Hydrothermal stability of silica-based membranes

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ECN-M—09-130 November 2009

ECN

Energy research Centre of the Netherlands

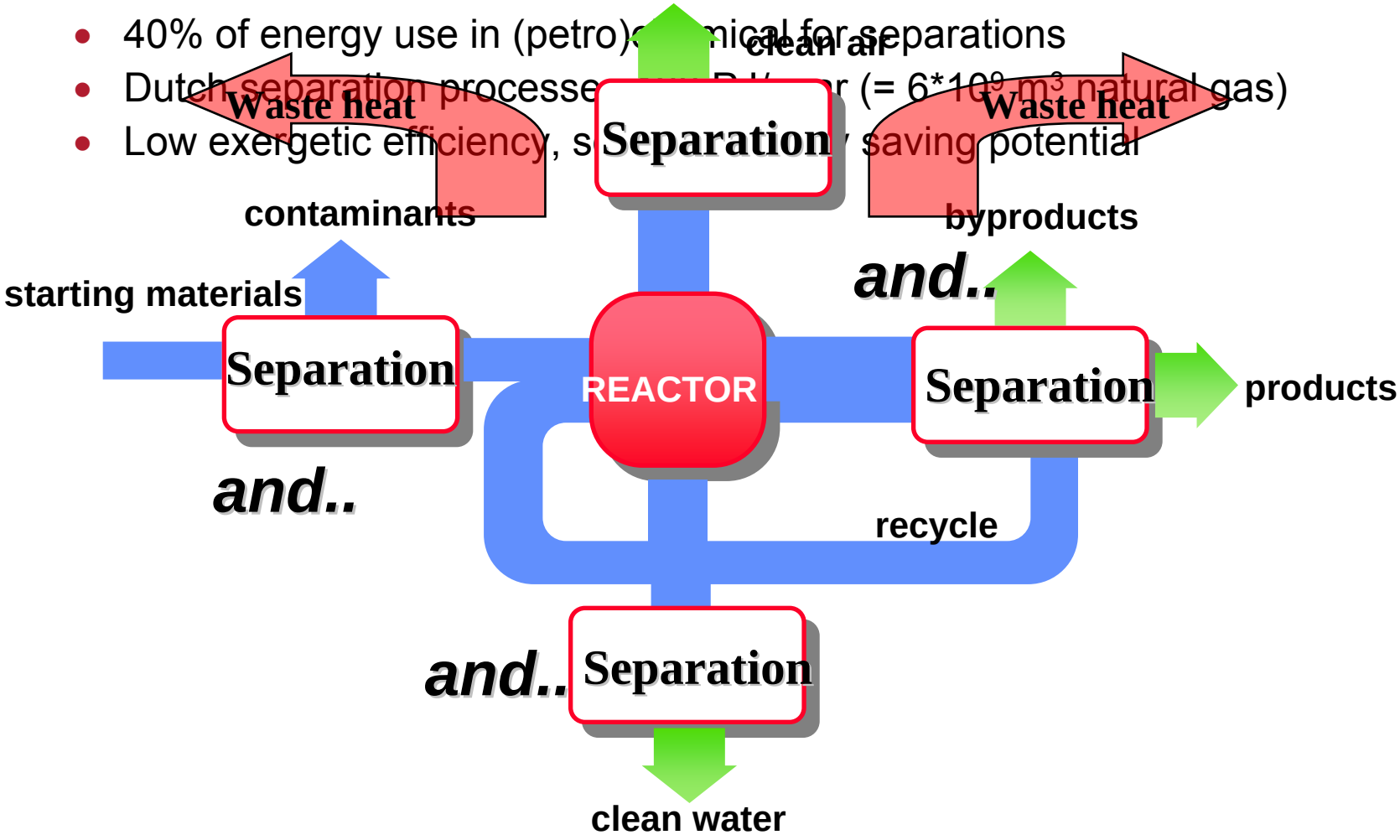
Hydrothermal stability of silica-based microporous membranes

Robert Kreiter

Energy research Centre of the Netherlands

Incentive

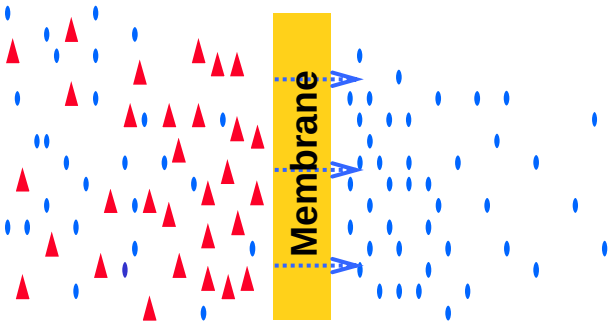
- 40% of energy use in (petro)chemical for separations
- Dutch separation processes [illegible] PJ/year (= 6*10^9 m^3 natural gas)
- Low exergetic efficiency, s[illegible] saving potential



Industrial membrane applications (PV/VP, GS)

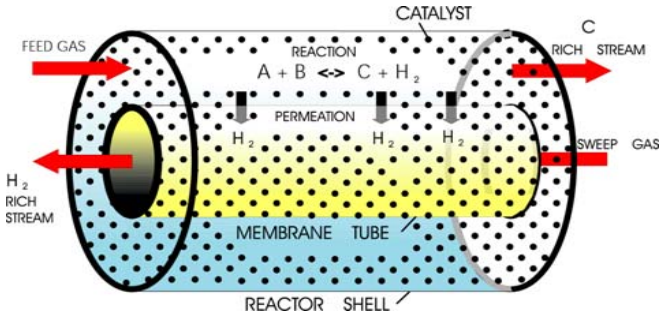
Case I: Pervaporation (PV)/ Vapor permeation (VP):

- Dewatering of organics, organic/organic



Case II: Gas separation (GS)

- H_2 from steam reforming/water-gas shift



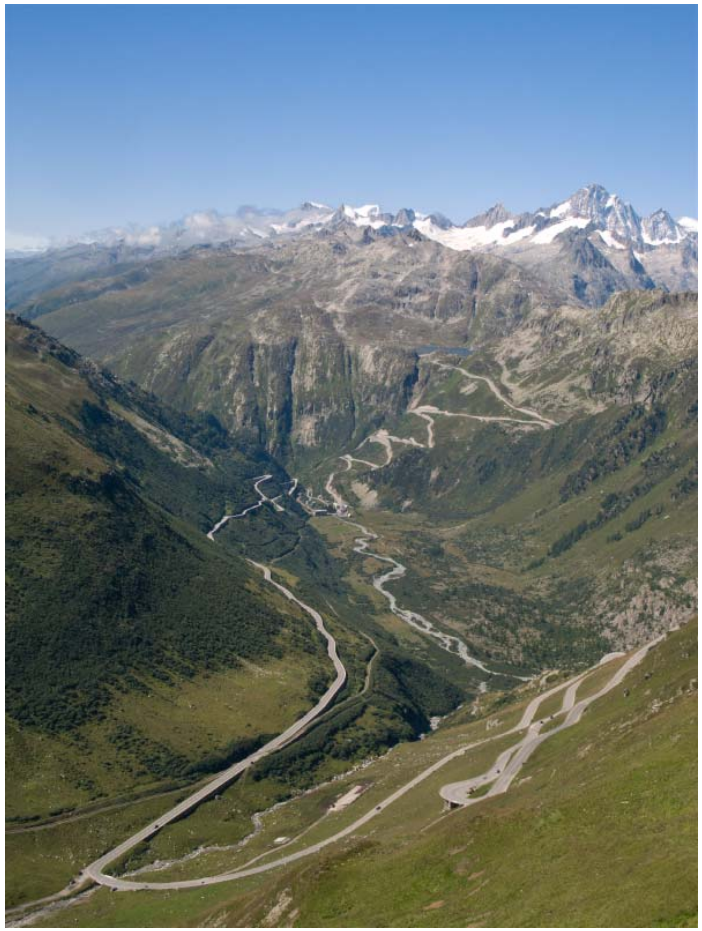
Mountains and microporous membranes

Membrane stability is challenged by:

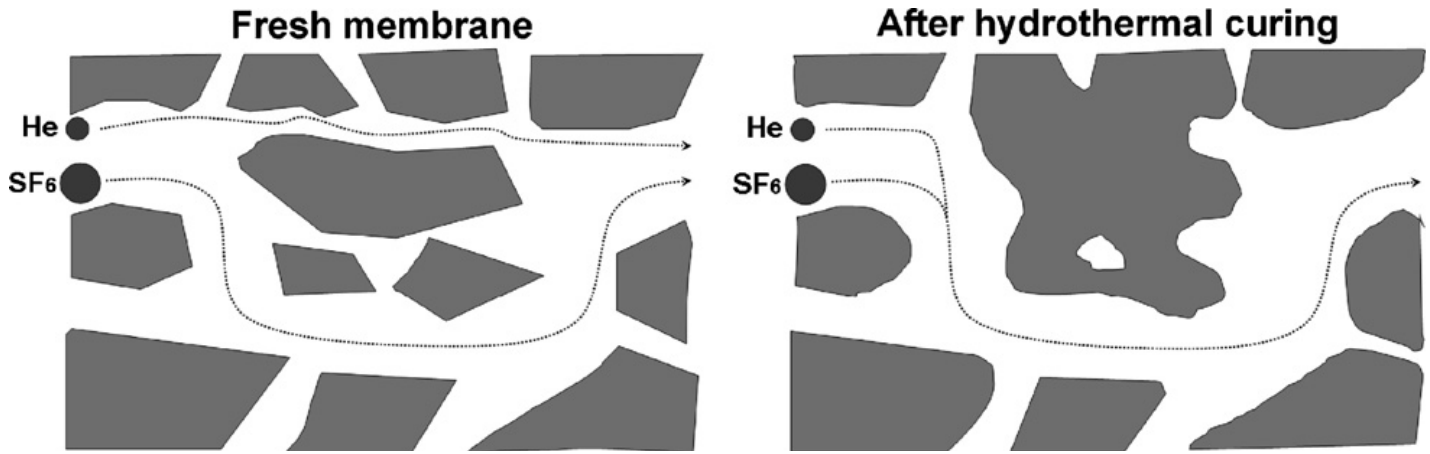
- (Hydro)thermal conditions
- Aggressive solvents
- Acids

Microporous sol-gel membranes

- Are thermodynamic mountain tops
- Are highly reactive or soluble
- Densify / change phase



Improving hydrothermal stability of silica: Mixed oxides

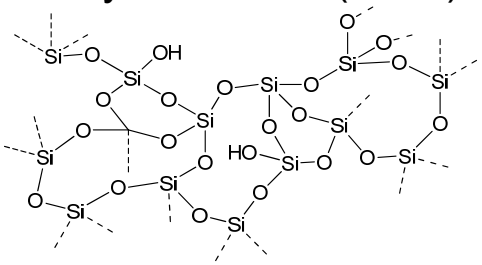


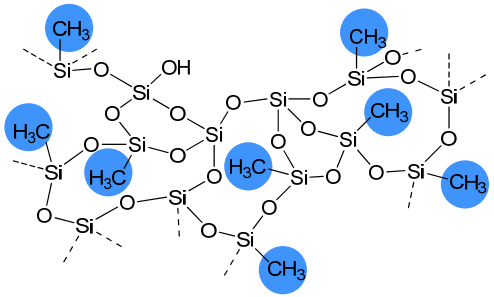
Si-M, M = Zr, Co, Ni, Nb, Fe, Al

- Kanezashi, Asaeda, Tsuru et al., *J.Membr.Sci.* 2006, 271, 86; *Mater.Res.Soc.Symp.Proc.* 2003, 752, AA10.3, 213
- S. Battersby, *Sep.Pur.Technol.* 2009, 66, 299
- Boffa, *J.Membr.Sci.* 2008, 319, 256

Improving hydrothermal stability of silica: Organics and carbon

Methylated silica (MeSi)



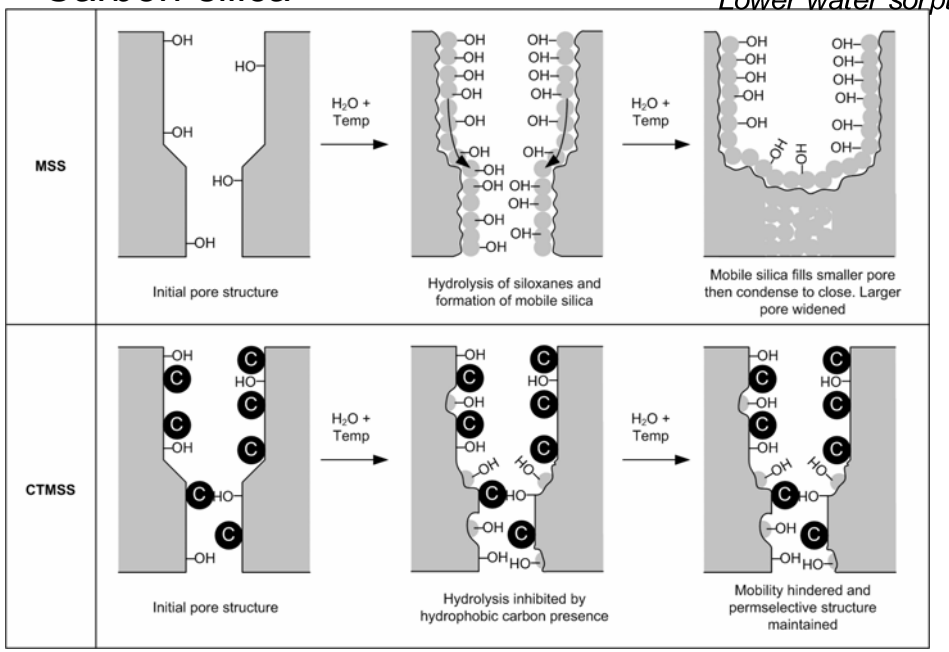


De Vos, Verweij,

J.Membr.Sci. 1999, 158, 277

Carbon-silica

Lower water sorption



Duke, Diniz da Costa et al.

Adv.Funct.Mat. 2006, 16, 1215

Our approaches towards hydrothermal stability

Previous developments:

- SiO_2 to MeSi

More recent:

- Ceramic-supported polyimide membranes

  J.Membr.Sci. 2008, 319, 126

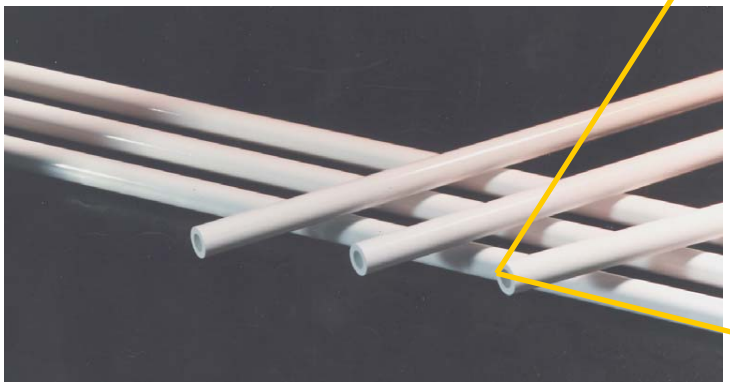
- Microporous titania and zirconia membranes

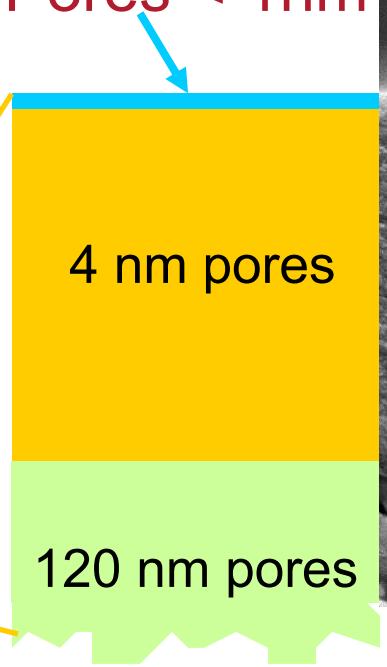
  J.Sol-gel Sci.Technol. 2008, 48, 203

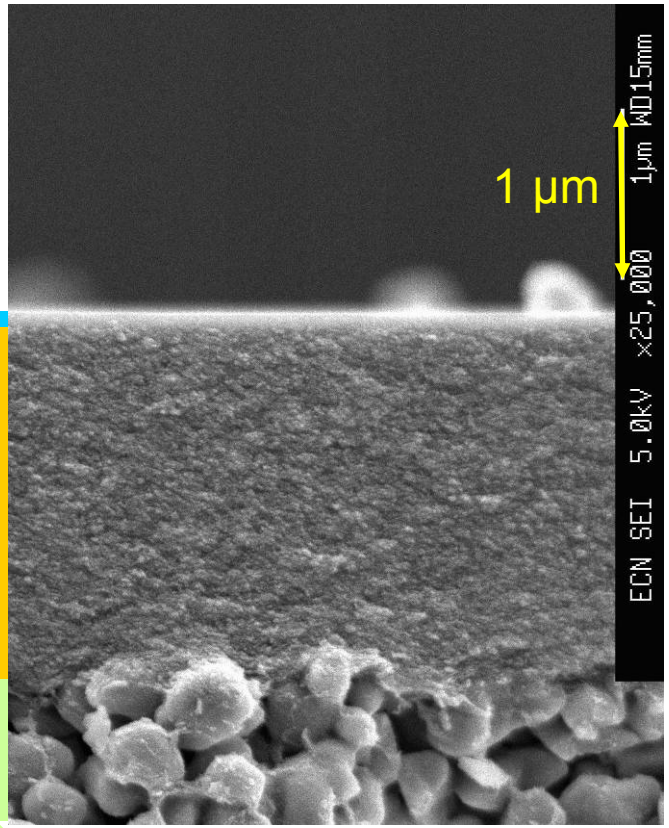
Latest development: **This presentation**

- Organic - inorganic hybrid silica

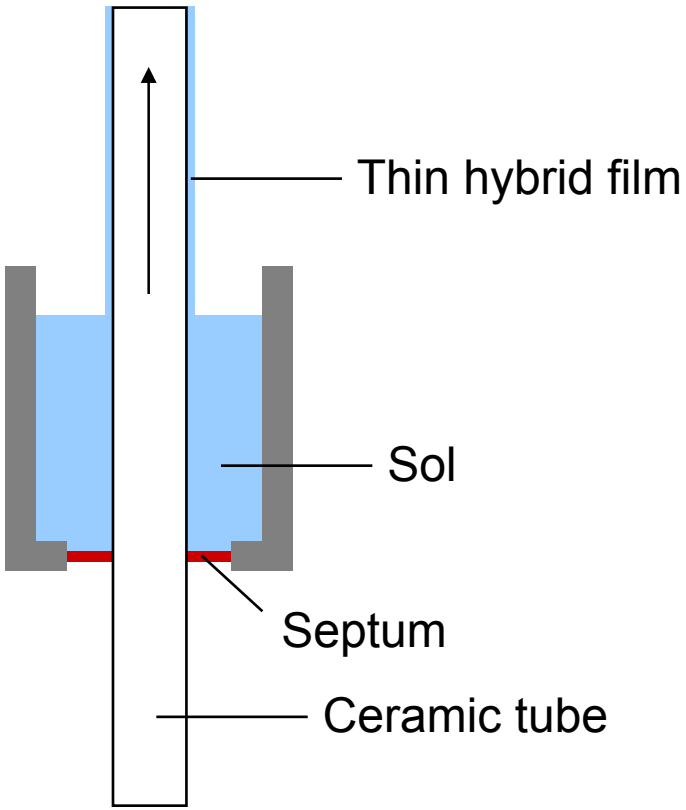
Tubular microporous membranes

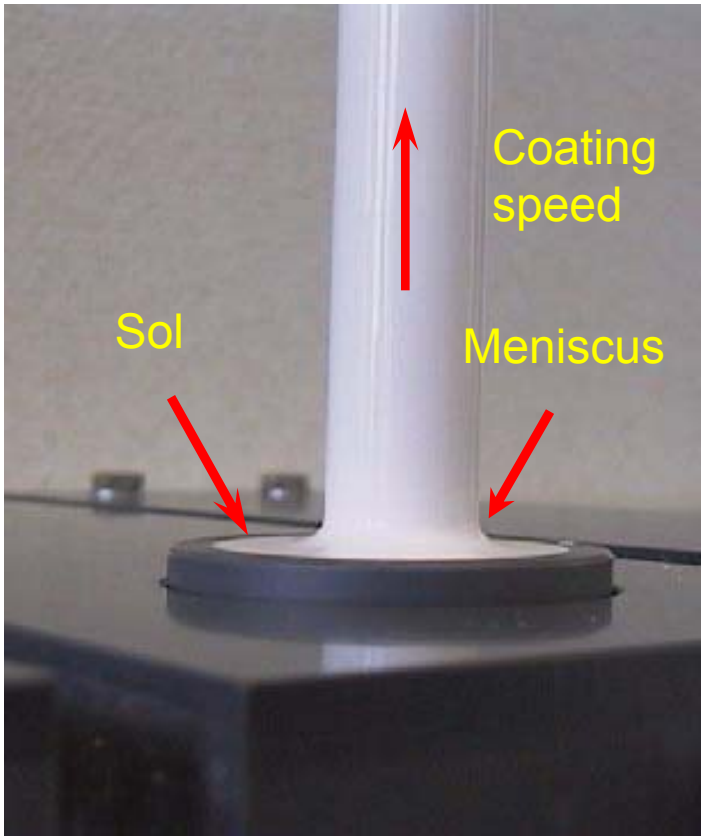






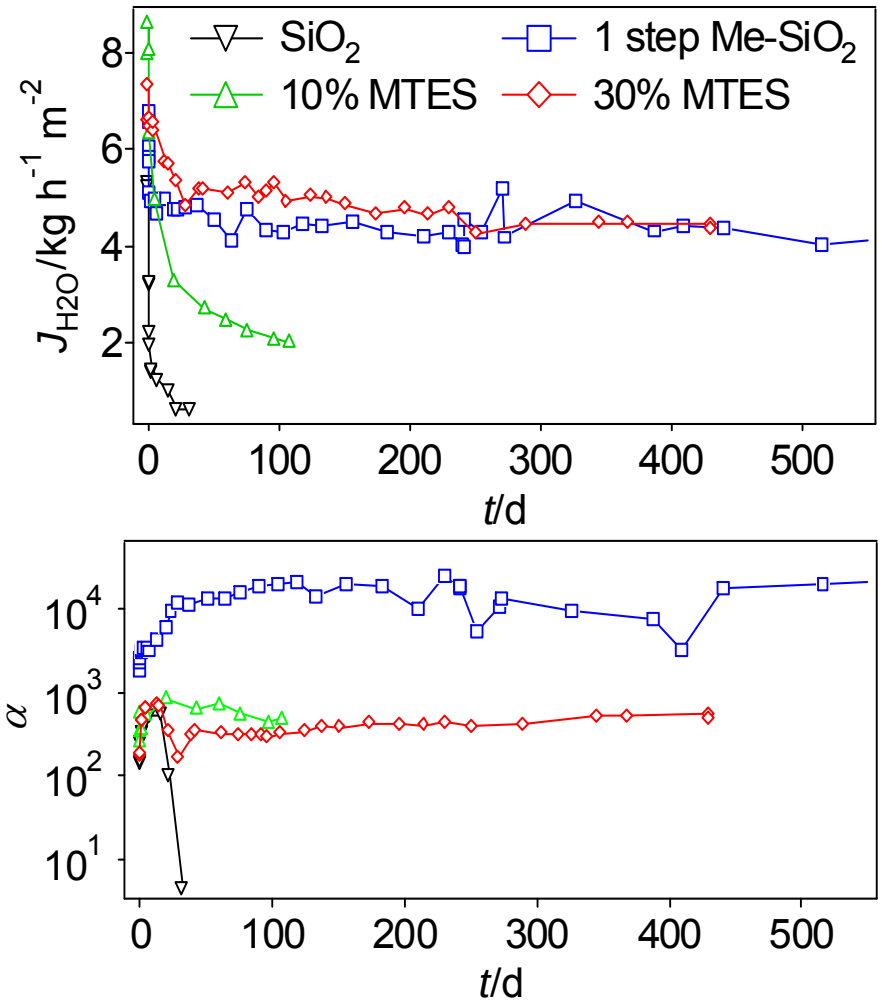
Membrane preparation





Tubes: 30 – 100 cm

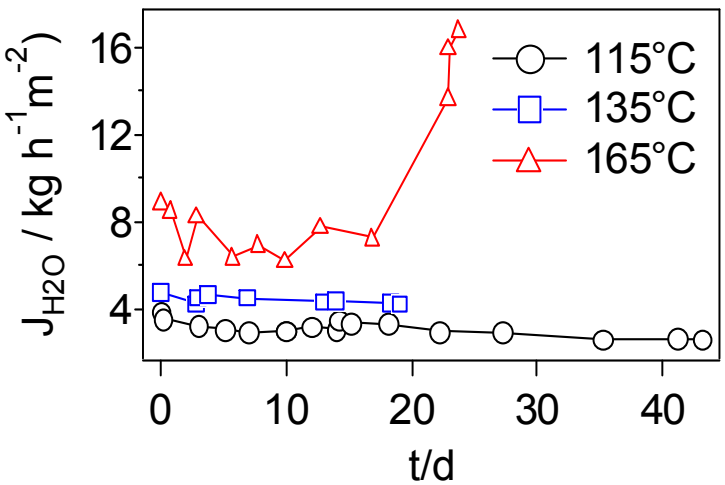
SiO_2 and MeSi pervaporation results (95ºC)

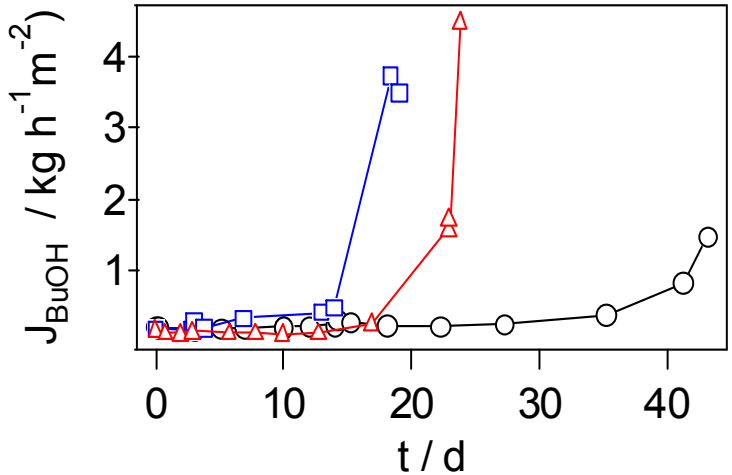


- 5 wt.% H_2O in BuOH, 10 mbar
- Addition of MTES gives better performance with time
- Constant performance for >18 months!

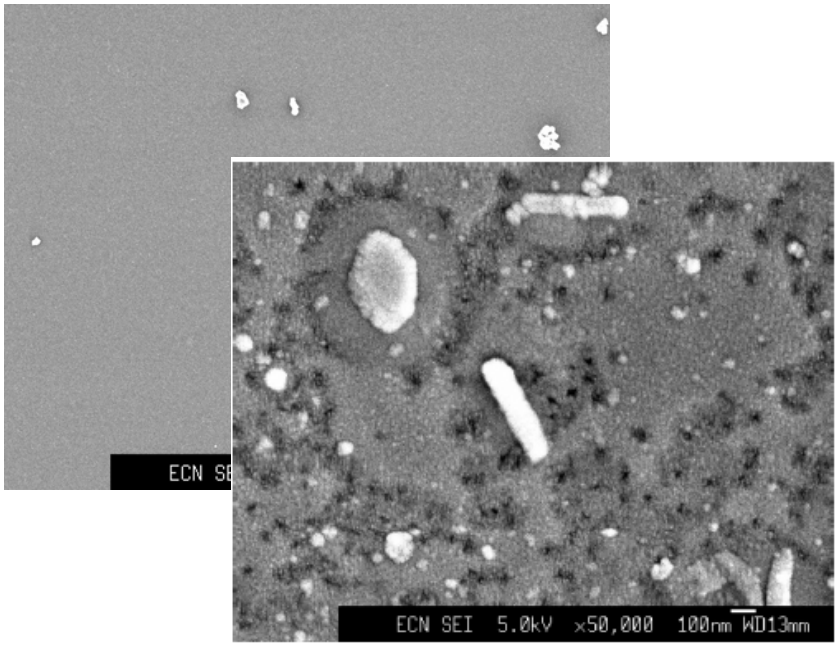
Chem.Commun. 2004, 834-835

MeSi pervaporation up to 165ºC



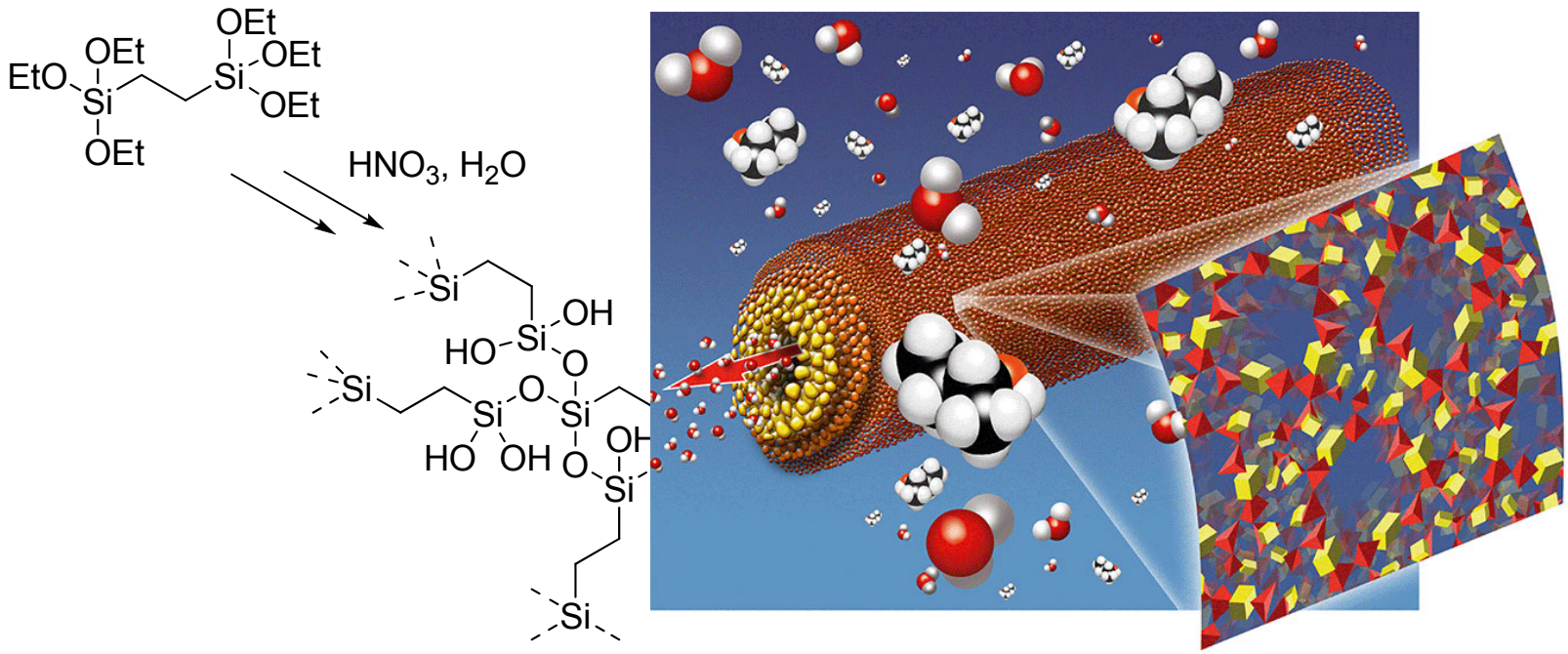


- 2.5 wt.% H_2O in BuOH, 10 mbar
- Failure within weeks
- No clear relation with temperature



HybSi® membranes from bridged silica precursors

Strategy: replace Si—O—Si bonds by Si—C—Si bonds

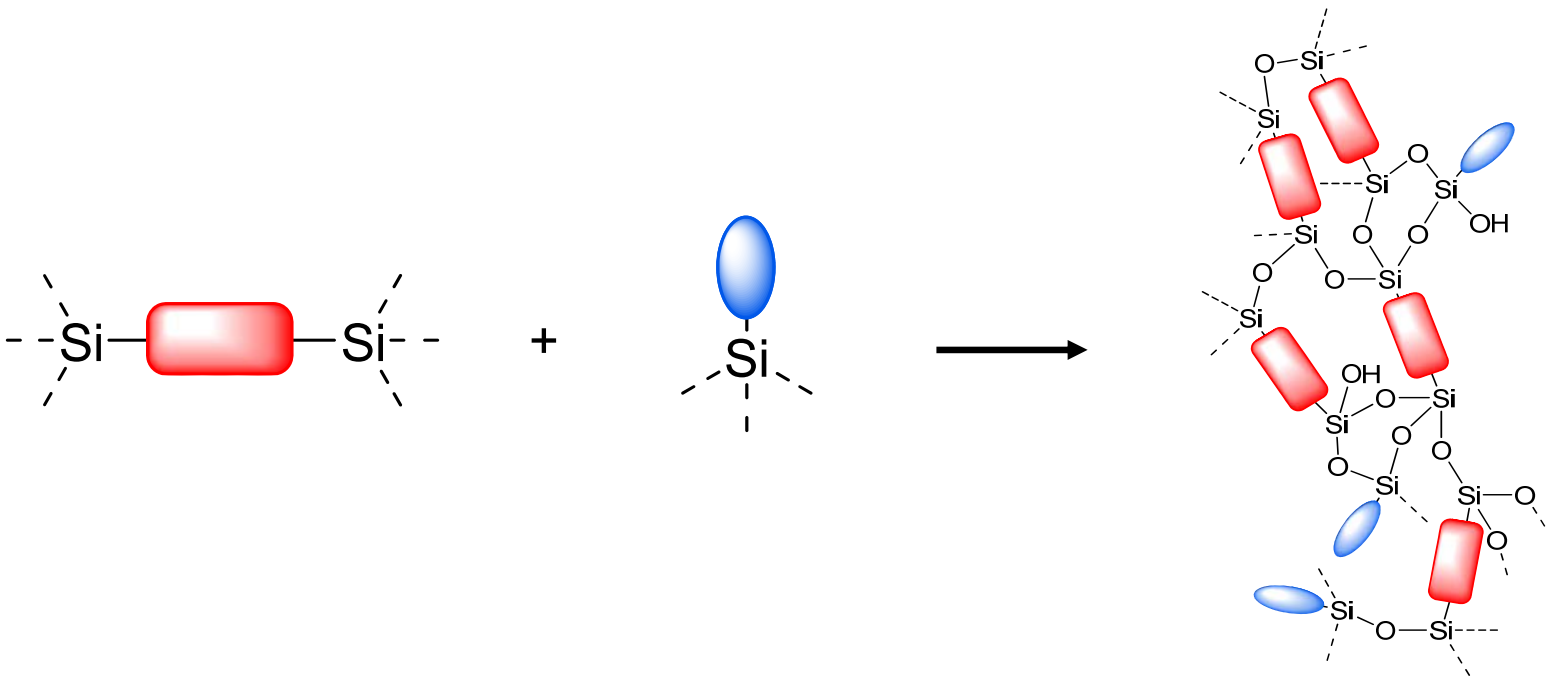


Collaboration with Universities of Twente and Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer), started in 2003

WO2007081212, 2006; *Chem. Commun.* 2008, 1103-1105

Screening precursors for HybSi® membranes

Tailored network



Overview of precursors: D.A. Loy, K.J. Shea *Chem.Rev.* 2005, 1431

High-throughput screening (HTS) of hybrid silica sols

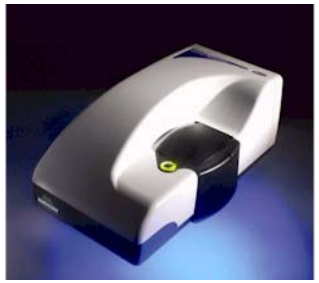
Automated synthesis of sols was performed varying:

- Precursor type
- Temperature
- H_2O/OR
- H^+/OR

Chemspeed ASW1000

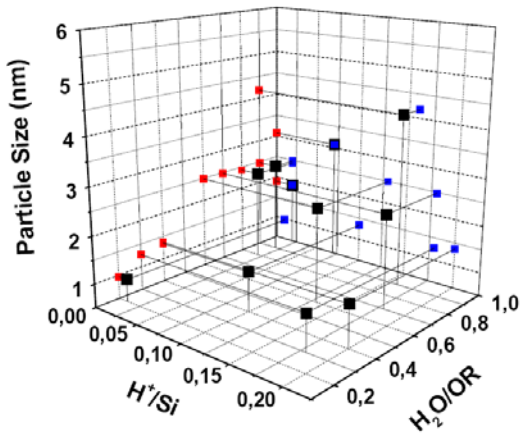
Total of ~160 individual sol preparations

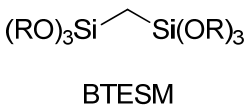
- 6.5 mL scale
- 1 standard in each run
- Analysis using DLS



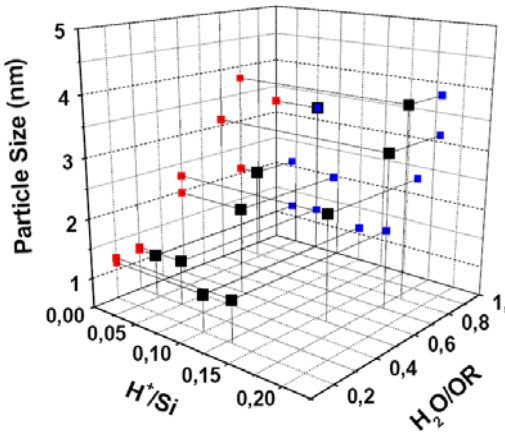
Malvern Zetasizer Nano ZS

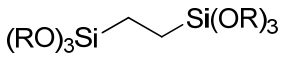
HTS – Example results



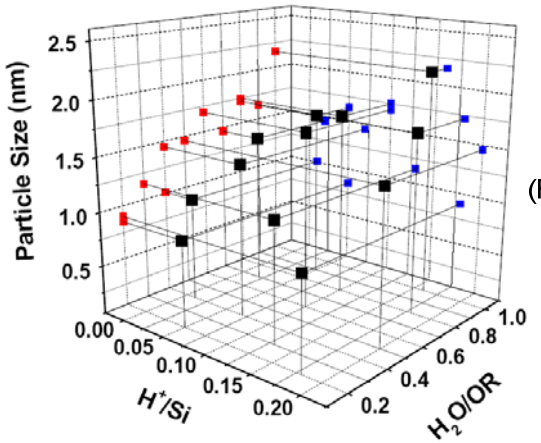


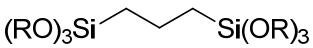
BTESM



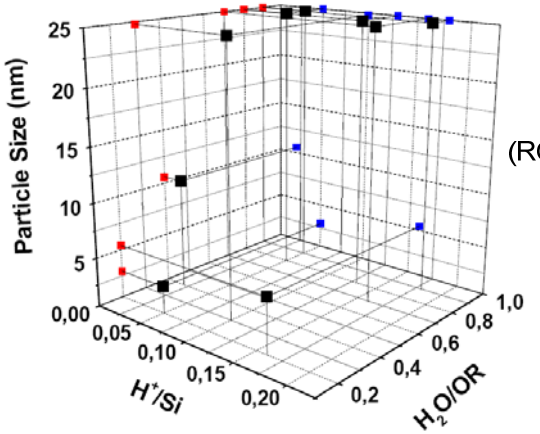


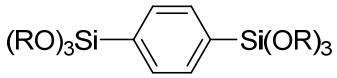
BTESE





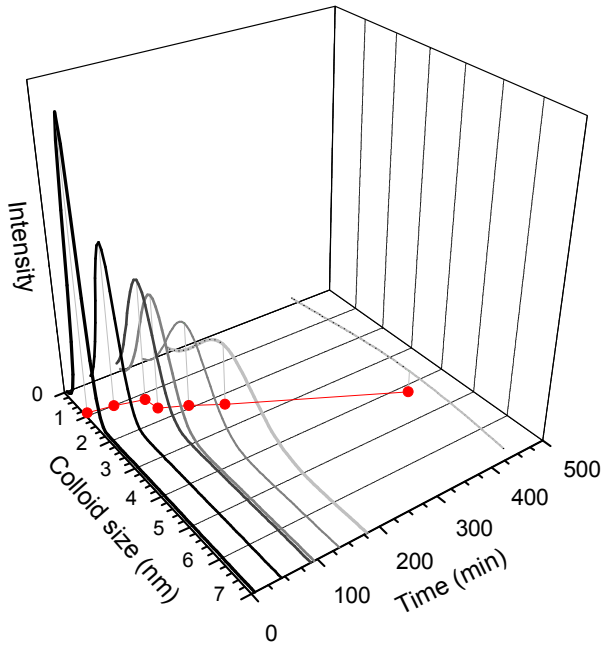
BTESP

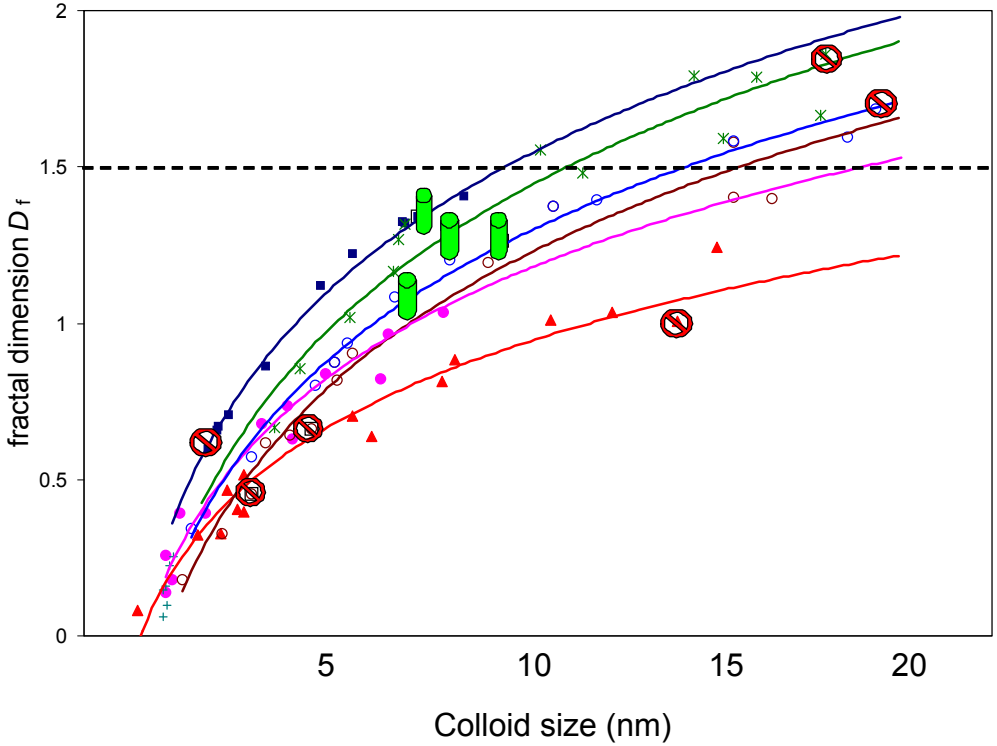




BTESB

SAXS and DLS





Particle sizes = 5-10 nm

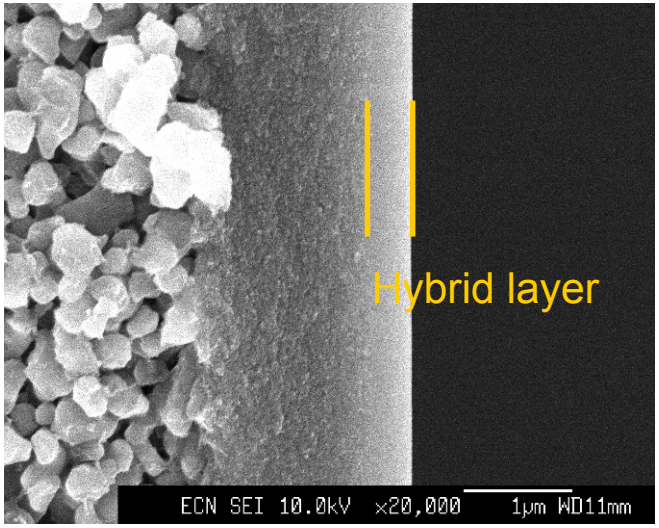
D_f = 1-1.5

Case I: pervaporation

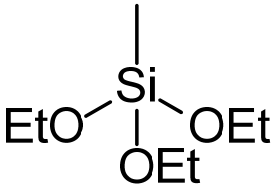
Precursors and PV performance

Precursors:

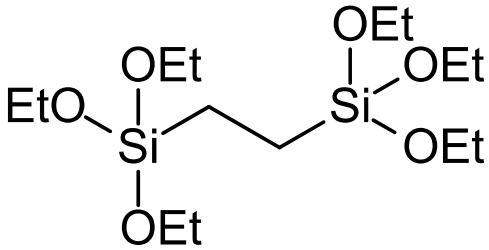
- BTESE + MTES
- BTESE
- BTESM



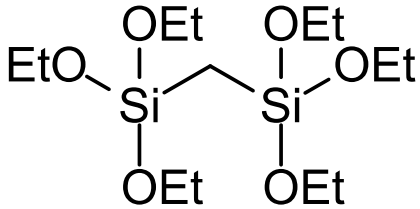
MTES



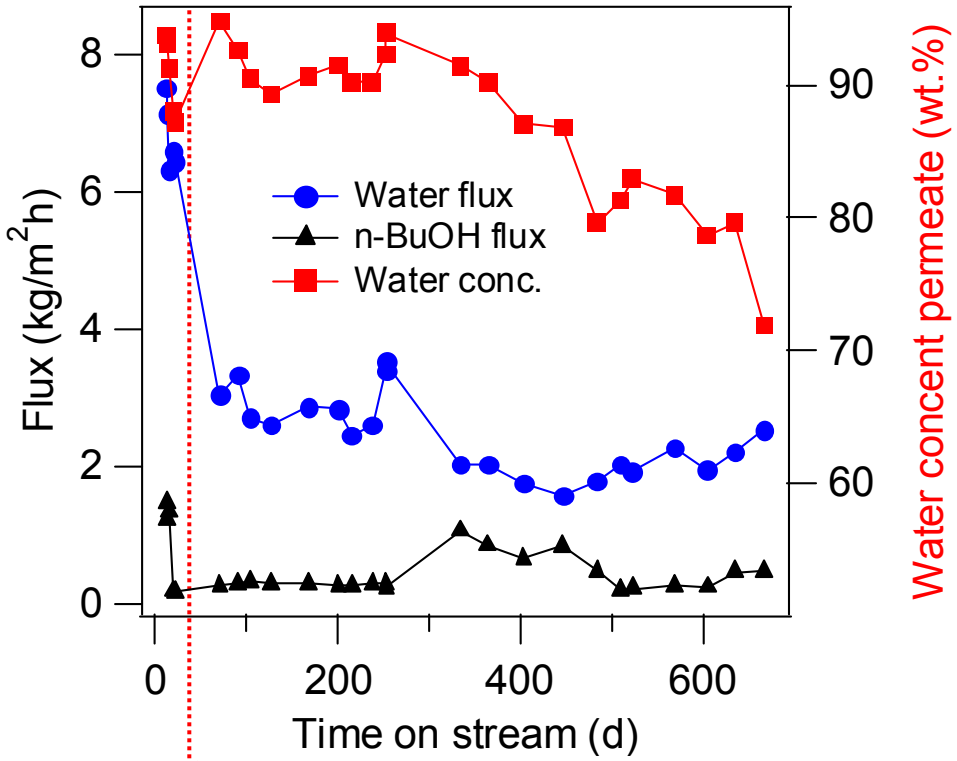
BTESE



BTESM



Performance hybrid membranes, 150°C



Life time state of the art methylated silica

Feed = 5 wt.% water in *n*-BuOH

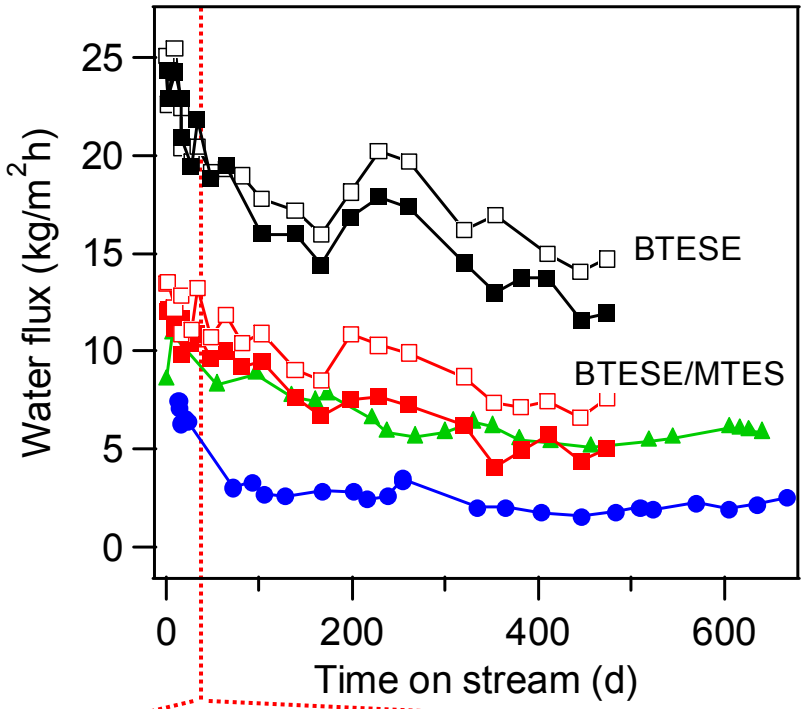
First membrane made BTESE/MTES

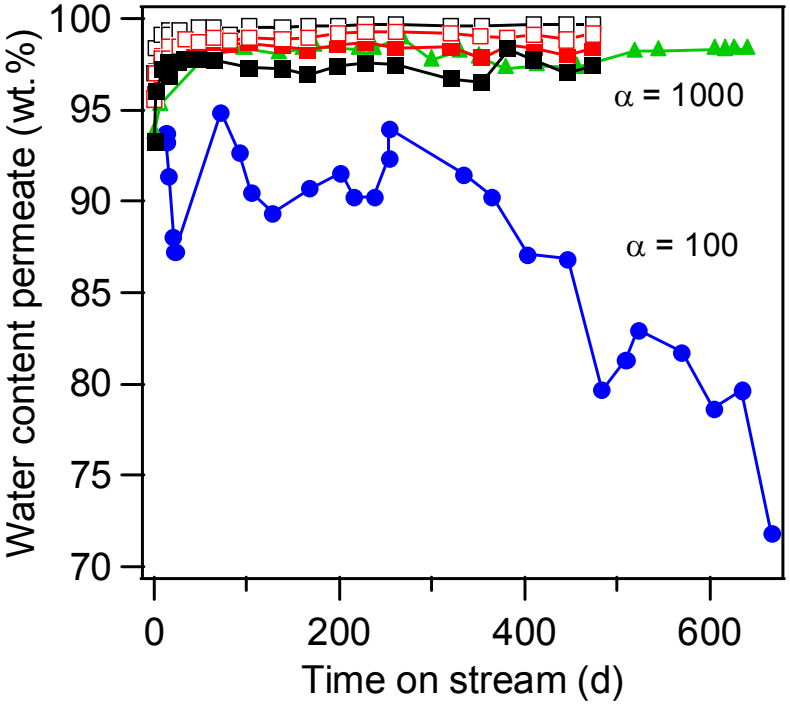
Life time >650 days

J. Mater. Chem. 2008, 18, 2150-2158

Performance hybrid membranes, 150°C

Feed: 5 wt.% water in *n*-BuOH



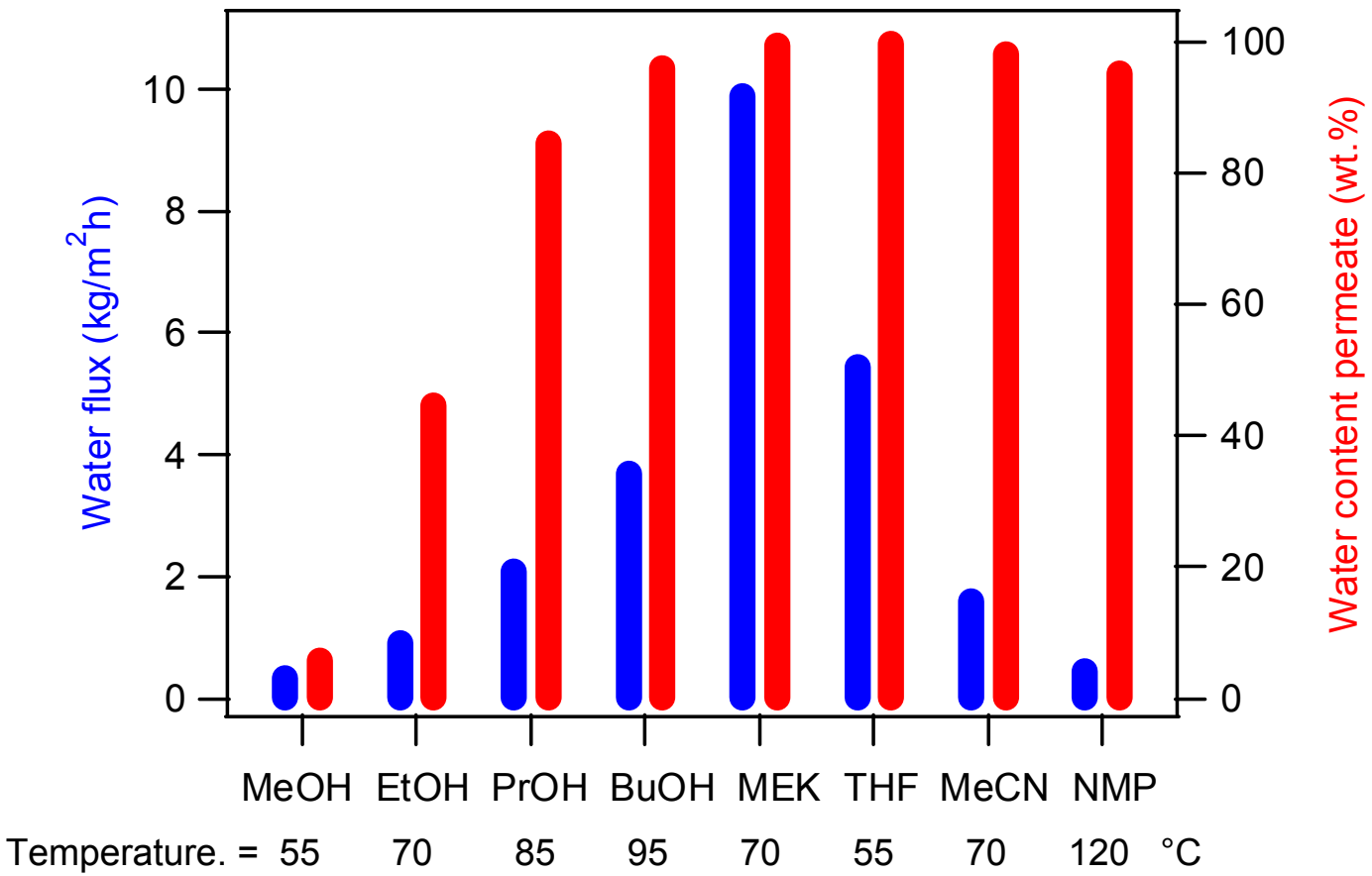


Life time state of the art methylated silica

J. Membr. Sci. 2008, 324, 111-118

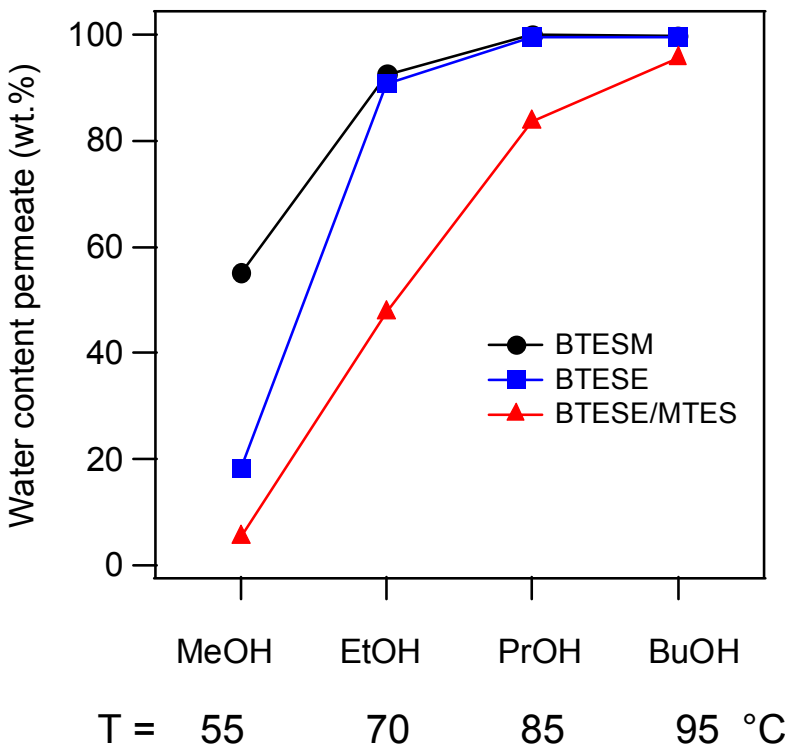
Application testing - solvents

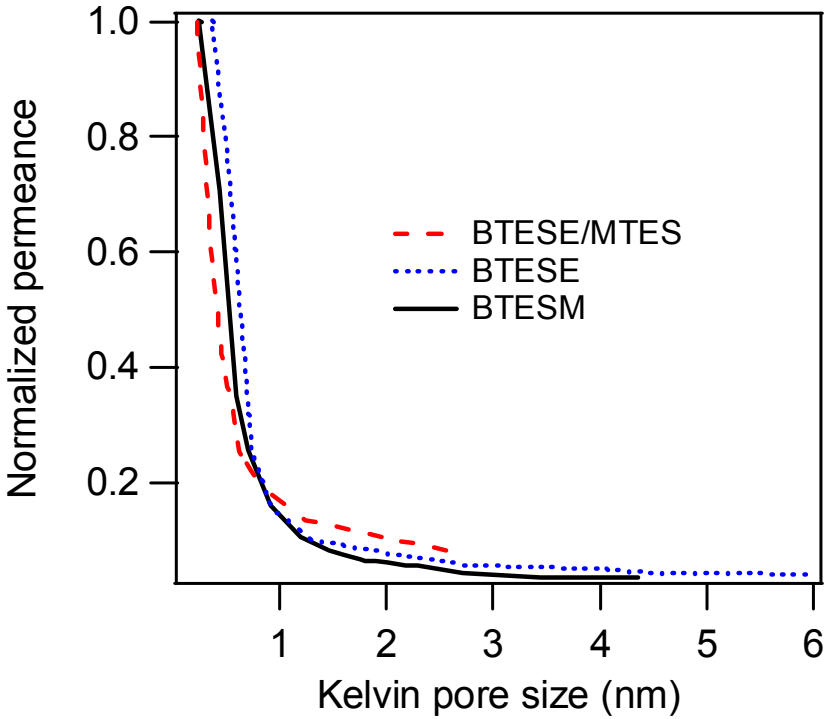
Feed = 5 wt.% water in solvent; BTESE/MTES



Application testing - alcohols

Feed = 5 wt.% water in alcohol

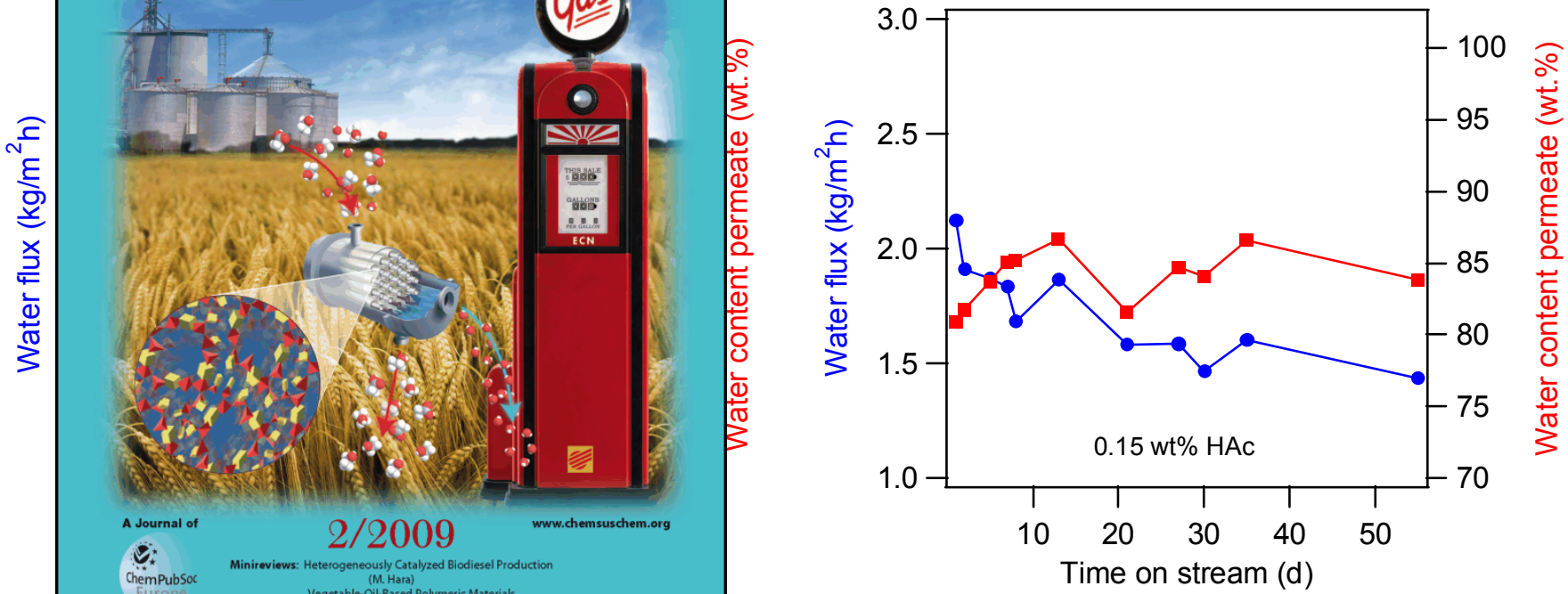




ChemSusChem 2009, *2*, 158-160

Acid stability

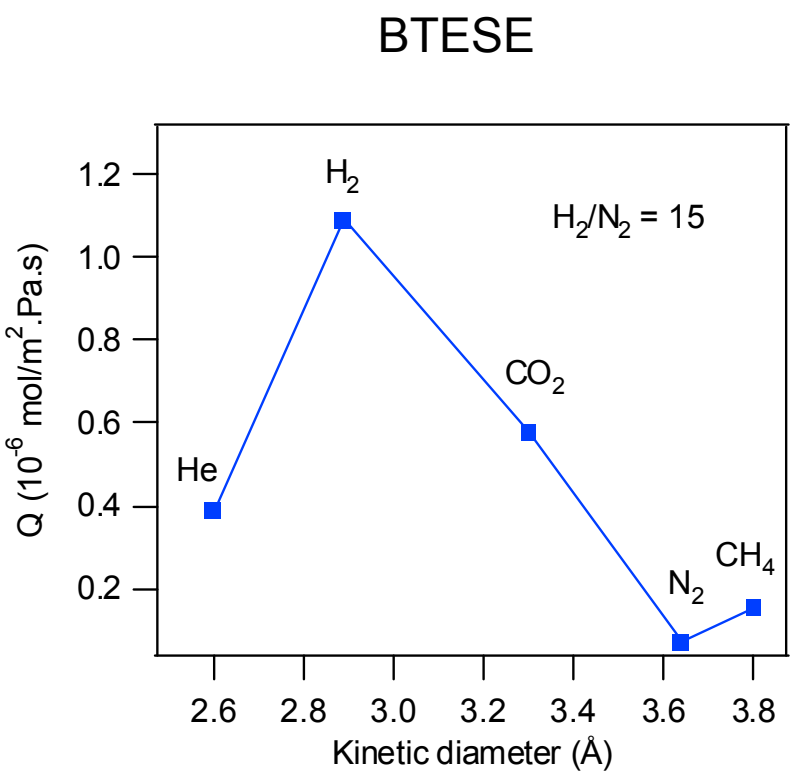
Feed : 5 wt.% water in EtOH
0.1 wt% HAc
BTESM

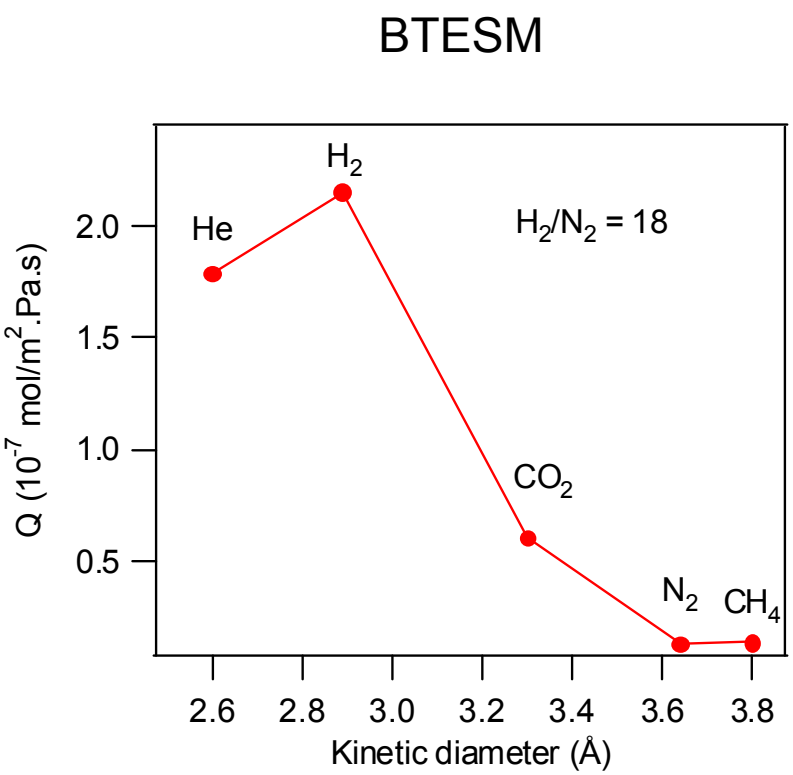


ChemSusChem 2009, *2*, 158-160

Case II: gas separation

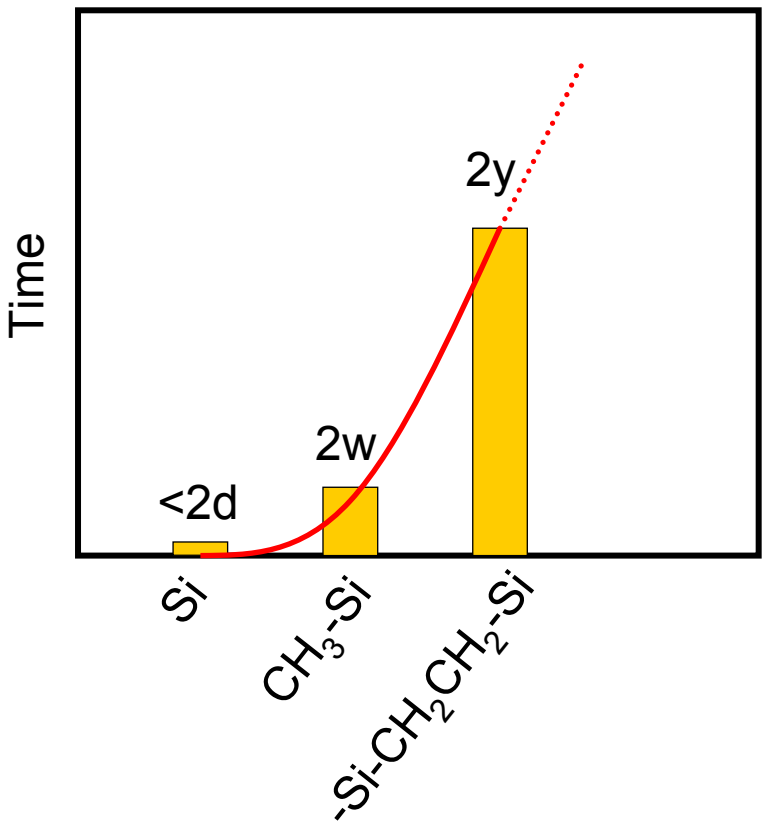
Hydrogen selectivity

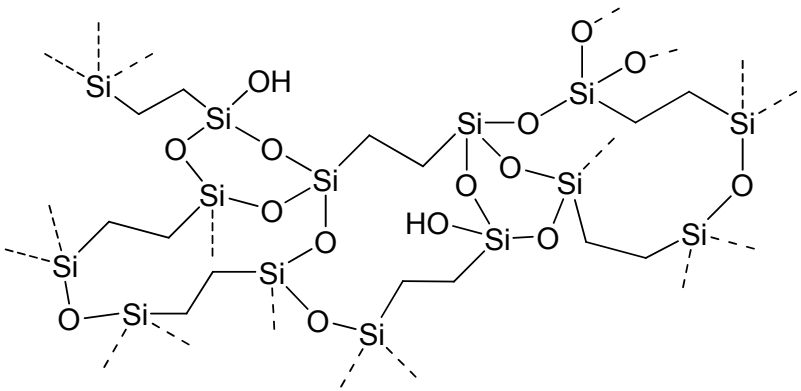




Similar findings by: M. Kanezashi, *JACS* 2009, 131, 2, 414

Origins of hydrothermal stability of HybSi®

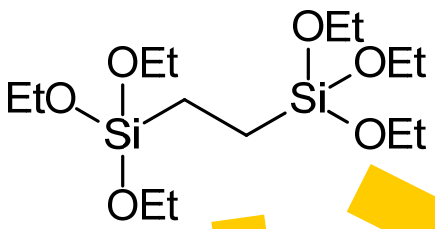


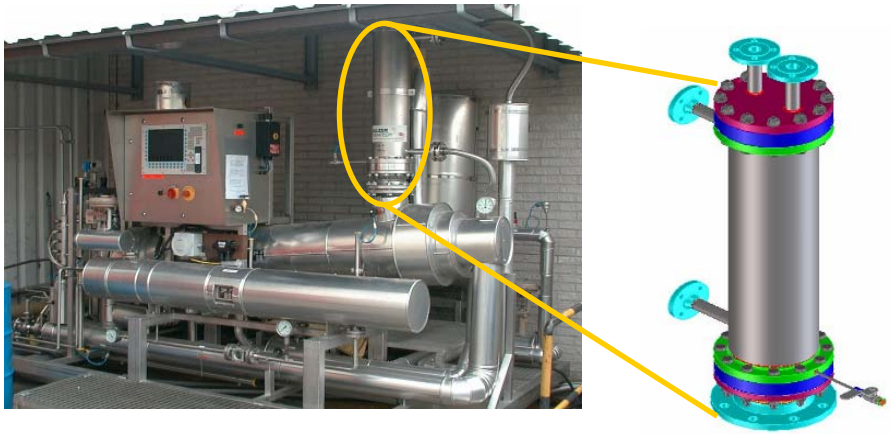


- Non-hydrolysable bonds
- Lower surface diffusion coefficient
- Lower solubility
- Crack propagation limited

Mechanical properties of Hybrid silica films: Dubois et al., *Adv.Mater.* 2007, 19, 3989

Scaling up



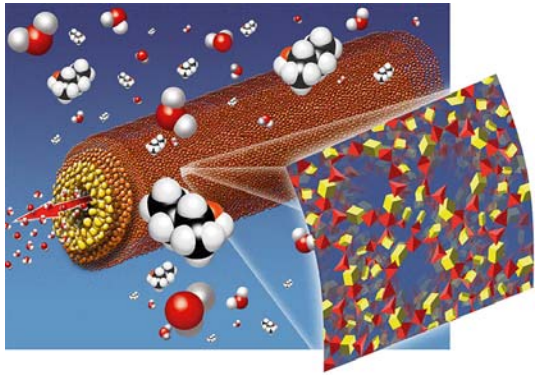


Pilot plant installation (PV/VP), 1000 litre liquid
A_{mem}= 1 m^2 (24 tubes)
T_{max} = 150°C
P_{max} = 10 bar

Single tube test module (GS)
A_{mem}= 40 cm^2
T_{max} = 650°C
P_{max} = 50 bar

Check www.HybSi.com and www.HySep.com
for pilot test equipment

Conclusions



- Hybrid silica sols
  - Preparation is straightforward
  - Automated synthesis is possible
  - A wide range of precursors can be used
  - Particle size and fractal dimension can be tuned

- HybSi® membranes:
  - Have a high hydrothermal stability
  - Show excellent PV performance
  - Show potential in H_2 separation
  - Are highly acid stable
  - Are readily scaled up and reproduced

Acknowledgement

Castricum, Kreiter, Ten Elshof, Vente et al.

Chem. Commun. 2008, 1103-1105

J. Mater. Chem. 2008, 18, 2150-2158

J. Sol-Gel Sci.Technol. 2008, *48*, 203-211

J. Membr. Sci. 2008, *324*, 111-118

ChemSusChem 2009, *2*, 158-160

Patent: WO2007081212

ECN

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