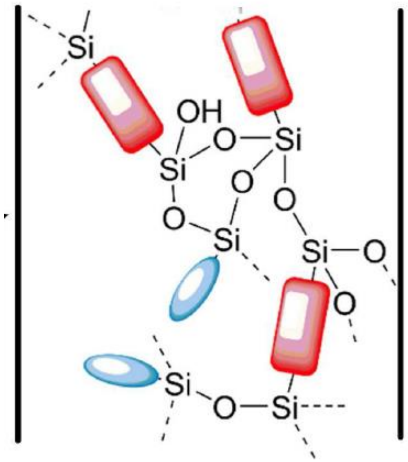
Water interaction: adsorption calorimetry

$$q\ (\rho) = (q_0 - q_e)\ exp(-\rho/\rho_c) + q_e$$

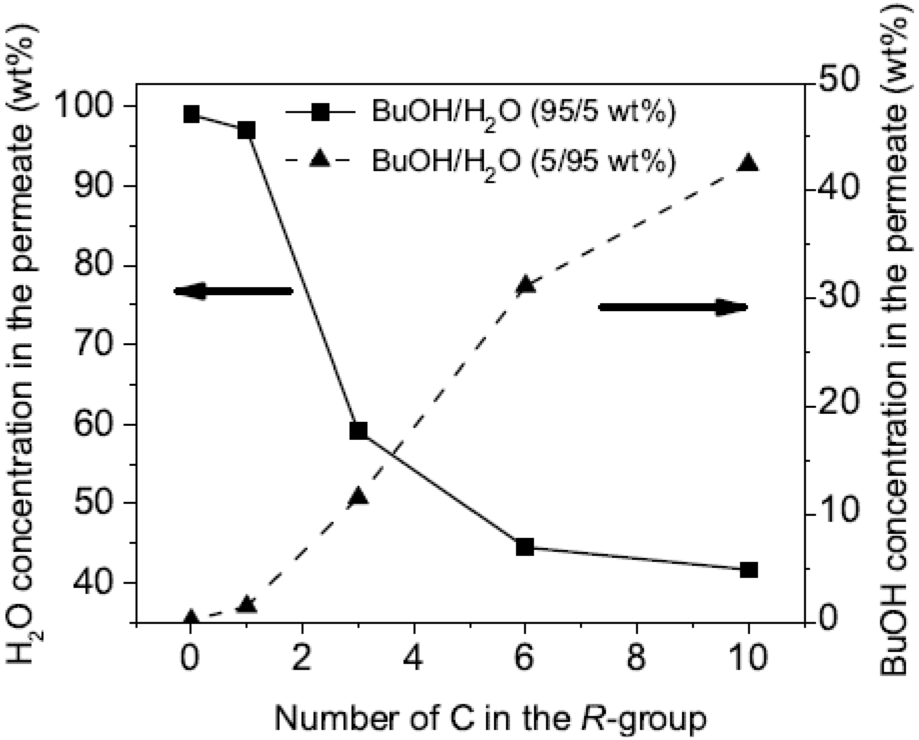




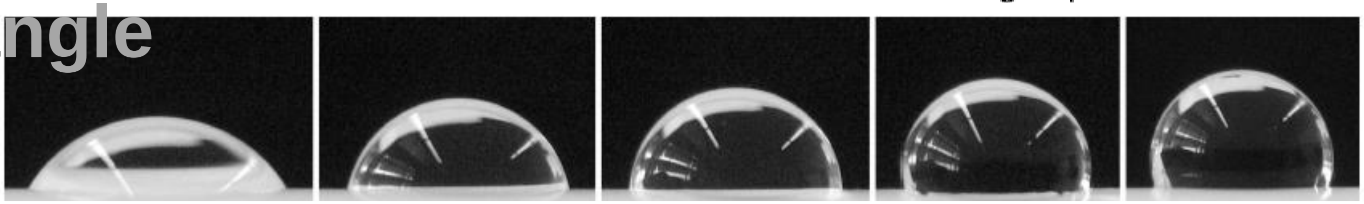
Hybrid organosilica



Pervaporation experiments: (water-butanol)



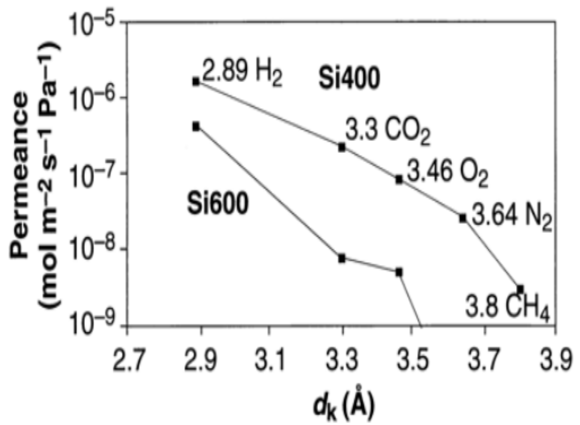
Contact angle



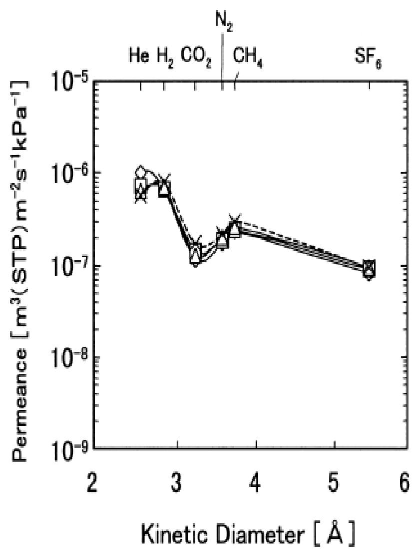
0 1 3 6 10

Number of C in the *R*-group

Gas–selective silica membranes

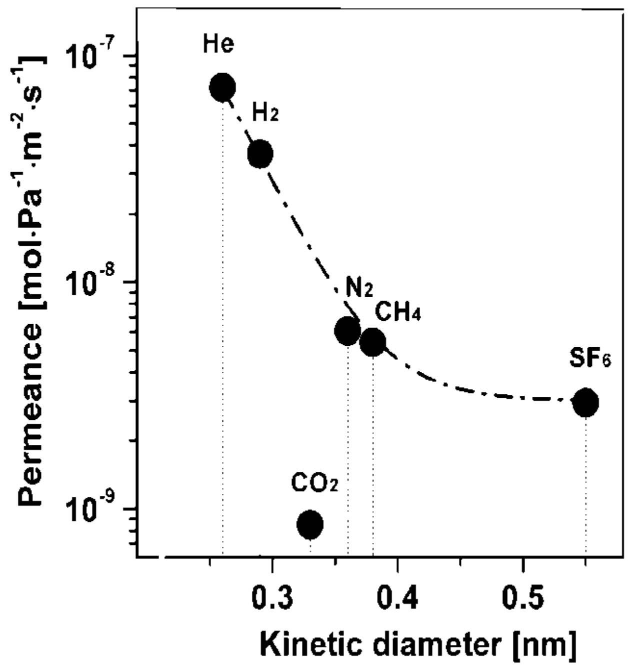


´R.M. De Vos et al. 1998 Science. 279, 5357.



(c) S5–Z5

M. Asaeda et al. 2001 J. Chem. Eng. Jap. 4, 523.



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

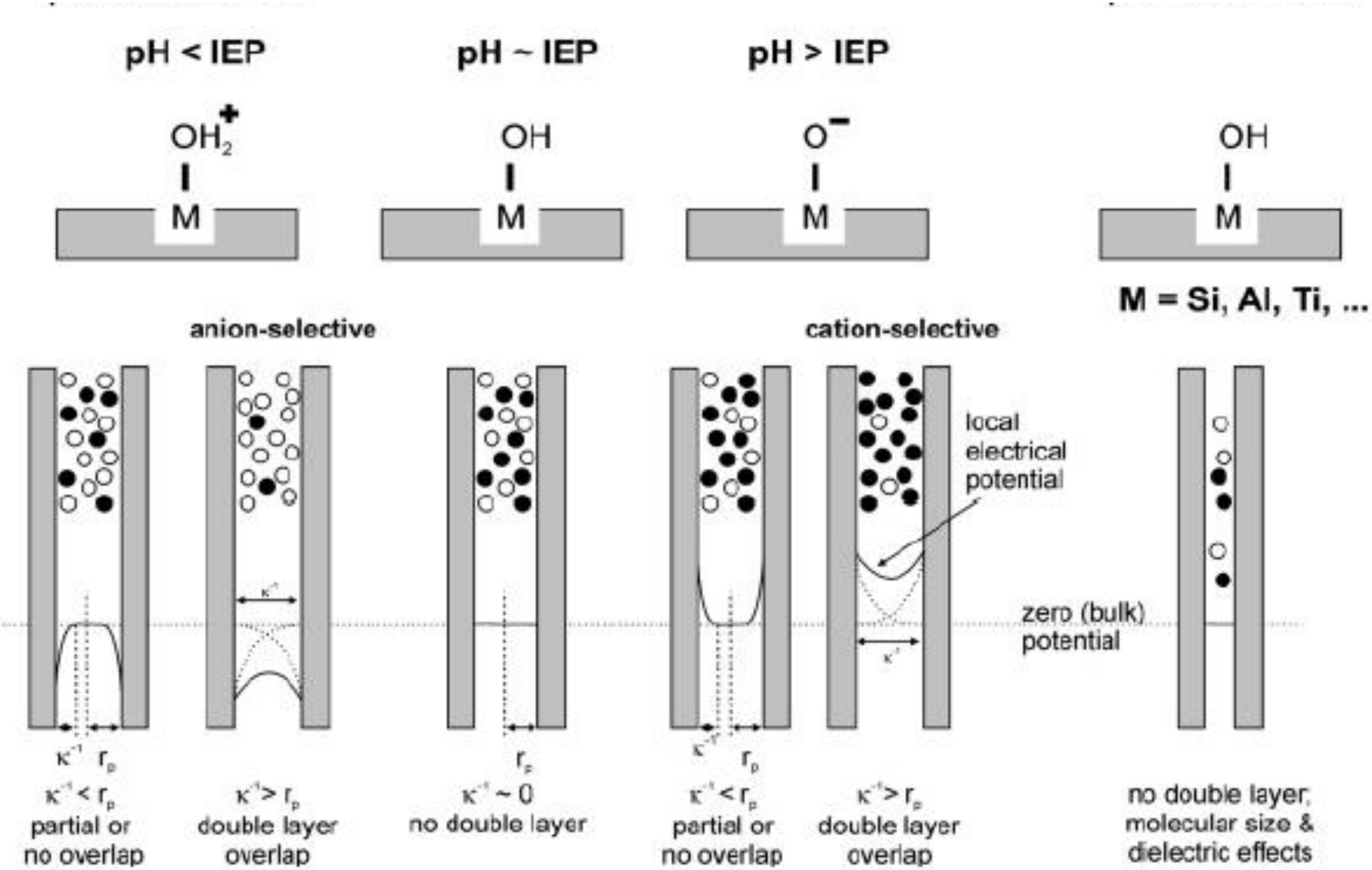
Stable membranes

Defect-free membranes

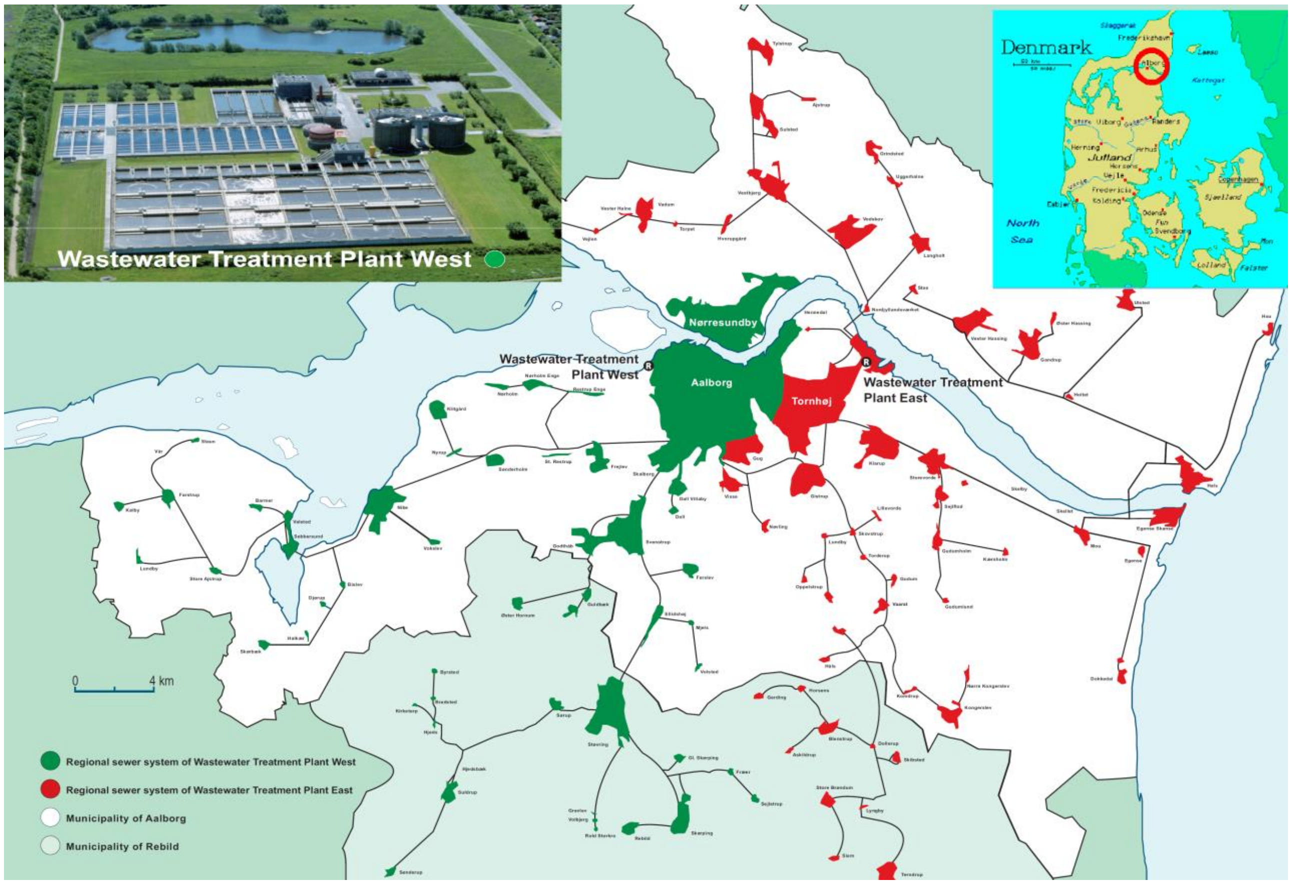
Functional membranes

1980 1990 2000 2010

Nanofiltration - Ultrafiltration

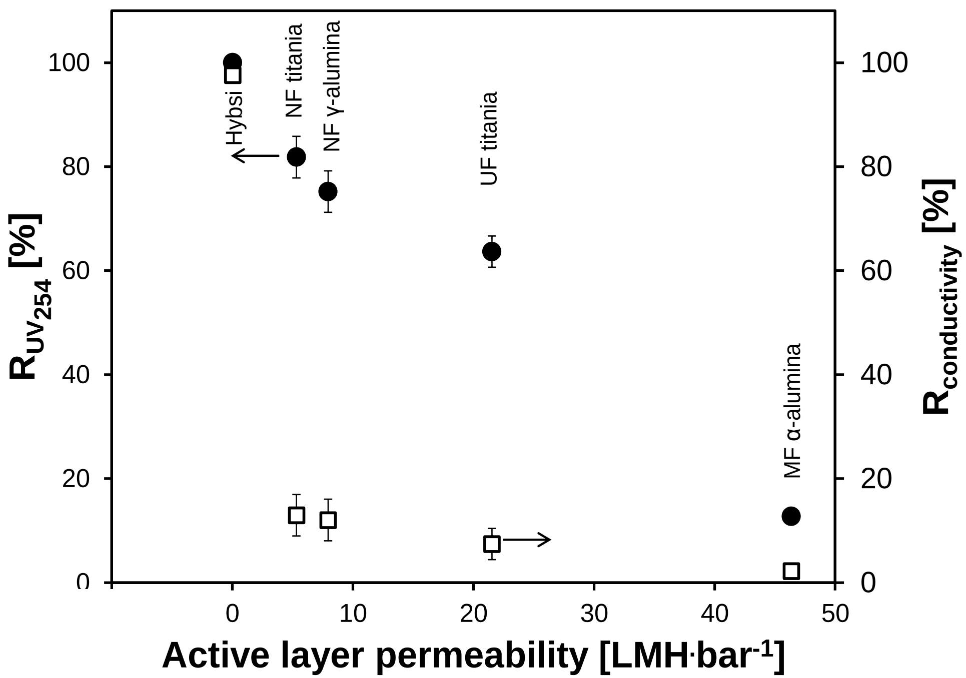


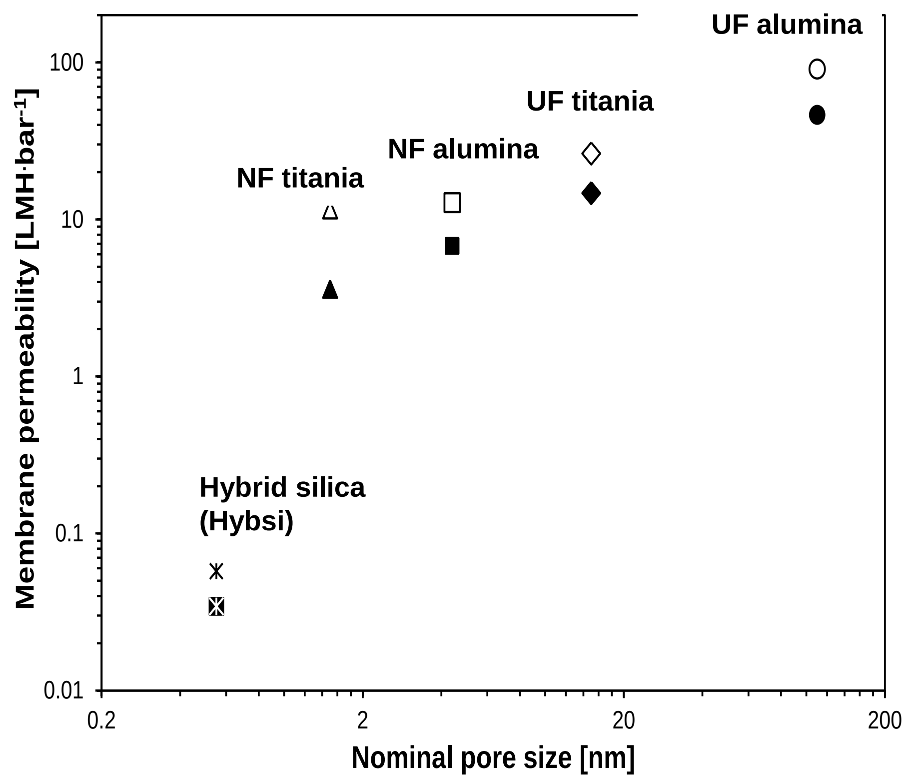
Tertiary treatment



Aalborg WEST WWTP plan

Tertiary treatment





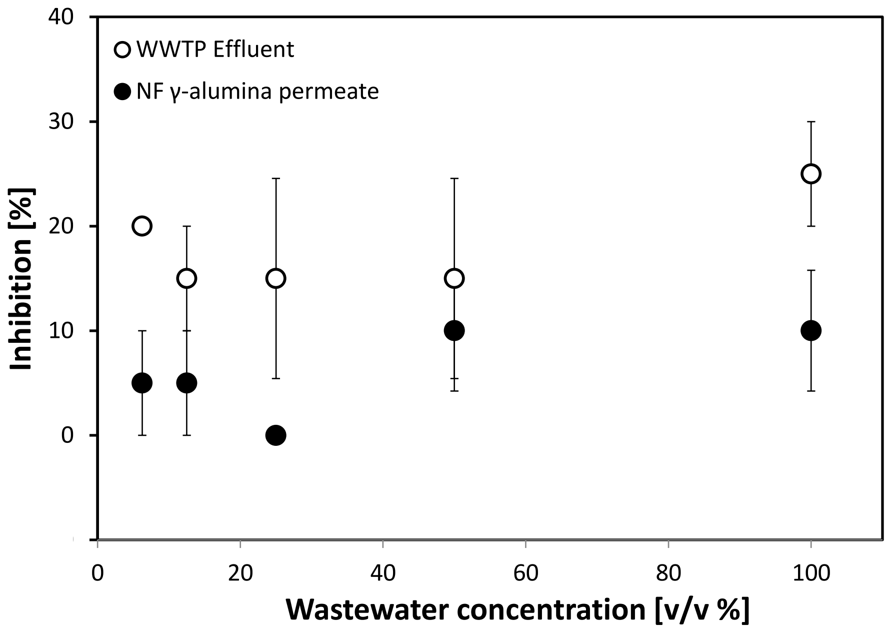
TMP= 6 bar

A. Farsi et al., Ind. Eng. Chem. Res., 54 (2015) 3462–3472

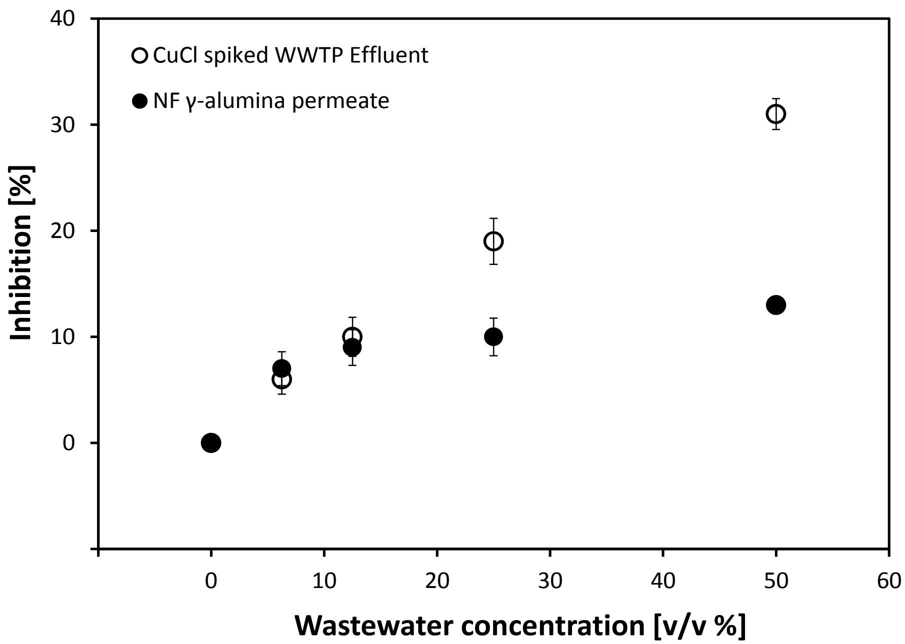
Tertiary treatment

Toxicity tests

D. magna



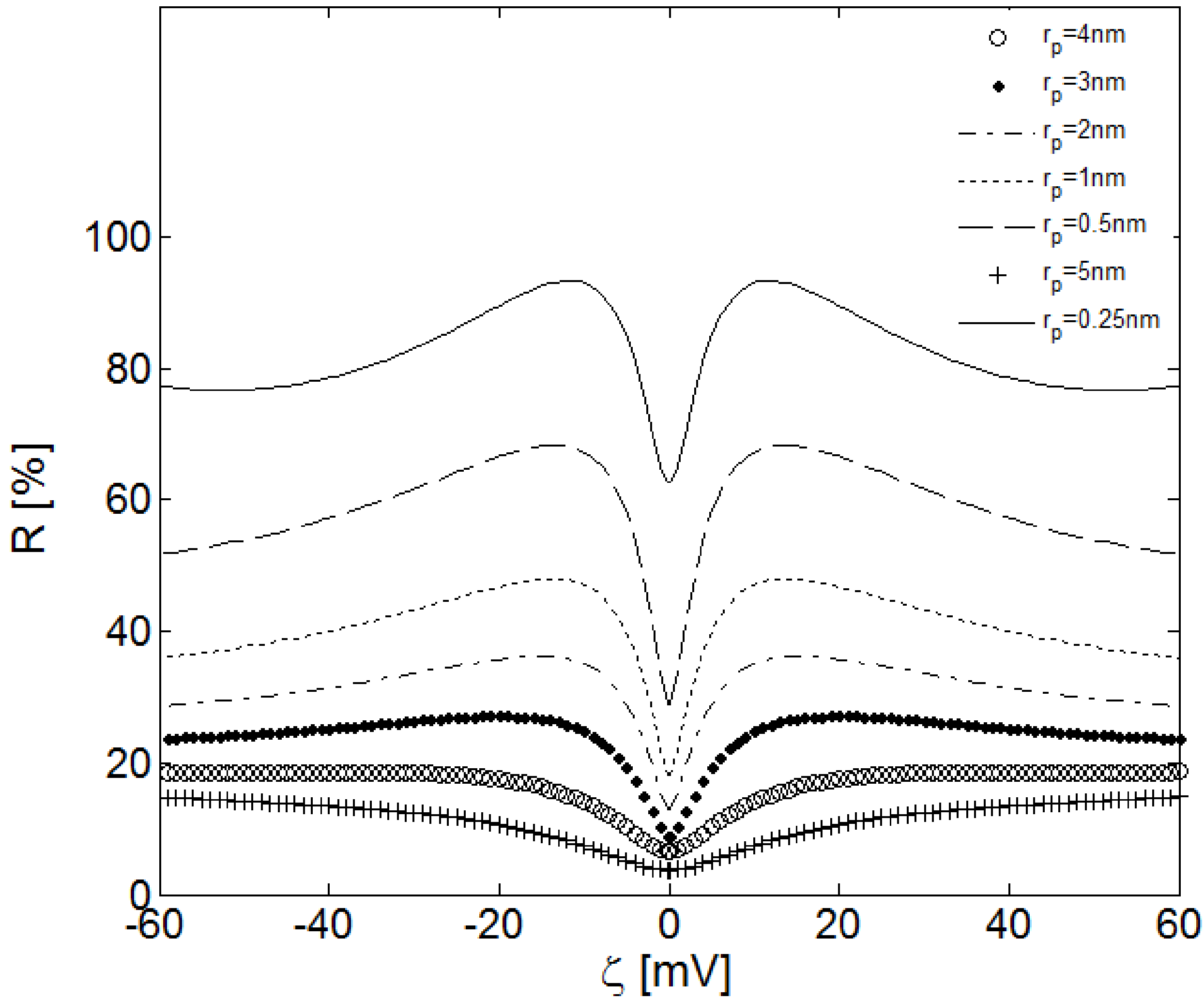
A. fischeri (CuCl spiked)



A. Farsi et al., Ind. Eng. Chem. Res., 54 (2015) 3462–3472.

Desalination

Sodium chloride rejection

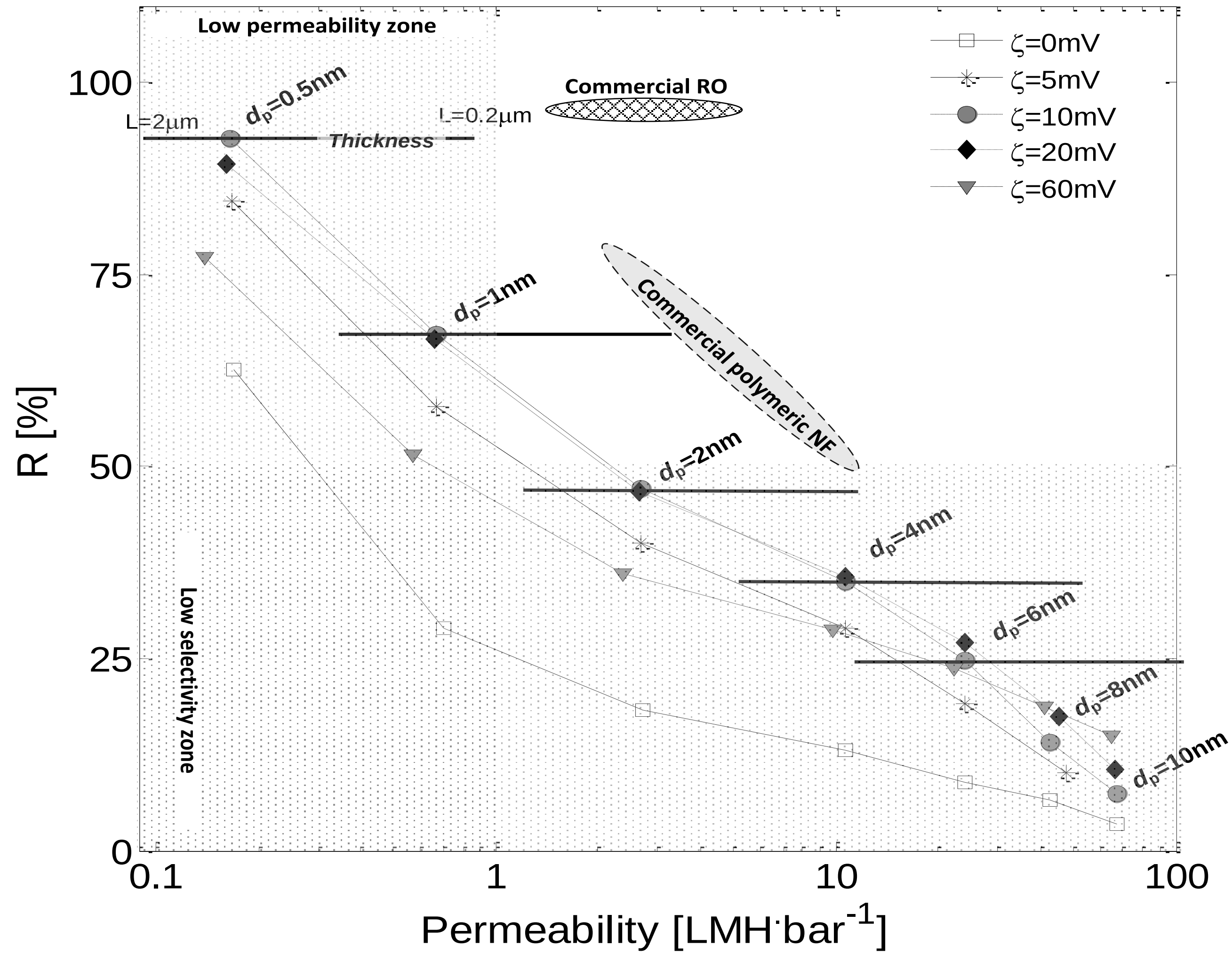


Transport governed by:

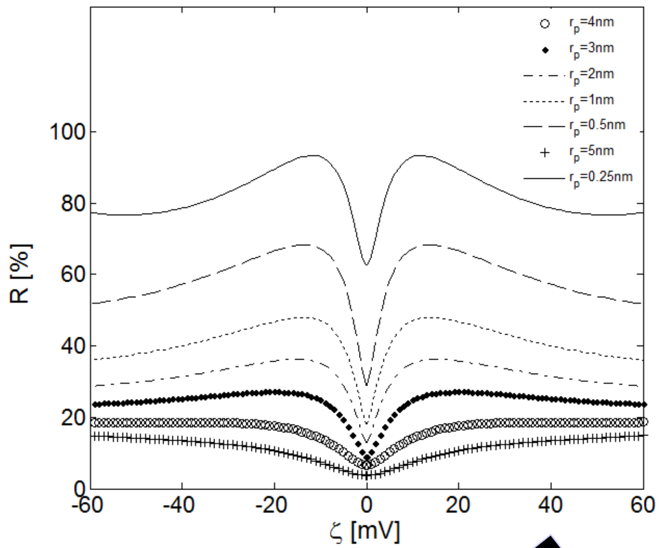
- **Convection;**
- **Diffusion;**
- **Electromigration**

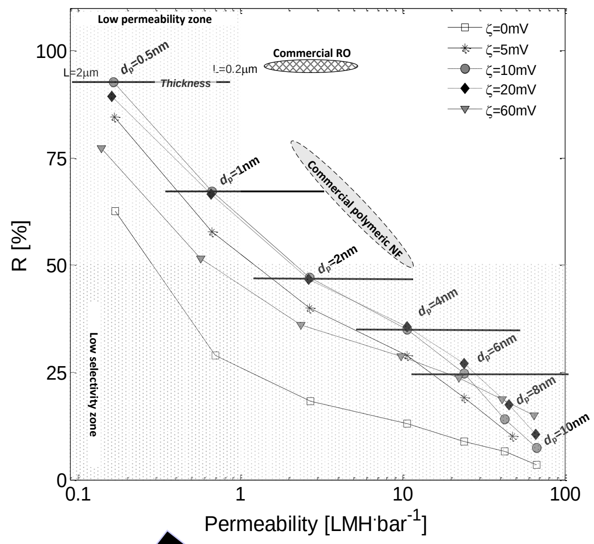
Electroviscous effect

Desalination



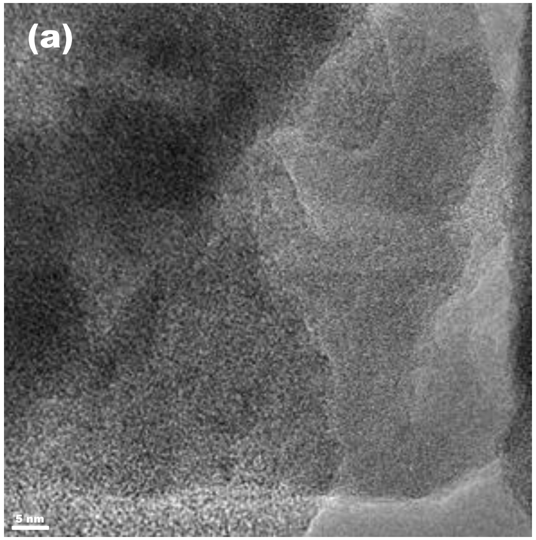
Desalination

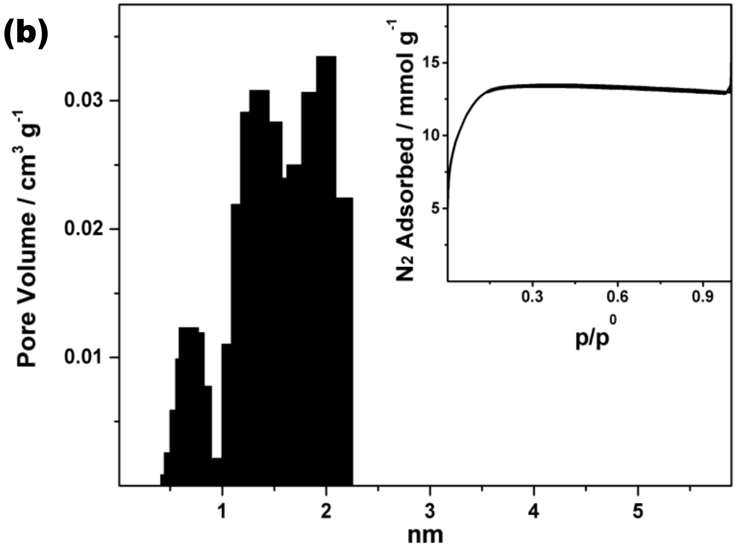




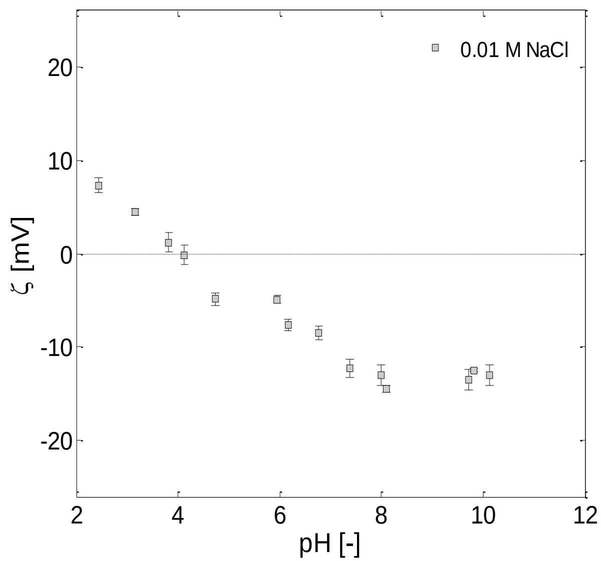
Fabrication criteria

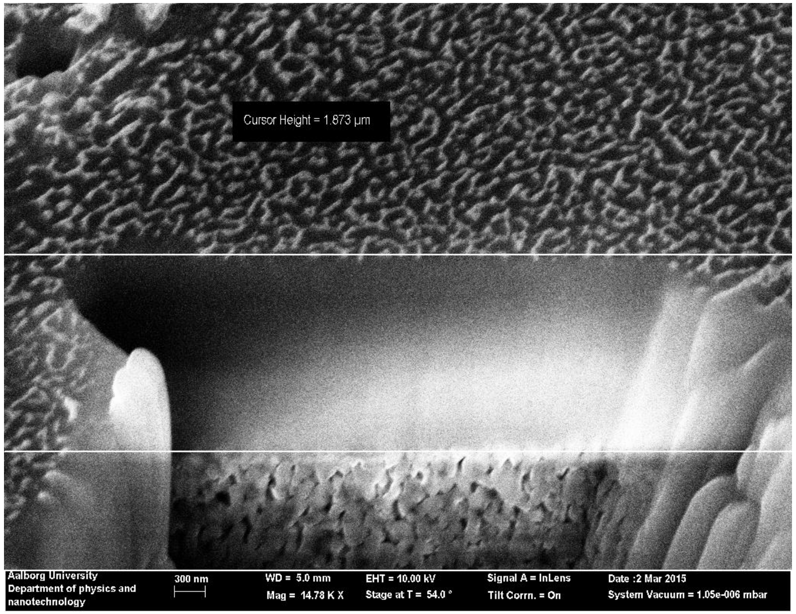
- Pore size: 1-2 nm;
- membrane thickness: < 1 µm;
- optimum |ζ| at pH and ionic strength suitable for desalination applications.





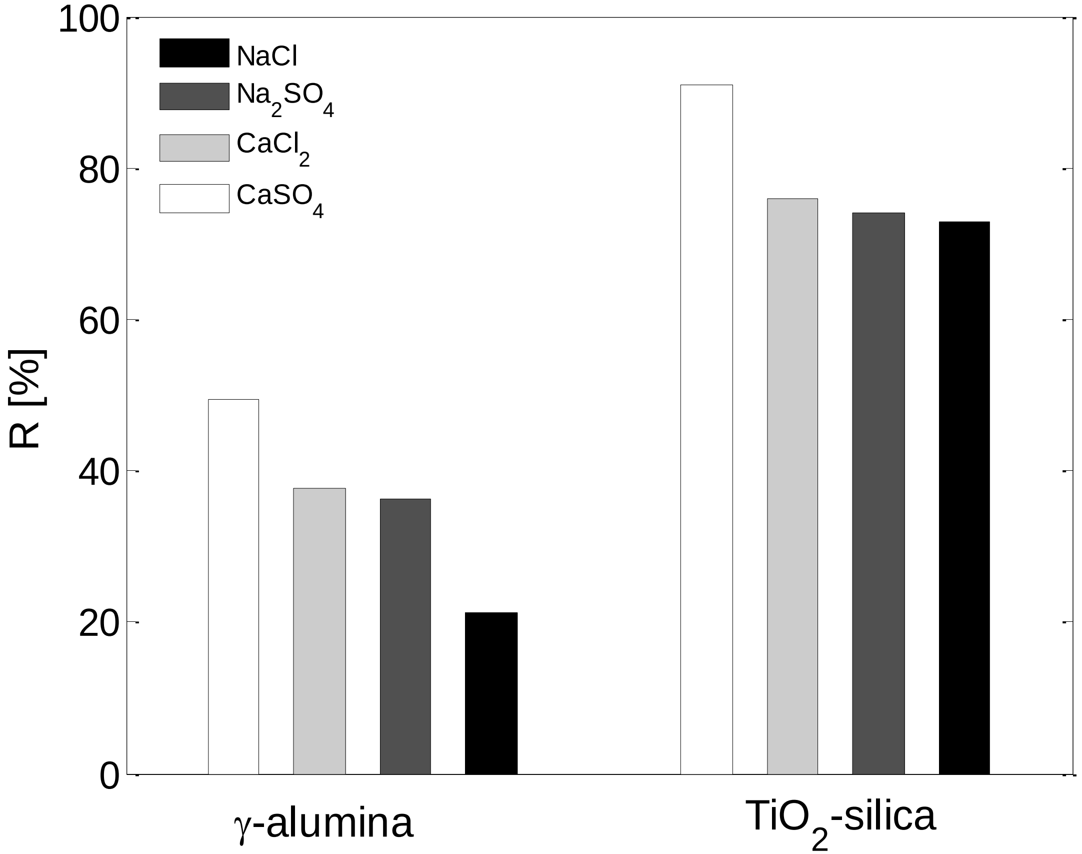
Surfactant templated TiO2-doped silica membrane



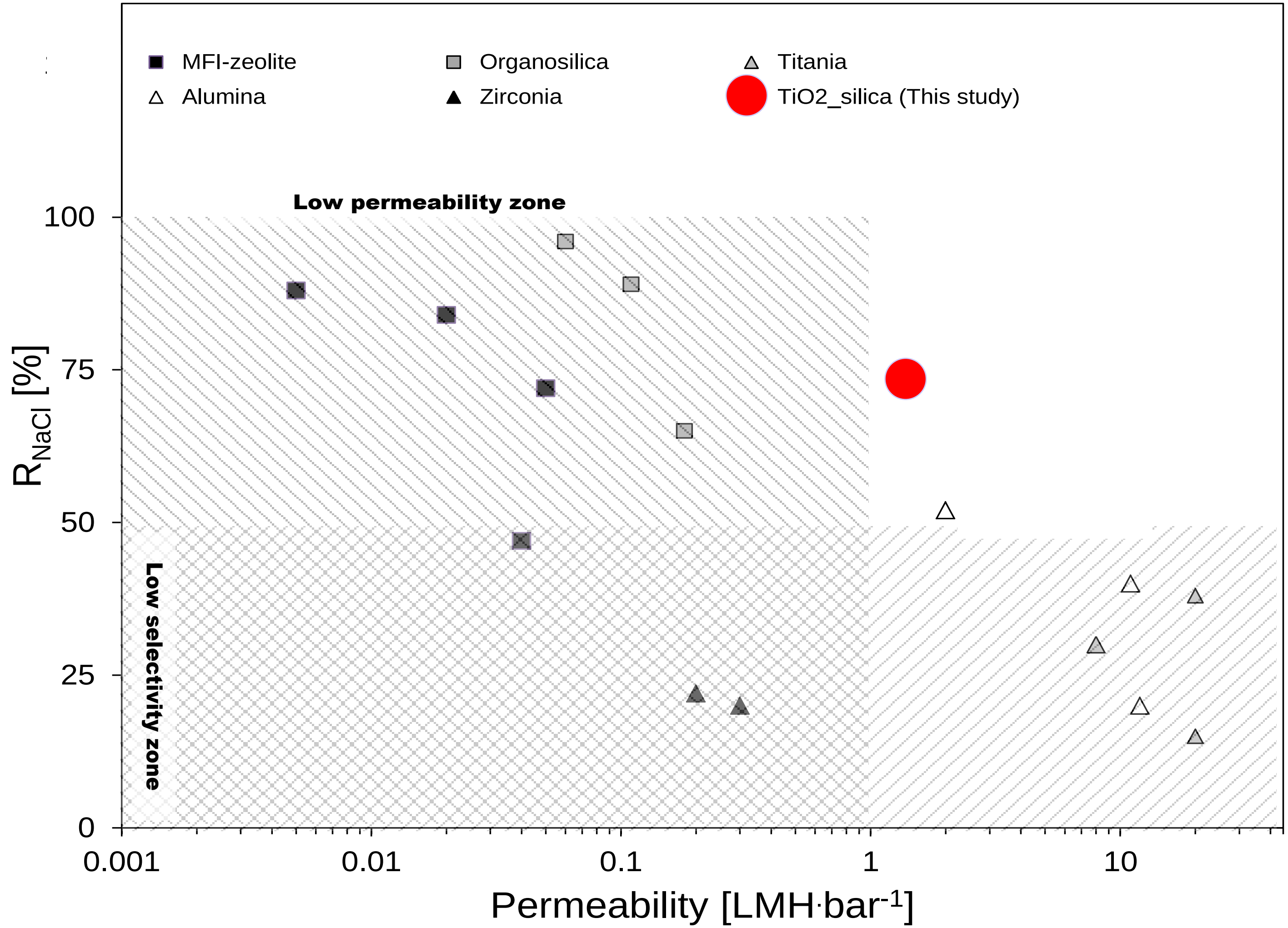


A. Farsi et al. , J. Membrane Sci., under review

Desalination

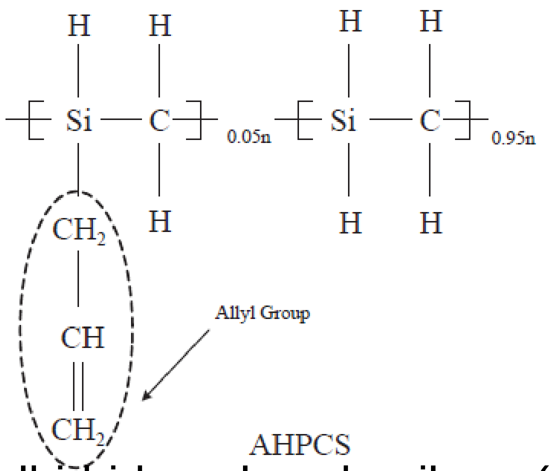


(ΔP=4-10bar, T=20-30°C and pH=5-7).

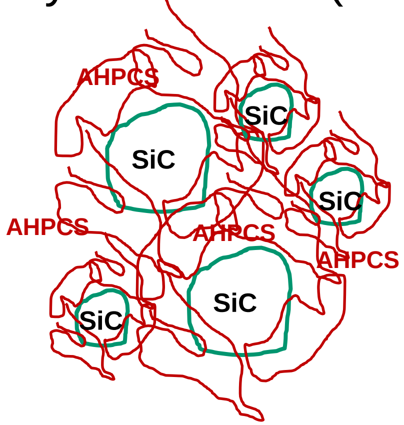


A. Farsi et al. , J. Membrane Sci., under review

SiC membranes



Allylhidrido polycarbosilane (AHPCS)

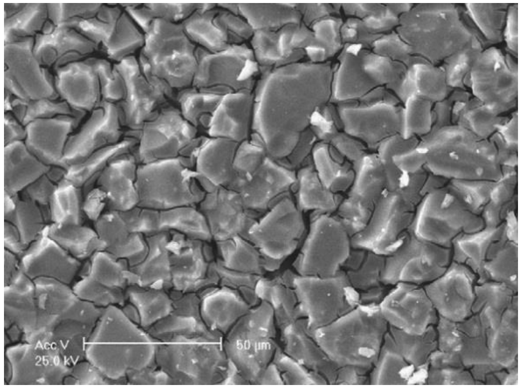


Ultrastable nanofiltration membranes

Silicon Carbide (SiC) is a highly covalent material with high melting point, hardness, and chemical stability

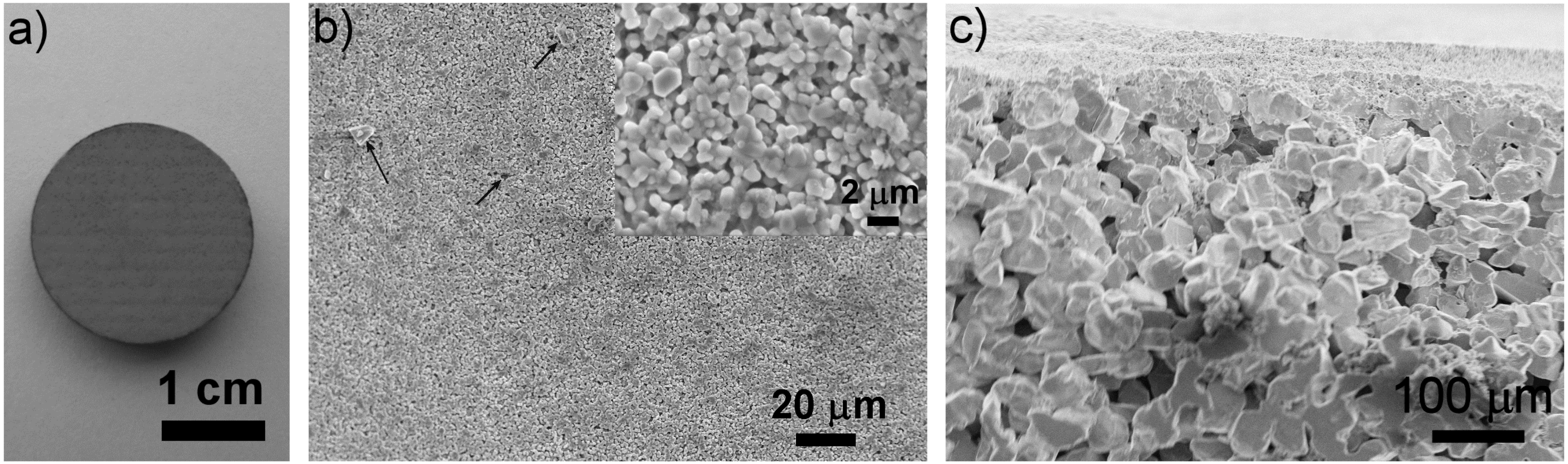
PYROLYSIS

750°C, Ar



R.J. Ciora et al., Chemical Engineering Science 59 (2004) 4957-4965
A. R. Maddocks et al., Materials Chemistry and Physics 113 (2009) 861–86

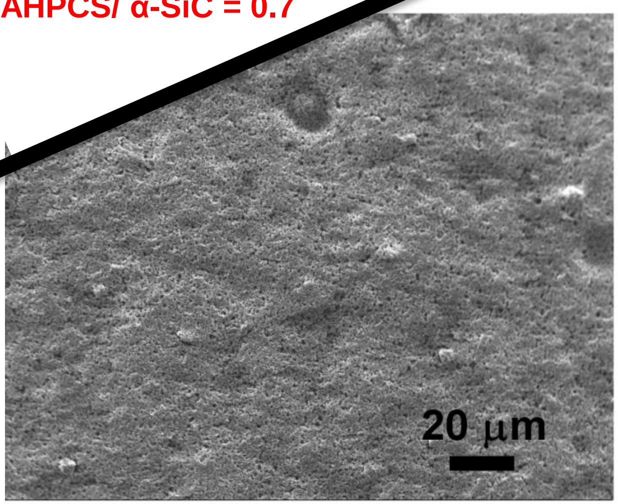
SiC membranes



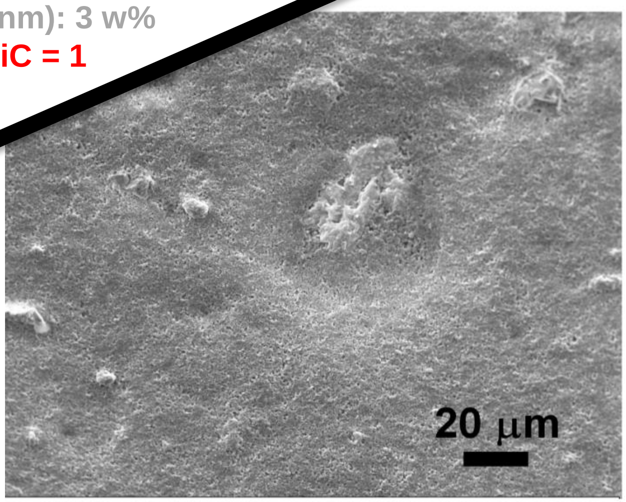
SiC membranes

Coating suspension:
1) Solvent: alkane
2) Filler: α-SiC (200 nm)
3) Precursor: AHPCS

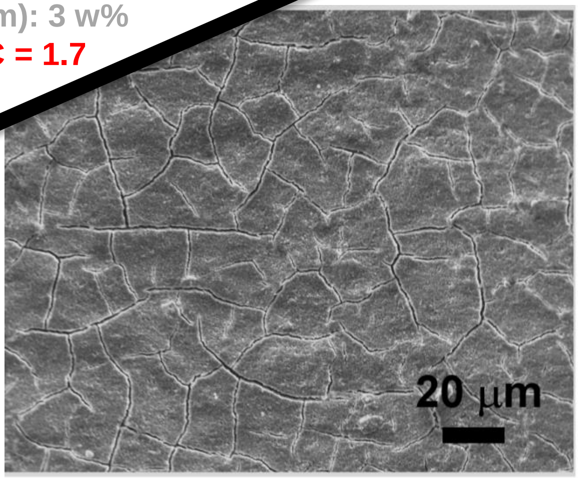
1) n-hexane/ tetradecane (70:30)
2) α-SiC (200 nm): 3 w%
3) AHPCS/ α-SiC = 0.7



1) n-hexane/ tetradecane (70:30)
2) α-SiC (200 nm): 3 w%
3) AHPCS/ α-SiC = 1

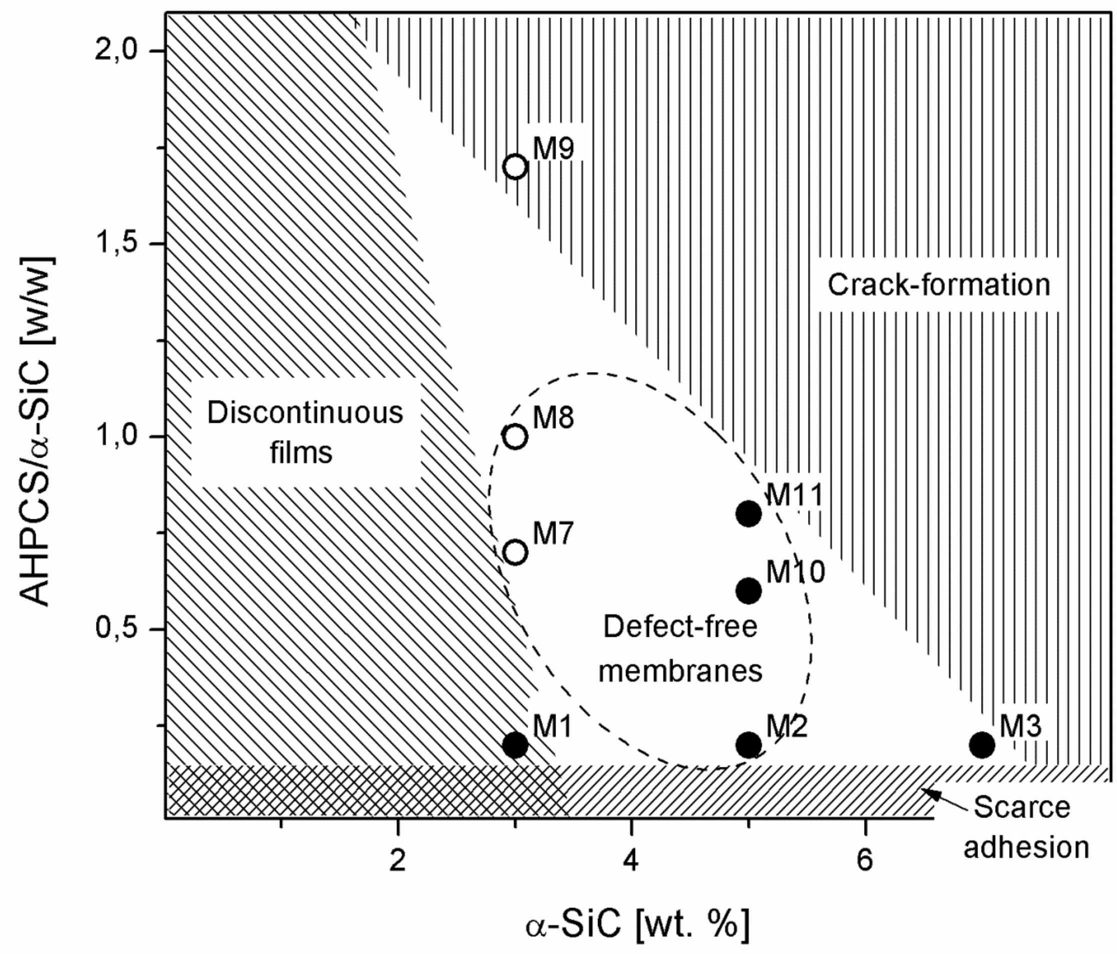


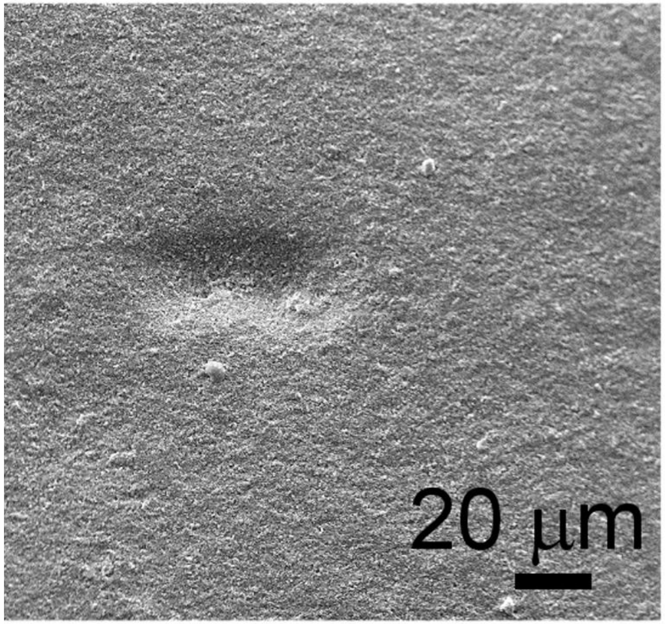
1) n-hexane/ tetradecane (70:30)
2) α-SiC (200 nm): 3 w%
3) AHPCS/ α-SiC = 1.7



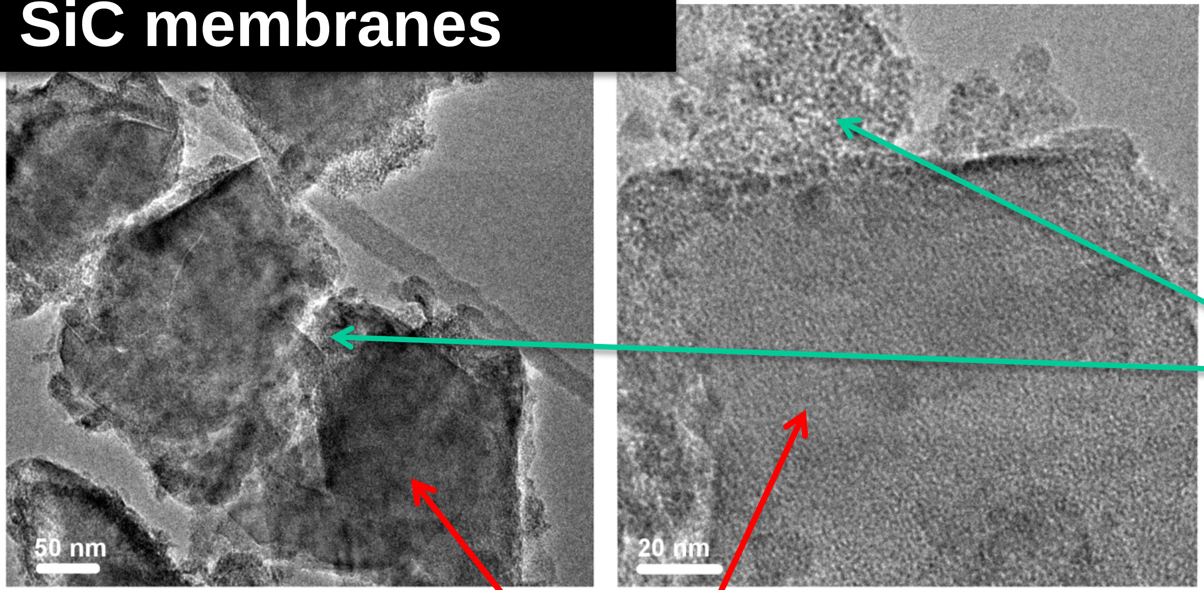
K. König et al., Journal of Membrane Science, 472 (2014) 232–240

SiC membranes



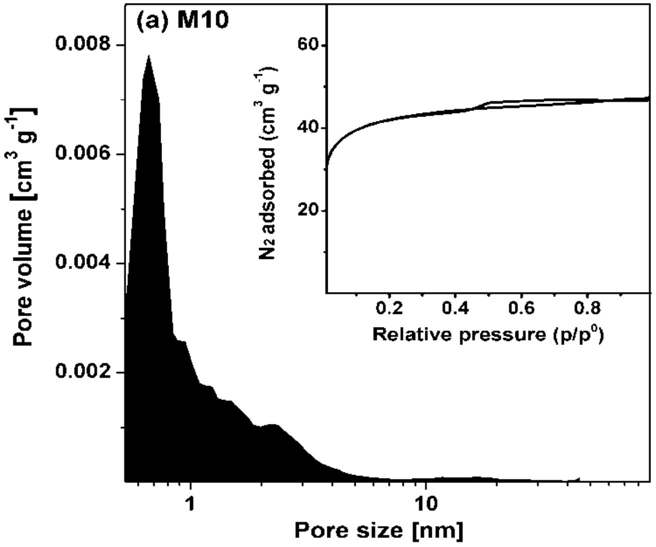


SiC membranes

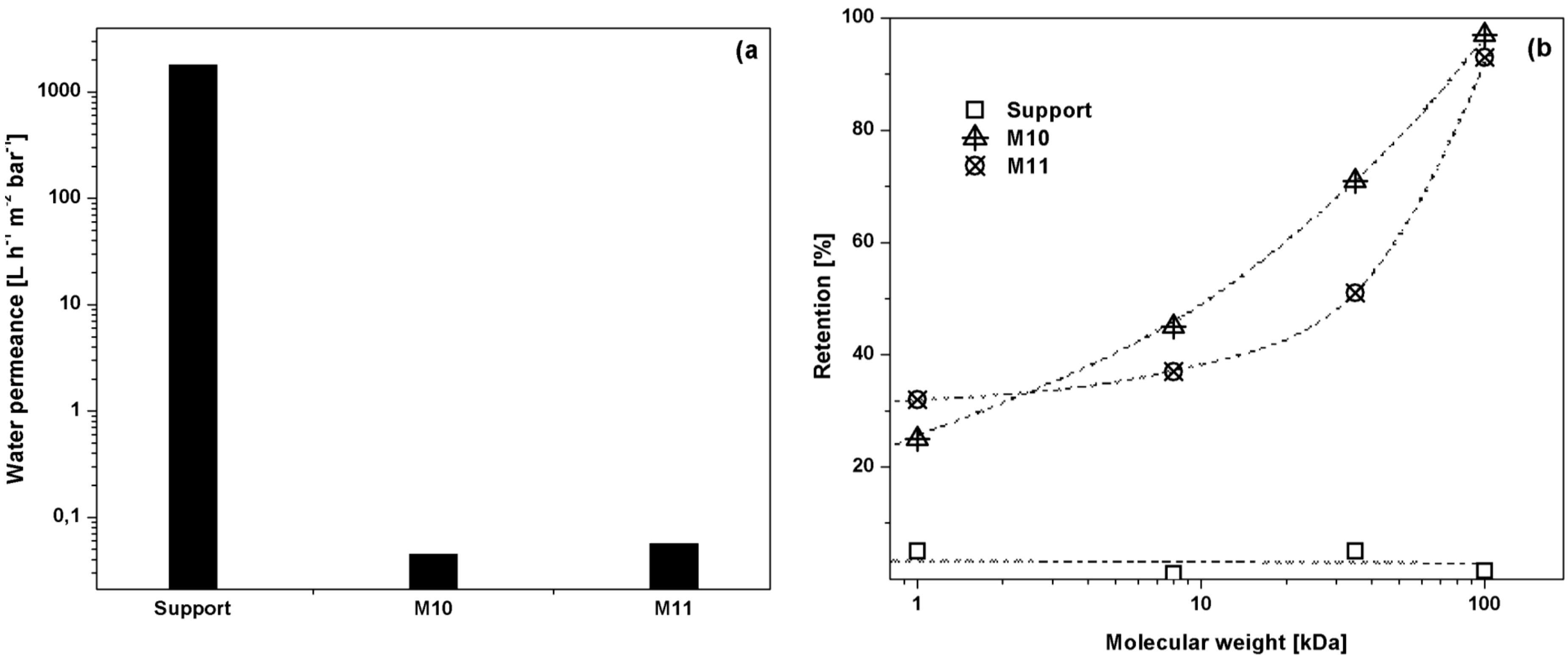


Porous amorphous SiC

α-SiC crystals



SiC membranes

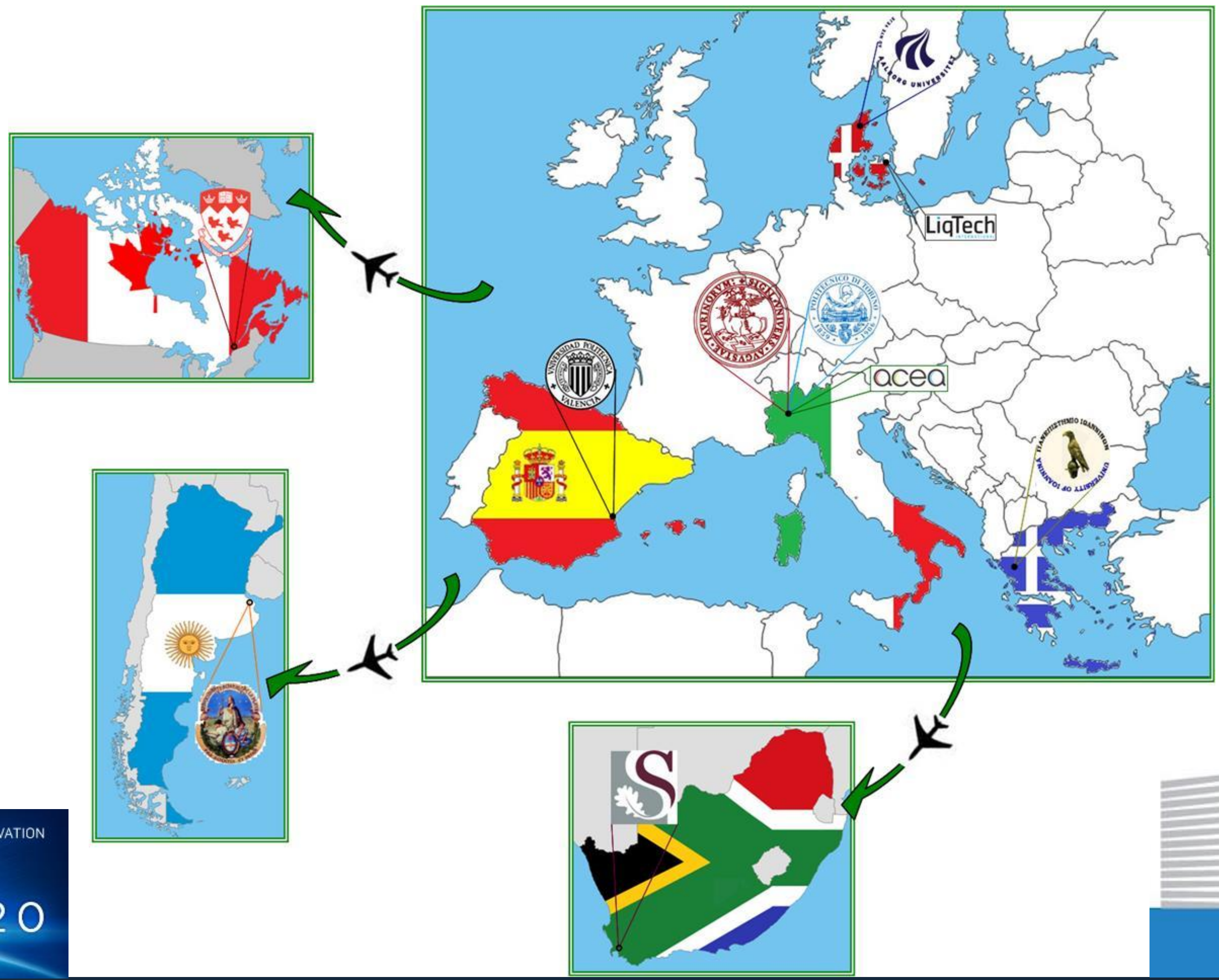


K. König et al., Journal of Membrane Science, 472 (2014) 232–240.

MAT4TREAT AALBORG UNIVERSITET

«Enhancing water quality by developing novel materials for organic pollutant removal in tertiary water treatment»

MSCA-RISE-2014: Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) Grant Agreement no: 645551

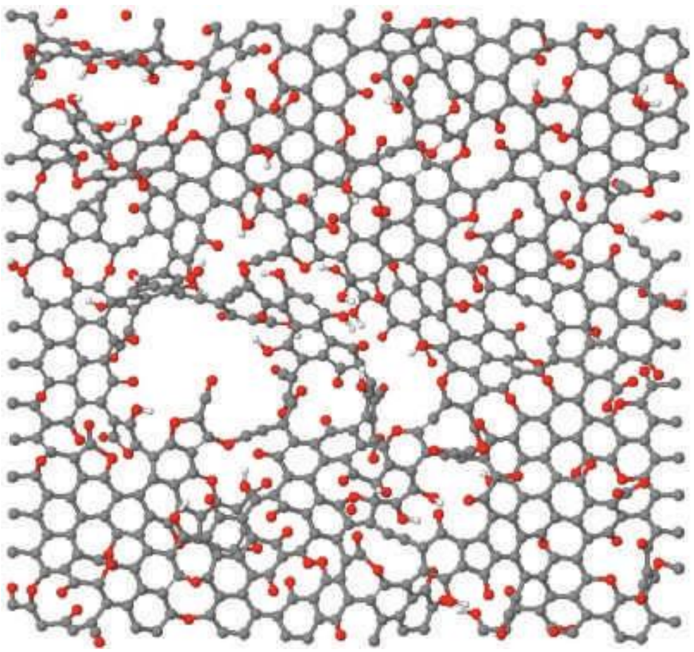


THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020

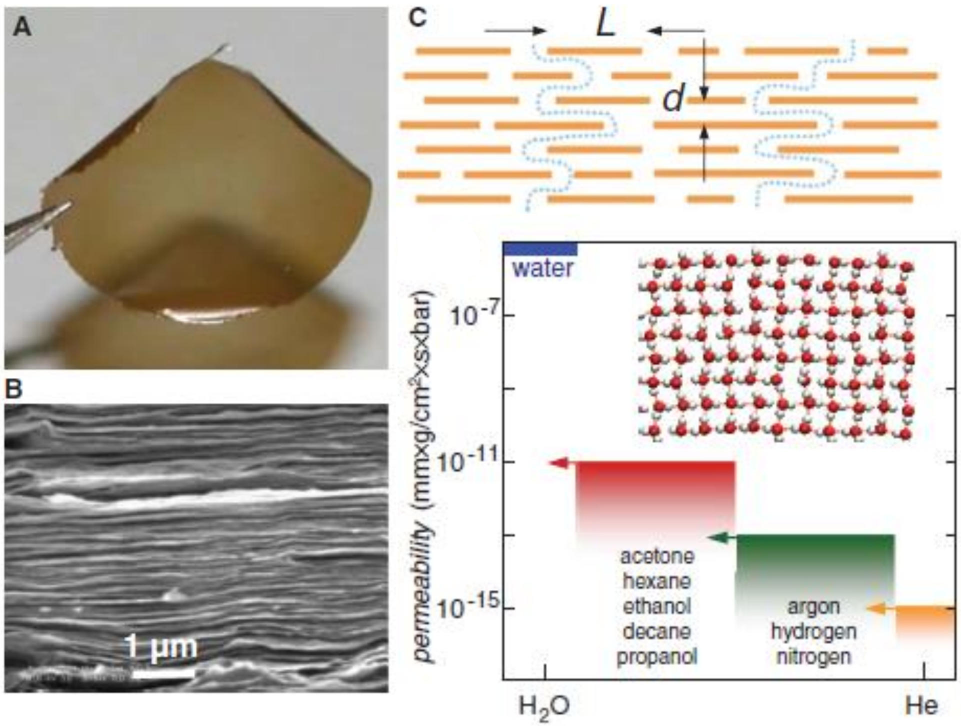
European Commission

GO membranes

Graphene oxide (GO) membranes



K.P. Loh et. al. Nature Chemistry 2 (2010) 1015

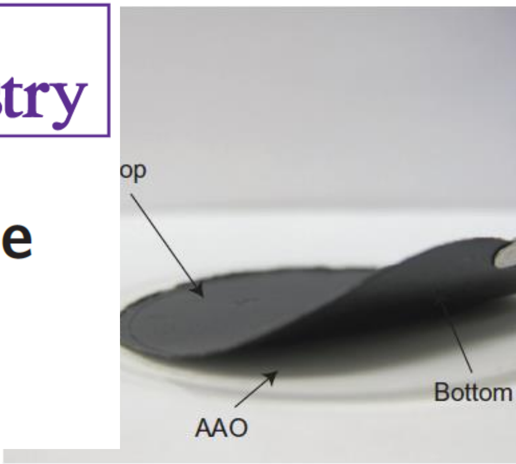


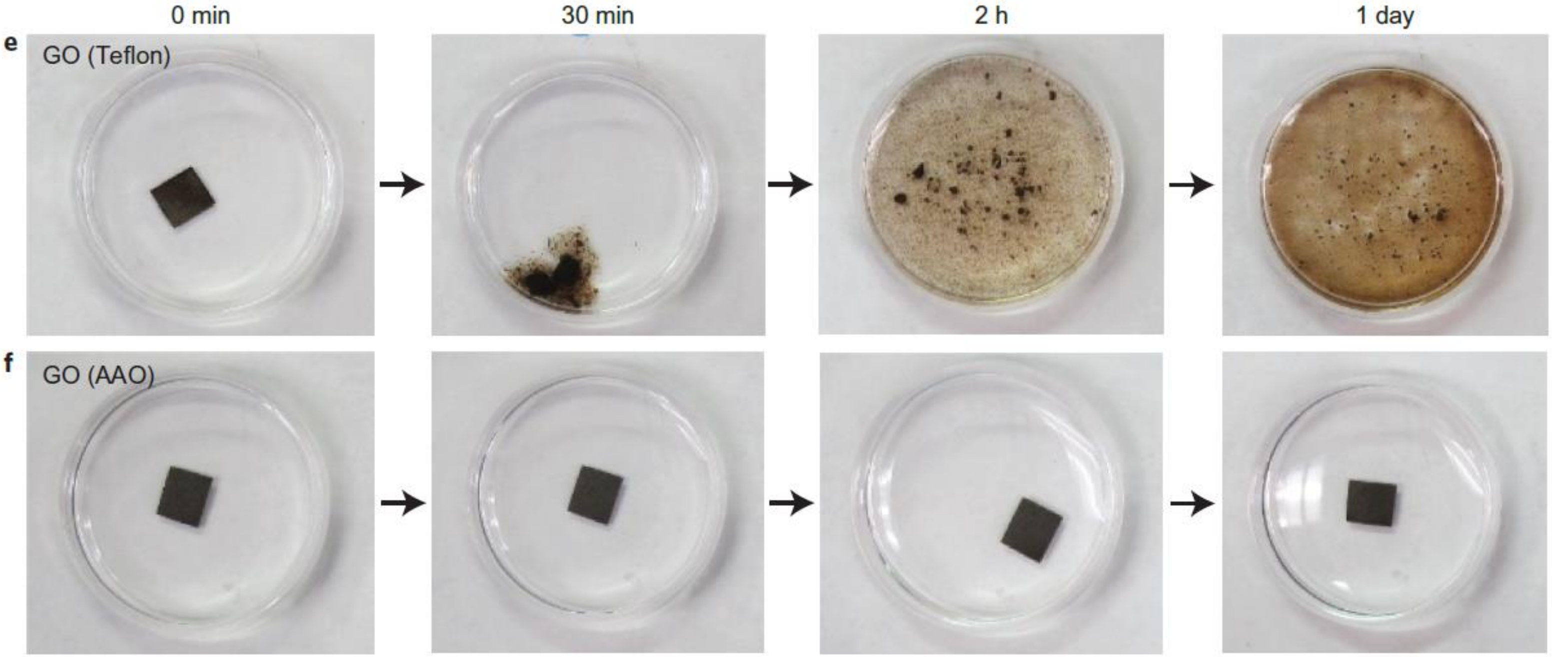
R.R. Nair et. al. Science 335 (2012) 442

ARTICLES
PUBLISHED ONLINE: 5 JANUARY 2015 | DOI: 10.1038/NCHEM.2145
nature chemistry

On the origin of the stability of graphene oxide membranes in water

Che-Ning Yeh[1], Kalyan Raidongia[1], Jiaojing Shao[1,2†], Quan-Hong Yang[2,3] and Jiaxing Huang[1*]





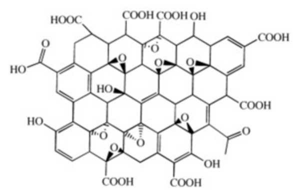
Casting

Inexpensive raw materials

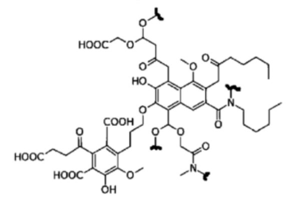
Natural graphite | **Compost from organic waste**

Simple extraction procedure

Nanomaterials



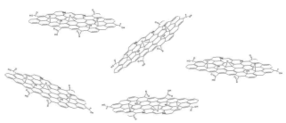
Graphene oxide (GO)



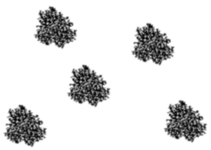
Humic acid-like substance (HAL)

Dispersion in aqueous ammonia pH = 9.8

Membrane building bloc



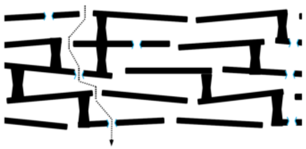
GO dispersion



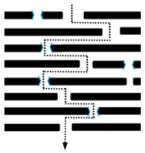
BOS solution

Mixing and casting

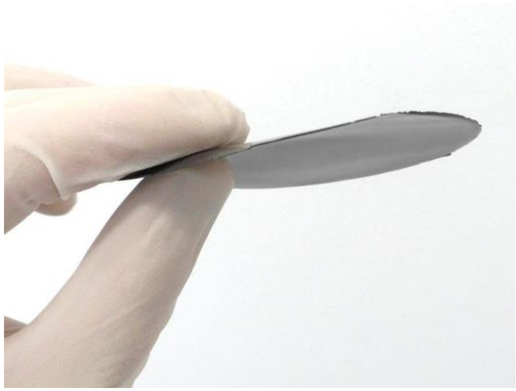
Self-assembly, drying and carbonization

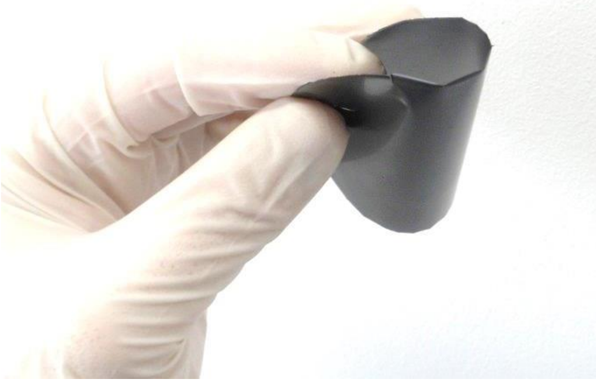


GOBOS membrane

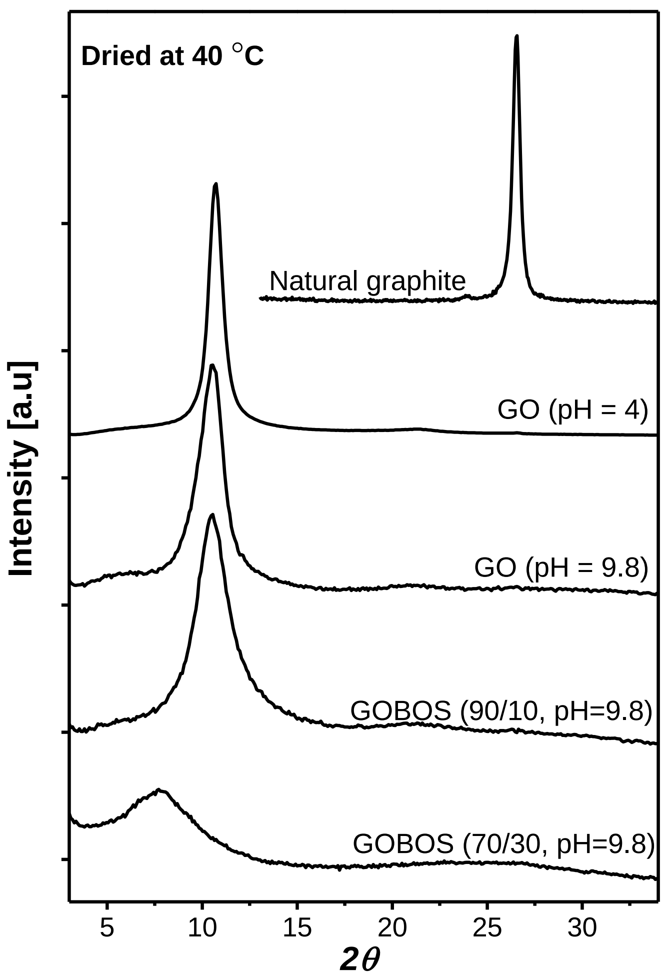


GO membrane

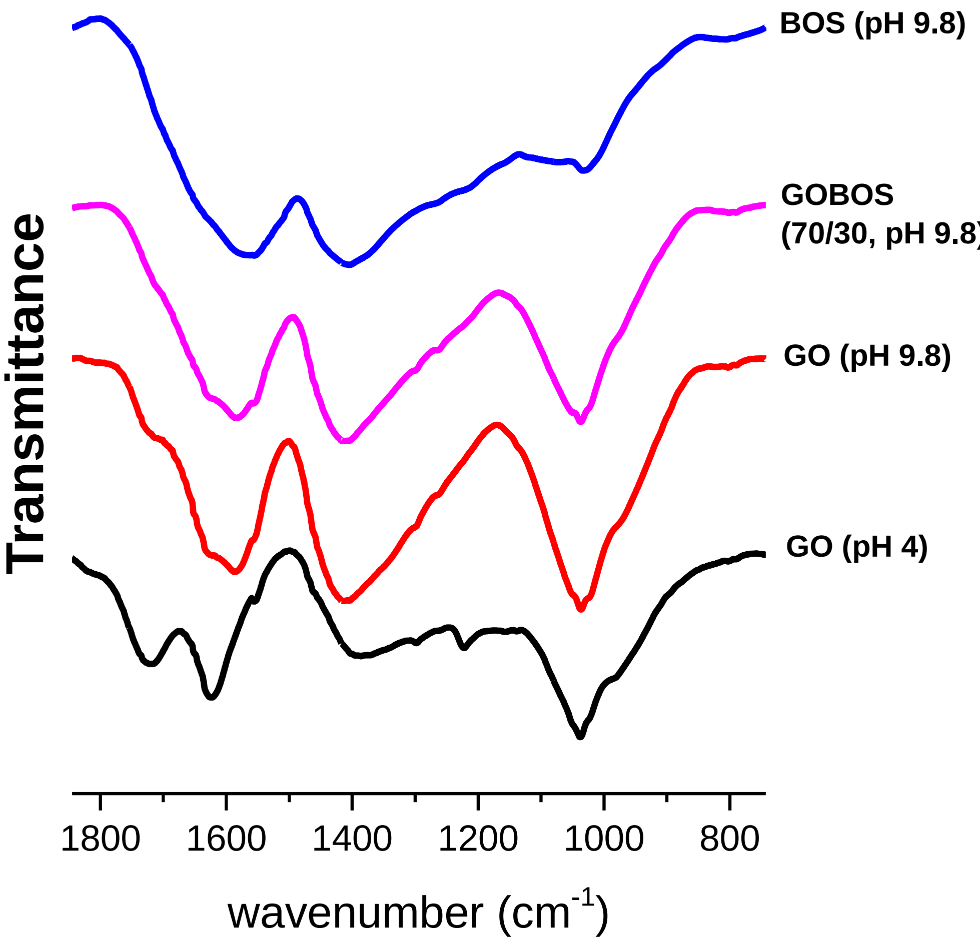




XRD analysis



ATR-FTIR analysis

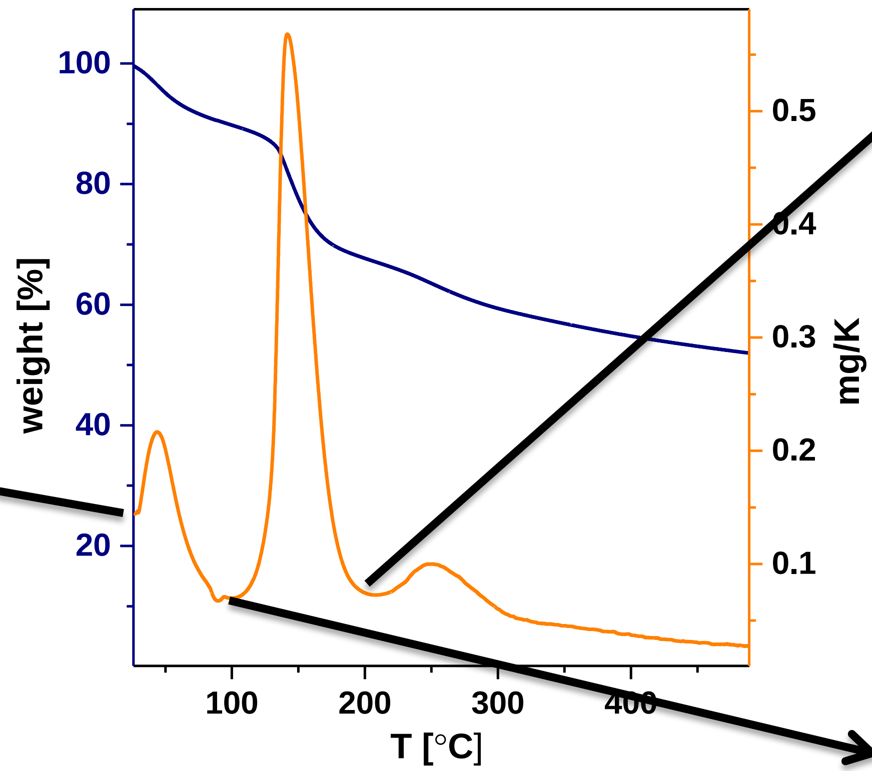


Thermal evolution

pH =9.8

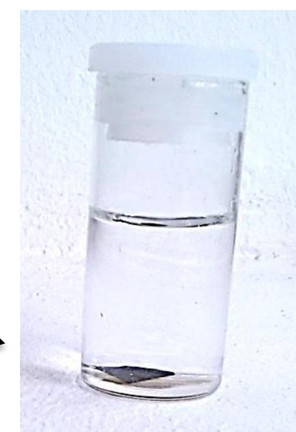
Dried at 40 °C

Ready for dispersion



Annealed at 200 °C

Hydrophobic

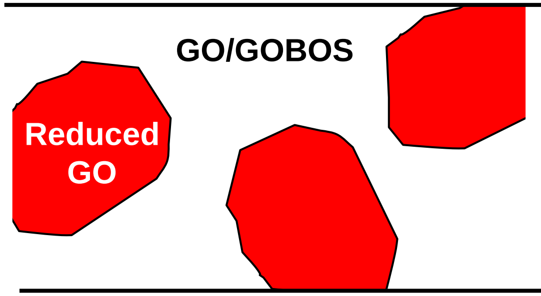


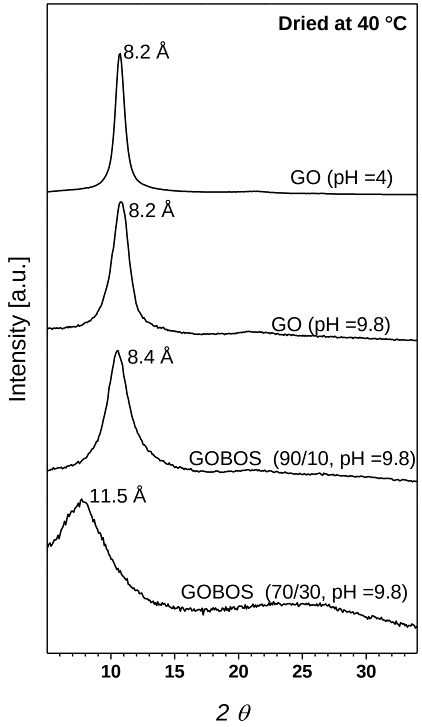
Annealed at 120 °C

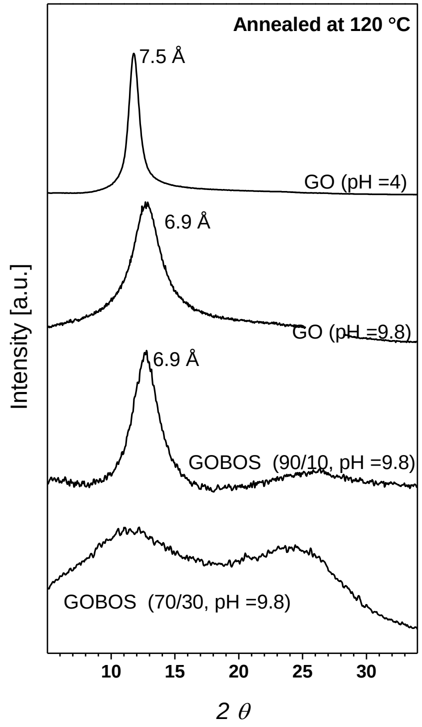
Hydrophilic

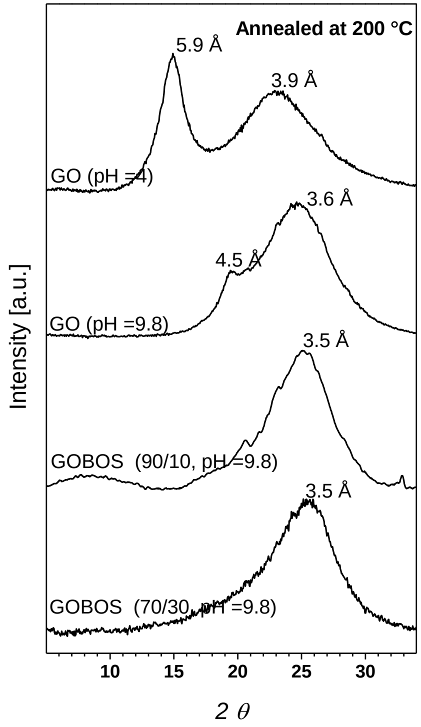
GO membranes

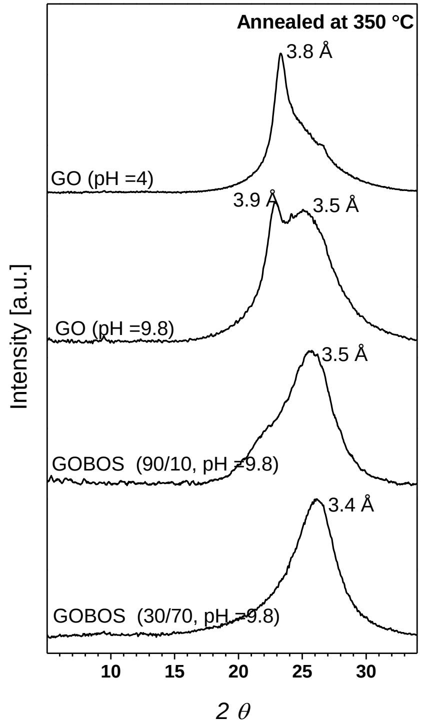
Thermal evolution





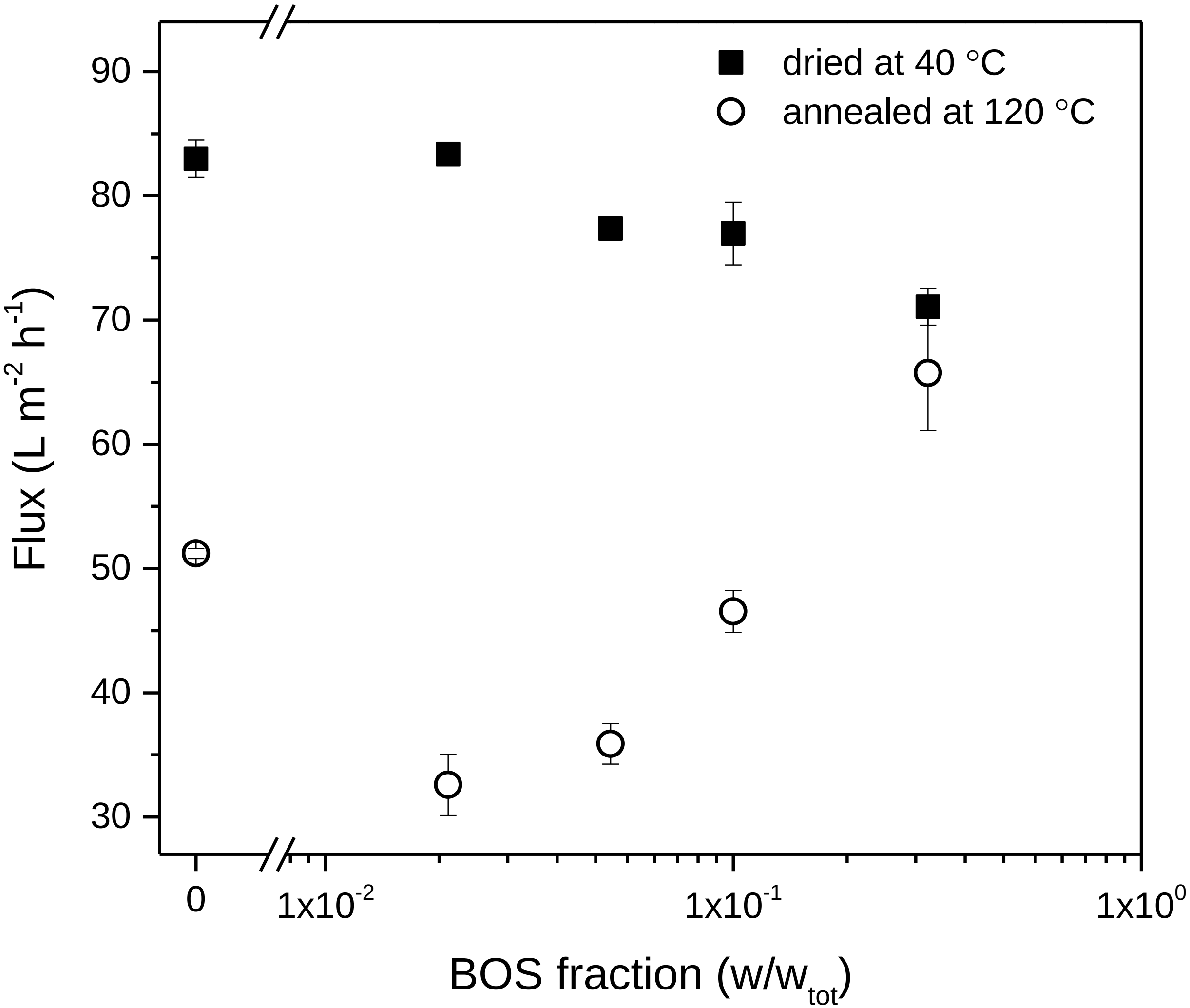






GO membranes

Water vapor permeation at 45 °C



Conclusions

- **Membrane-based separation processes are promising for water purification and for the upcoming green energy platforms;**

- **In many cases stability and perm-selectivity remain an issue;**

- **The future generations of membranes for advanced separation systems rely on the development of new functional and highly stable (micro)porous materials.**

Acknowledgements

Gas-selective silica

Prof. J. E. ten Elshof (Twente Univ)
Dr. H. Castricum (Amsterdam Univ)

SiC membranes

Dr. K. König (consulting)
LiqTech International A/S
Prof. Yuanzheng Yue (AAU)

Transport model

Dr. Morten L. Christensen (AAU)
Ali Farsi (AAU)

Adsorption analysis

Dr. Giuliana Magnacca (Turin Univ)

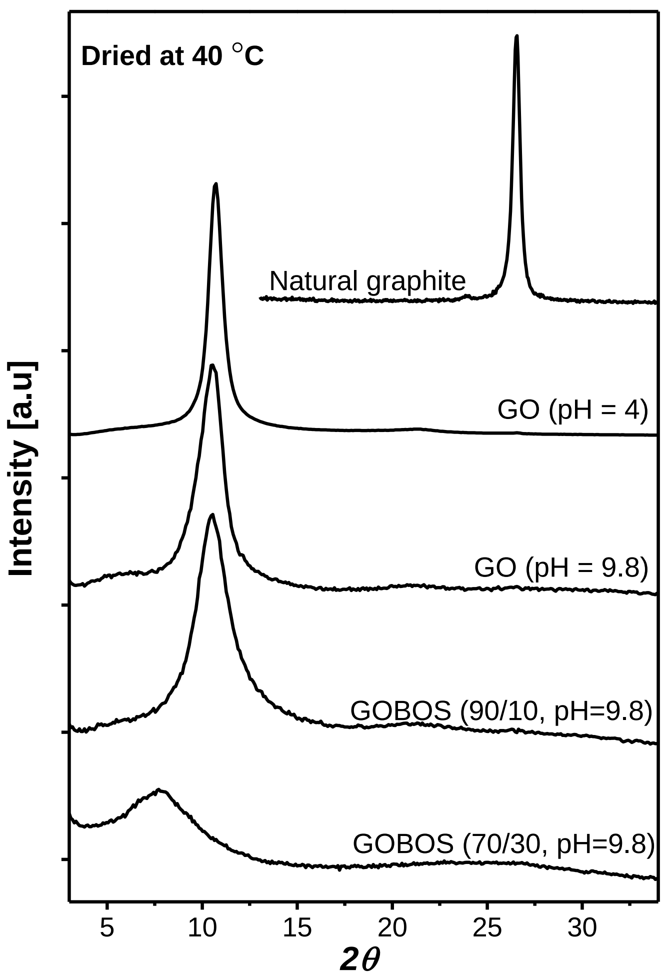
Graphene oxide membrane

Prof. Peter Mallon and all the members of his group, particularly Dr. Hussein Etmimi and Mr. Neil Basson

Dr. Vincent Smith
Dr. William Cloete

I was here thanks to MAT4TREAT: Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) Grant Agreement no: 645551

XRD analysis



ATR-FTIR analysis