Hydrothermal stability of silica-based membranes

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Hydrothermal stability of silica-based microporous membranes

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Incentive

- 40% of energy use in (petro)chemical for separations
- Dutch separation processes 190 PJ/year (= 6*10^9 m^3 natural gas)
- Low exergetic efficiency, so large energy 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)
• H₂ 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

Improving hydrothermal stability of silica: Organics and carbon

Methylated silica (MeSi)

Carbon-silica

De Vos, Verweij,
*J. Membr. Sci.* 1999, 158, 277

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
  

Latest development: **This presentation**
- Organic - inorganic hybrid silica
Tubular microporous membranes

Pores < 1nm
4 nm pores
120 nm pores
1 μm
Membrane preparation

Tubes: 30 – 100 cm
SiO$_2$ and MeSi pervaporation results (95ºC)

- 5 wt.% H$_2$O 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 165°C

- 2.5 wt.% H₂O 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

Screening precursors for HybSi® membranes

High-throughput screening (HTS) of hybrid silica sols

Automated synthesis of sols was performed varying:

- Precursor type
- Temperature
- $\text{H}_2\text{O}/\text{OR}$
- $\text{H}^+\text{OR}$

Total of ~160 individual sol preparations

- 6.5 mL scale
- 1 standard in each run
- Analysis using DLS
HTS – Example results

- \((\text{RO})_3\text{Si} \longrightarrow \text{Si(OR)}_3\) BTESM
- \((\text{RO})_3\text{Si} \longrightarrow \text{Si(OR)}_3\) BTESE
- \((\text{RO})_3\text{Si} \longrightarrow \text{Si(OR)}_3\) BTESP
- \((\text{RO})_3\text{Si}-\text{Si}(\text{OR})_3\) BTESB
SAXS and DLS

Particle sizes = 5-10 nm
$D_f = 1.0 - 1.5$
Case I: pervaporation
Precursors and PV performance

Precursors:
- BTESE + MTES
- BTESE
- BTESM
Performance hybrid membranes, 150ºC

Feed = 5 wt.% water in n-BuOH

First membrane made
BTESE/MTES

Life time >650 days

Life time state of the art methylated silica

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

Water flux (kg/m$^2$/h)

Water content permeate (wt.%)

J. Membr. Sci. 2008, 324, 111-118
Application testing - solvents

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

Temperature: 55  70  85  95  120 °C

Water flux (kg/m² h)

Water content permeate (wt.%)
Application testing - alcohols

Feed = 5 wt.% water in alcohol

![Graph showing water content permeate vs. Kelvin pore size for different alcohols at various temperatures.](image)

ChemSusChem 2009, 2, 158-160
Acid stability

Feed: 5 wt.% water in n-BuOH
0.005 – 0.5 wt.% HNO₃

BTESE

3.0
2.5
2.0
1.5
1.0
0.5

Water flux (kg/m² h)

0.005    0.05     0.5 wt% HNO₃

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

BTESM

3.0
2.5
2.0
1.5
1.0
0.5

Water flux (kg/m² h)

0.15 wt% HAc

J.Mater.Chem. 2008, 18, 1-10
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
\( A_{\text{mem}} = 1 \, \text{m}^2 \) (24 tubes)
\( T_{\text{max}} = 150^\circ \text{C} \)
\( P_{\text{max}} = 10 \, \text{bar} \)

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

Check [www.HybSi.com](http://www.HybSi.com) and [www.HySep.com](http://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 H₂ separation
  - Are highly acid stable
  - Are readily scaled up and reproduced
Acknowledgement

**Castricum, Kreiter, Ten Elshof, Vente et al.**
*J. Mater. Chem.* 2008, 18, 2150-2158
*J. Membr. Sci.* 2008, 324, 111-118
*ChemSusChem* 2009, 2, 158-160

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