Stable HybSi® pervaporation membranes

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Presented at Euromembrane 2009, Montpellier, France, 6-10 September 2009

ECN-M—09-118 November 2009

ECN

Energy research Centre of the Netherlands

HybSi®

Pervaporation Membranes

Stable HybSi® pervaporation membranes

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Energy research Centre of the Netherlands

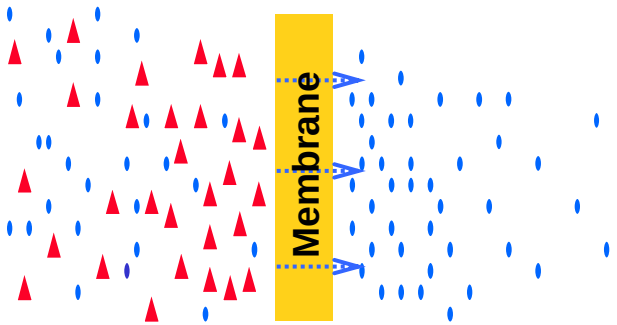
Energy research Centre of the Netherlands

- Non-governmental, non-profit institute
- One of the leading European institutes in energy research
- Develops technology for the transition to a sustainable energy system
- Bridges the gap between basic research and industrial application

Industrial membrane applications (PV/VP, GS)

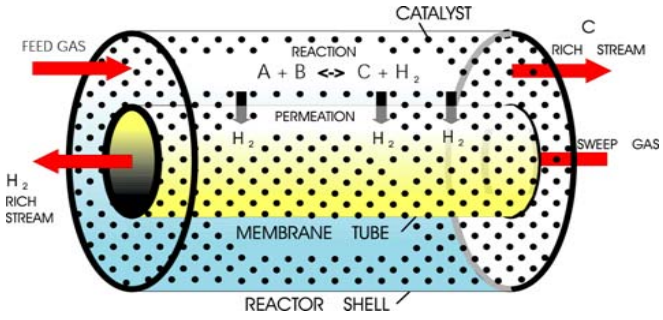
Pervaporation (PV)/ Vapor permeation (VP):

- Dewatering of organics, organic/organic



Gas separation (GS)

- H_2 from steam reforming/water-gas shift



- Also noble metal membranes
  www.hysep.com

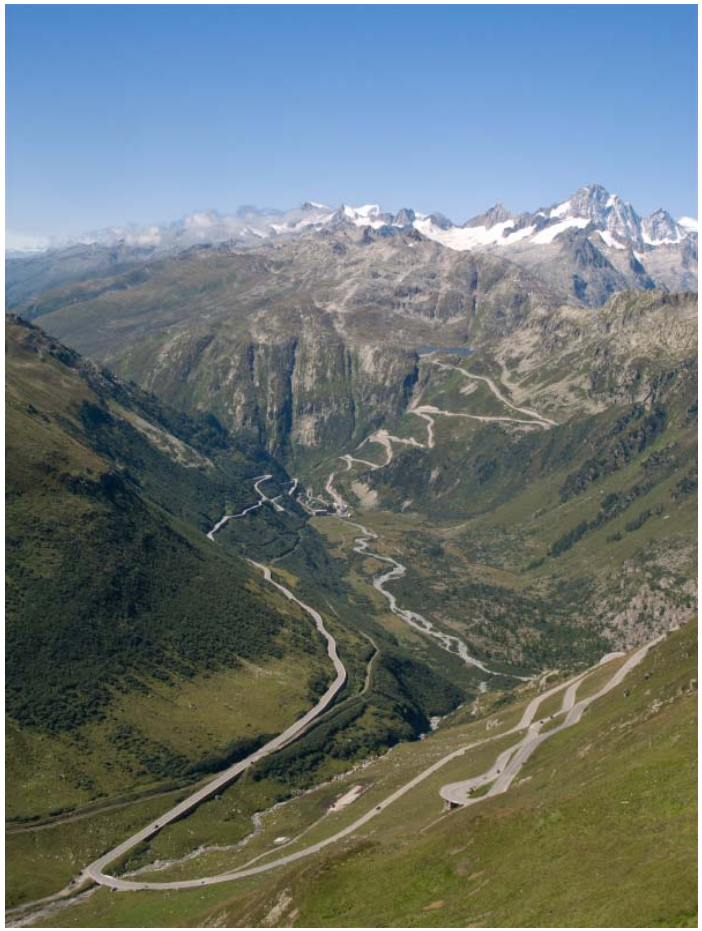
Mountains and microporous membranes

Membrane stability is challenged by:

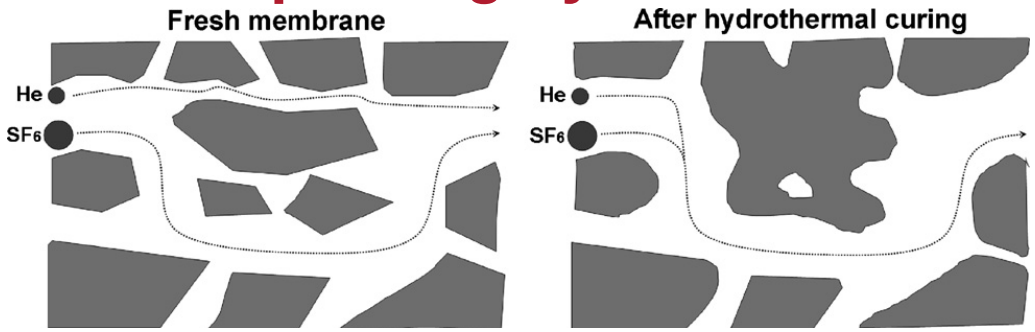
- (Hydro)thermal conditions
- Aggressive solvents
- Acids

Microporous sol-gel membranes

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



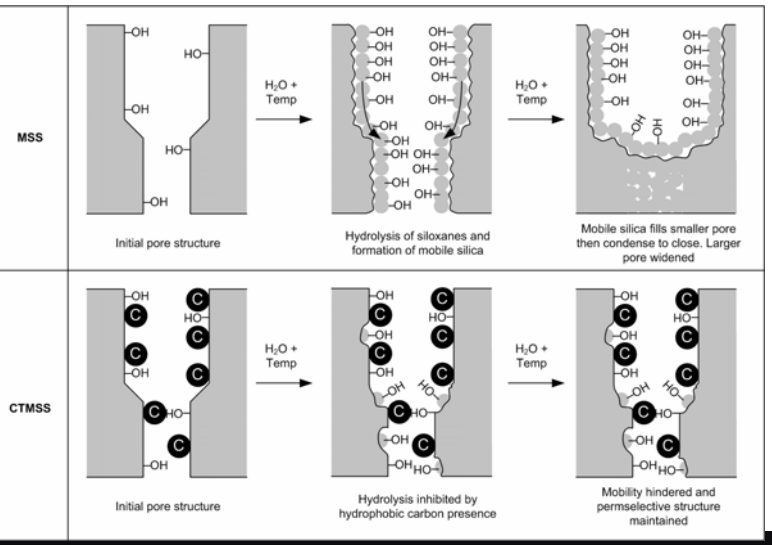
Improving hydrothermal stability of silica

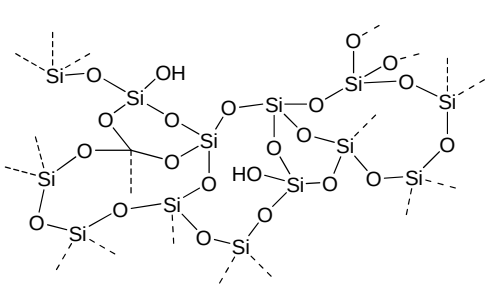


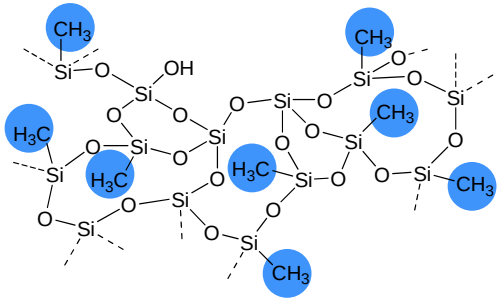
Mixed oxides (Zr, Co, Ni, Nb, Fe, Al)

Tsuru, *J.Membr.Sci.* 2006, 271, 86;
da Costa, *Sep.Pur.Technol.* 2009, 66, 299
ten Elshof, *J.Membr.Sci.* 2008, 319, 256

Carbon doped Silica da Costa.
Adv.Funct.Mat. 2006, 16, 1215





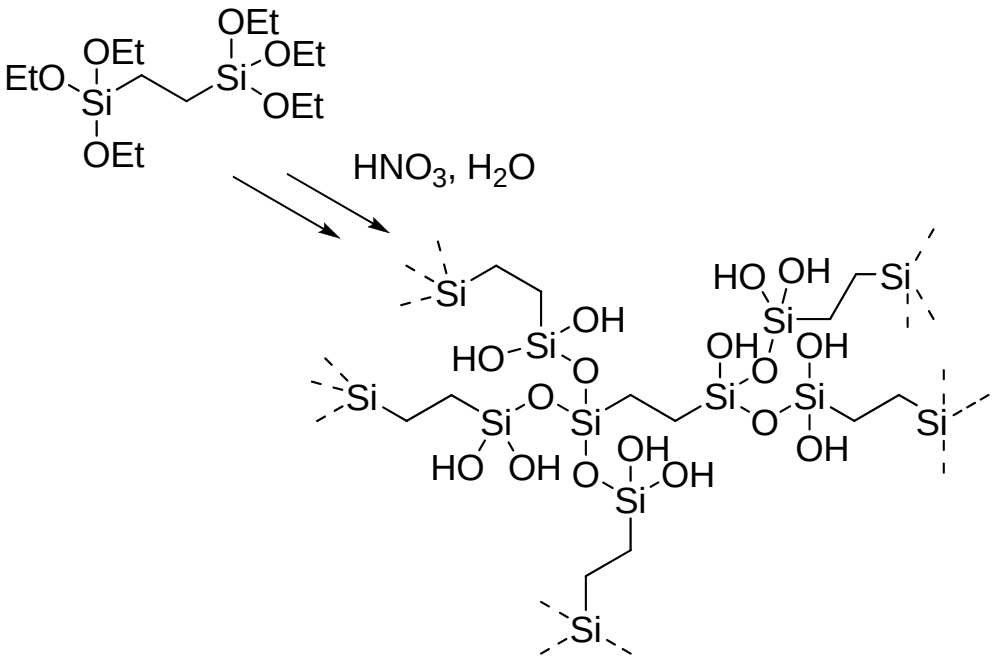


Lower water sorption

Methylated silica
Verweij, *J.Membr.Sci.* 1999, 158, 277

Our approach: bridged silica precursors

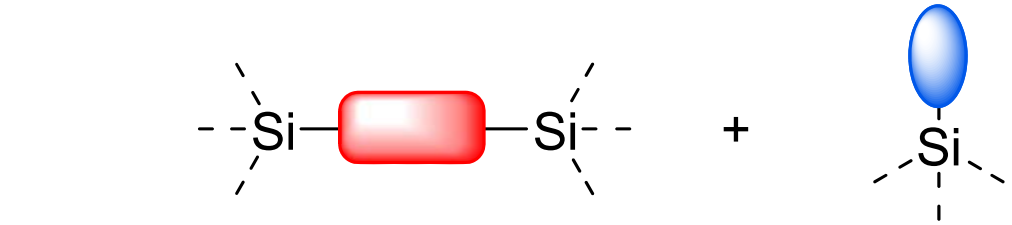
Strategy: replace Si—O—Si bonds by Si—C_nH_m—Si bonds



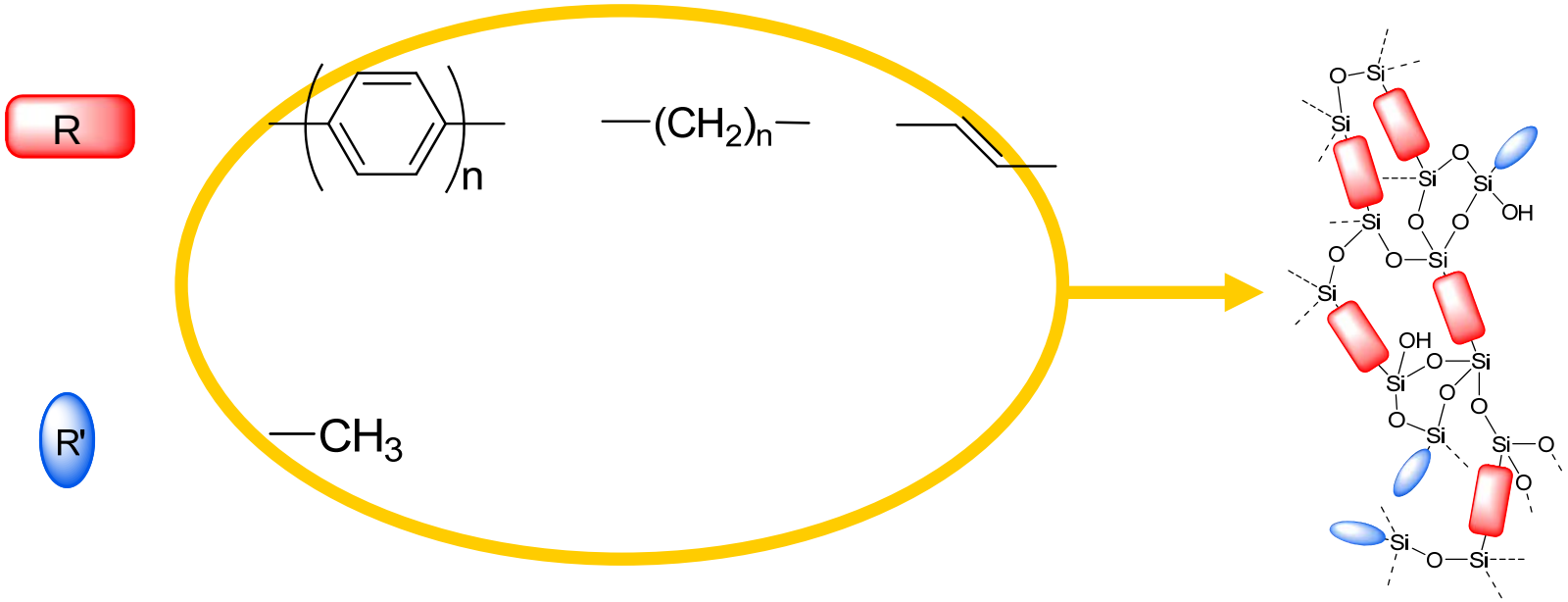
Development started in 2003

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 of hybrid silica sols

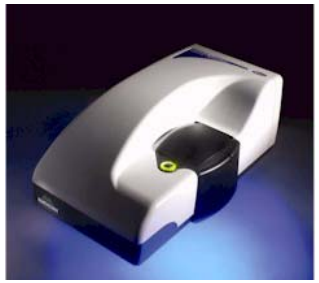
Automated synthesis of sols was performed varying:

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

Chemspeed ASW1000

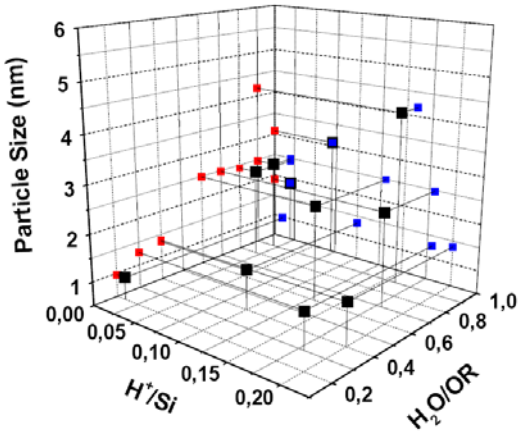
Total of ~160 individual sol preparations

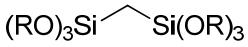
- 6.5 mL scale
- 1 standard in each run
- Analysis using DLS



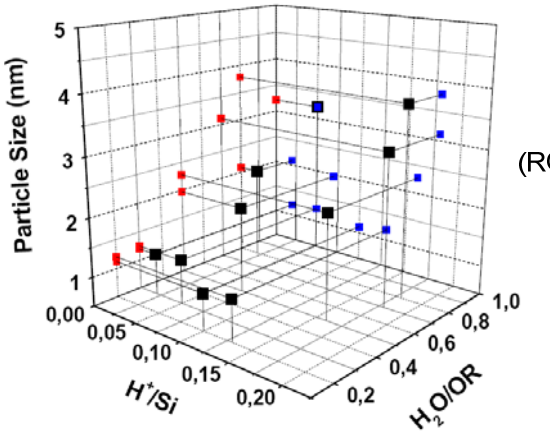
Malvern Zetasizer Nano ZS

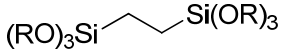
HTS – Example results





BTESM





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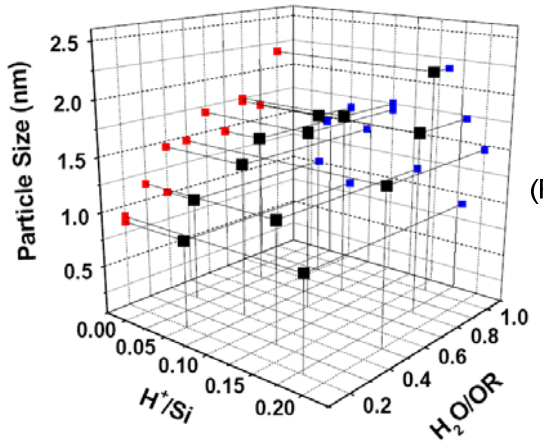

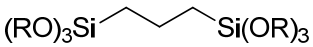

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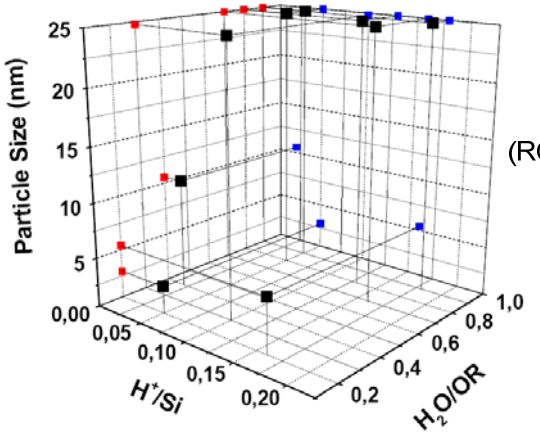
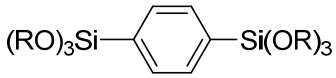
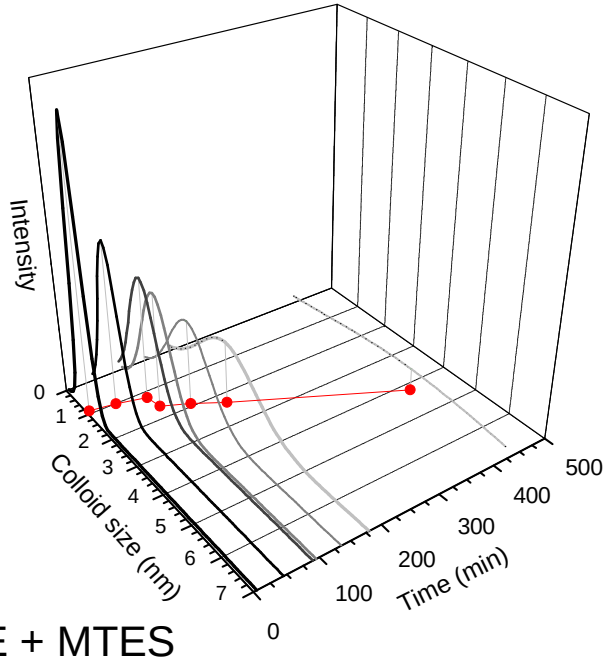


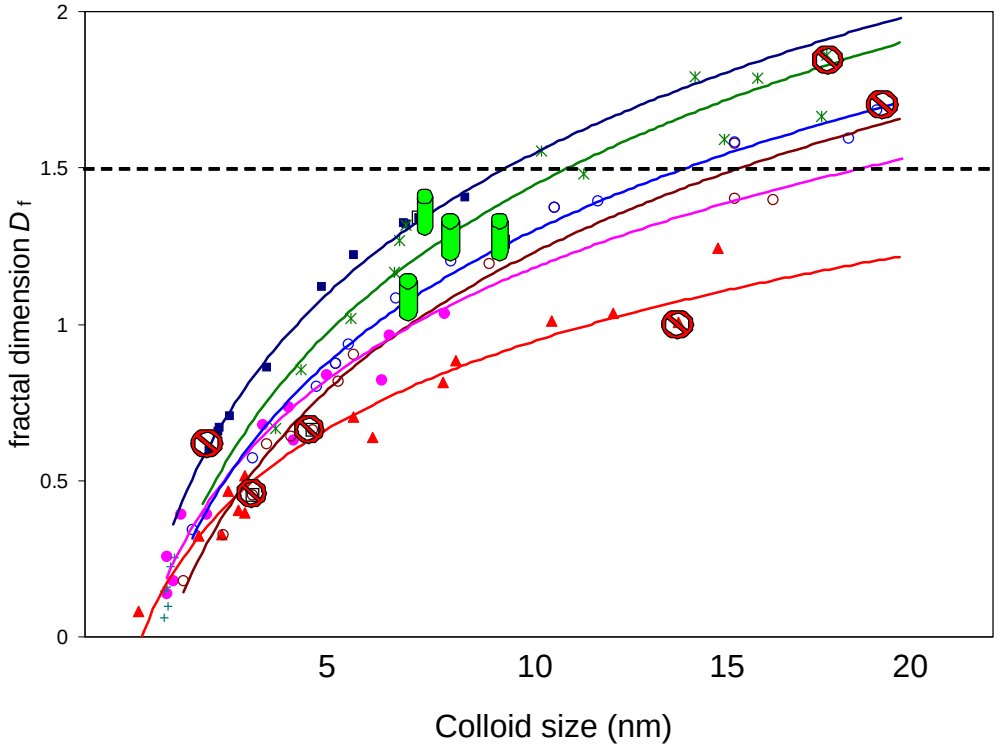


BTESB

DLS and SAXS



BTESE + MTES



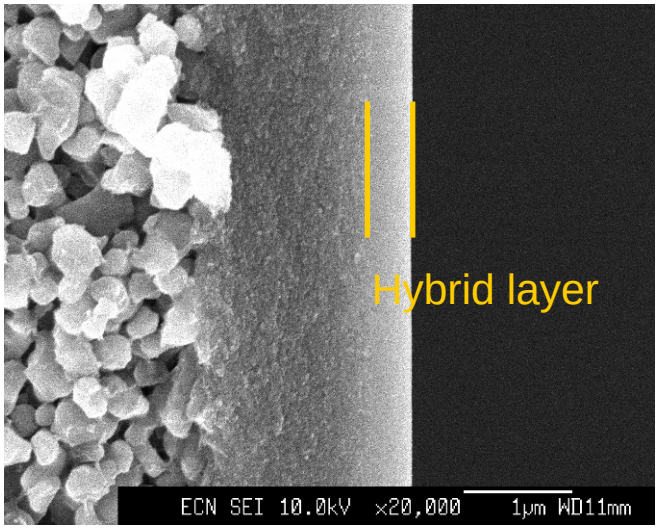
Particle sizes = 5-10 nm

D_f = 1-1.5

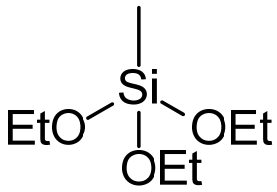
Precursors and PV performance

Precursors:

- BTESE + MTES
- BTESE
- BTESM



MTES



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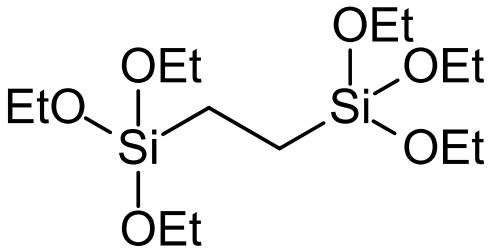

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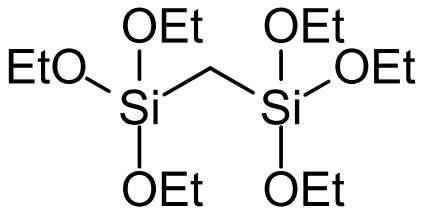
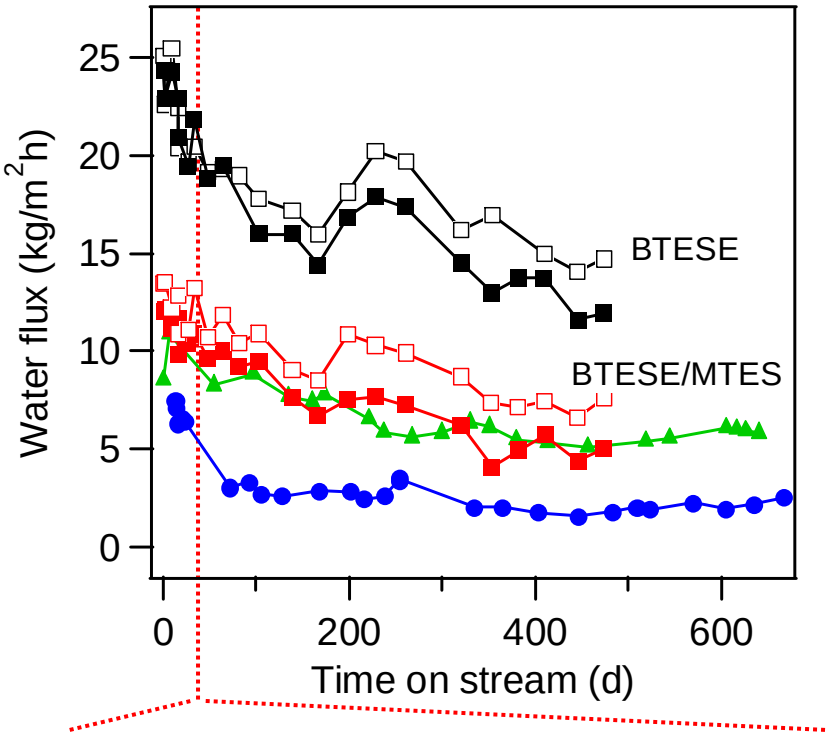
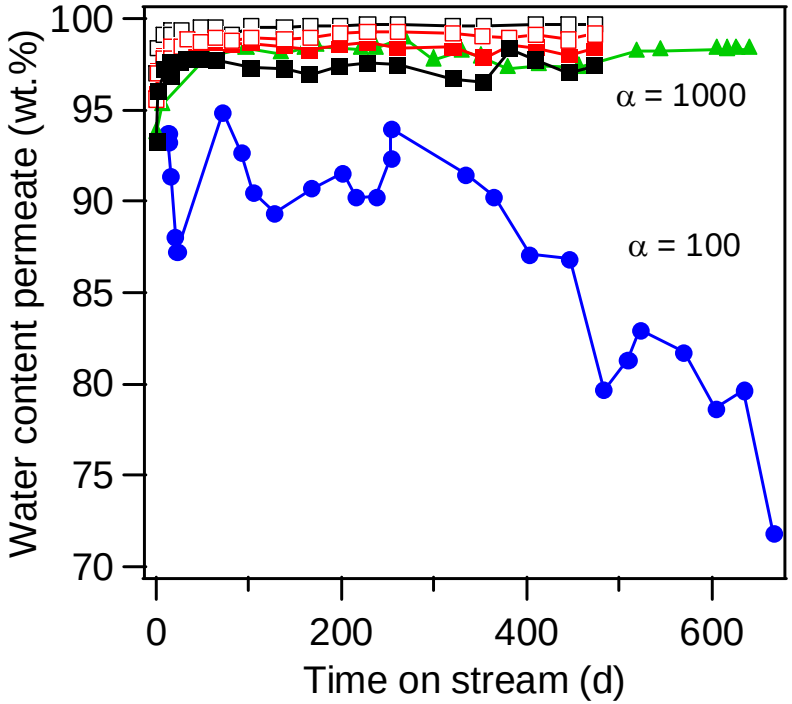


Performance hybrid membranes, 150°C

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



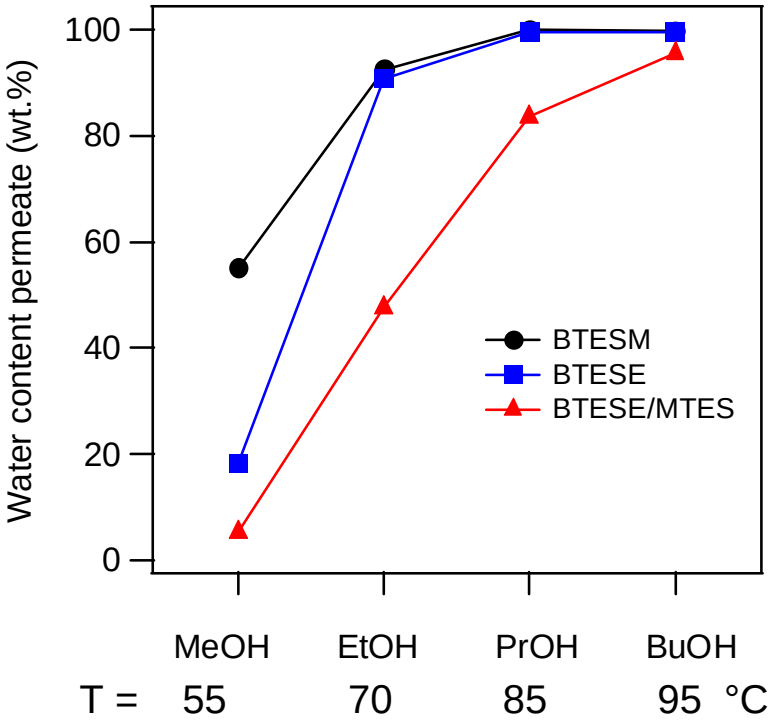
Life time state of the art methylated silica



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

Application testing – alcohols

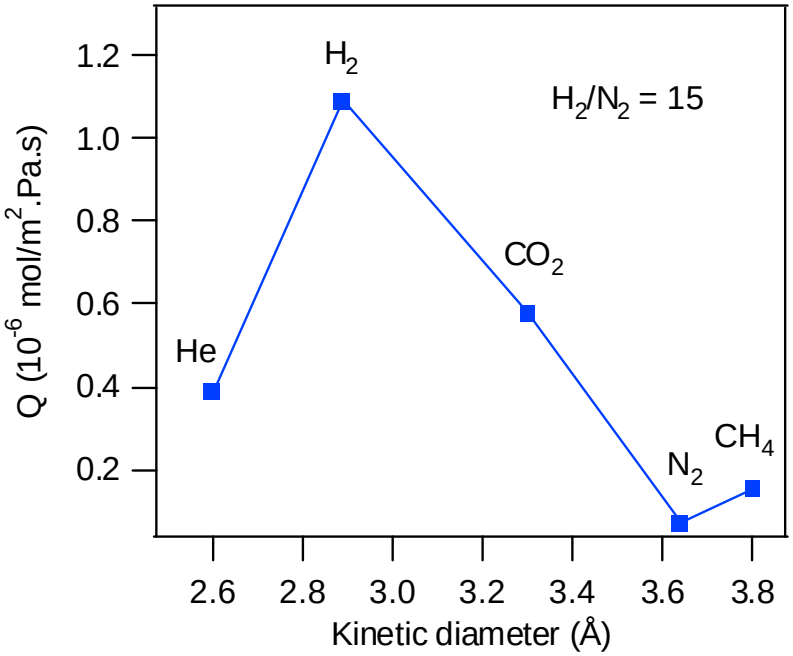
Feed = 5 wt.% water in alcohol



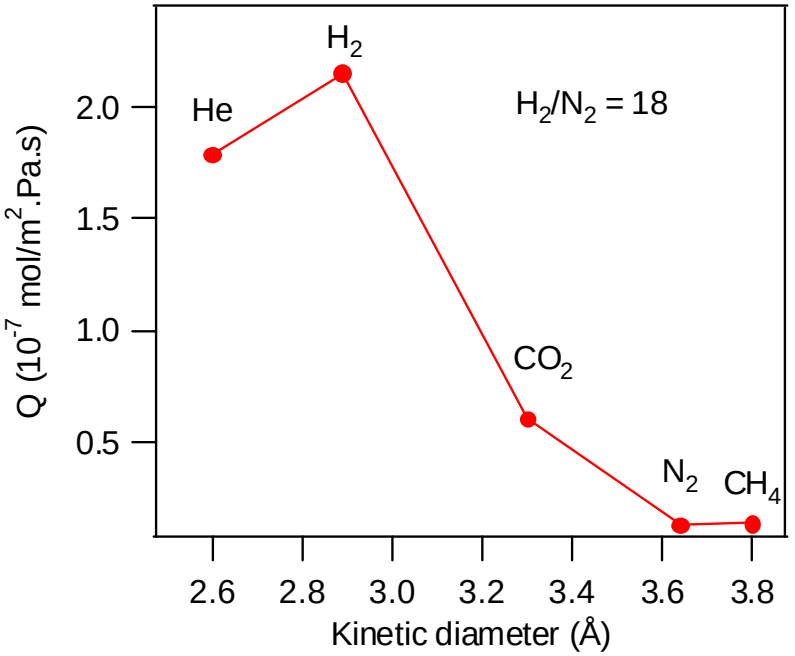
ChemSusChem 2009, 2, 158-160

Gas separation: hydrogen selectivity

BTESE

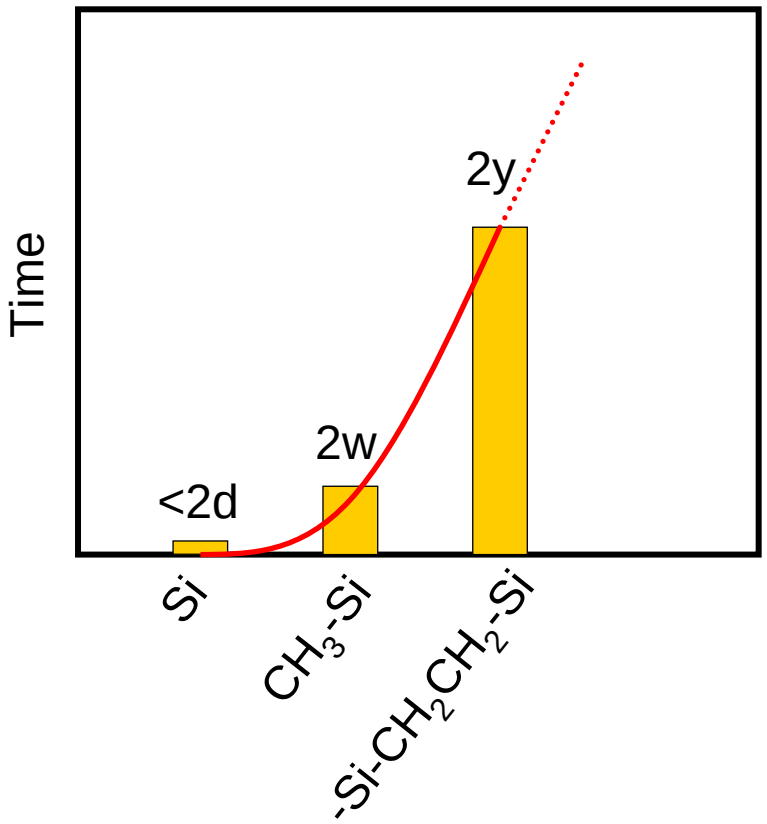


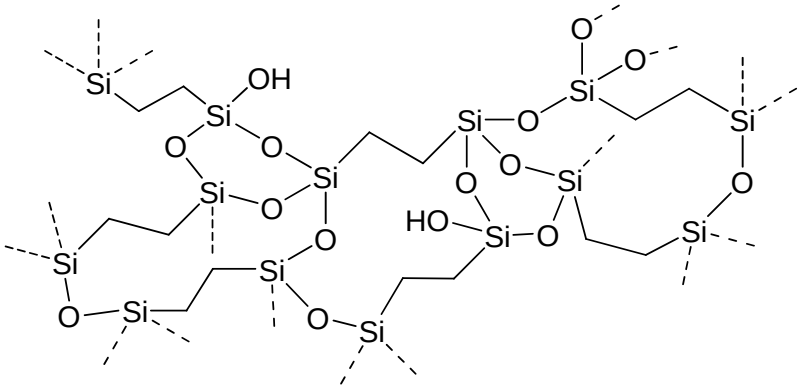
BTESM



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

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

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J.E. ten Elshof

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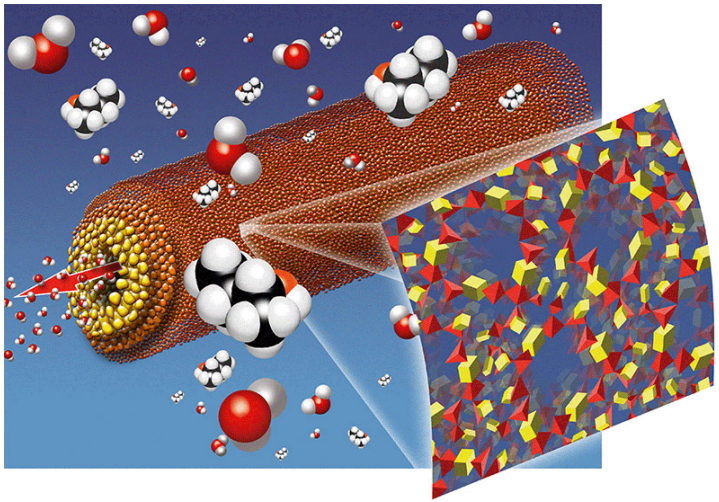

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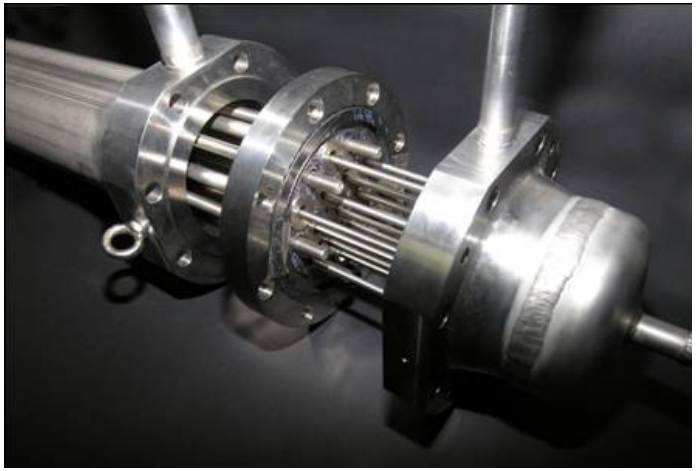
Hydrogen Separation Modules



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