Hydrothermal stable pervaporation membranes

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HYDROTHERMAL STABLE PERVERAPORATION MEMBRANES
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1 Abstract
Thermal separation processes like distillation consume a large amount of energy in the process industry. Replacing these processes by membrane pervaporation will lead to much lower energy consumption. The expected high chemical and thermal stability of inorganic membranes compared to polymer membranes has resulted in a growing research activity with the first aim of replacing polymer membranes with inorganic ones. The superior separation performance, i.e. selectivity and flux, of silica-based membranes in the dehydration of alcohols and solvents at elevated temperatures has raised the interest even further. The application depends on a reliable and good long-term performance. Unfortunately, information on this topic is still very limited. We have shown that silica and methylated silica membranes are not stable at temperatures above 100°C and the application window of state-of-the-art Me-SiO\textsubscript{2} membranes for use in dehydration processes is limited to 95°C [1]. For methanol separation from organic solvents the Me-SiO\textsubscript{2} membranes can be used at higher temperatures [2].

Hybrid silica materials are expected to have a much higher hydrothermal stability than (methylated) silica. The superior separation performance, i.e. selectivity and flux, of these hybrid membranes in the dehydration of alcohols and solvents at elevated temperatures has raised the interest [3]. High flux performance is required to decrease the membrane area needed and thereby the price to become competitive against the well know distillation technique. It is proven that the required water flux of at least 3 kg/m\textsuperscript{2}h, for the dehydration of 5wt.% water in butanol as a representative standard application, can be achieved easily. The profitable application of the membranes depends on a reliable, stable long-term behaviour and the broad applicability especially at temperatures above 100°C. We will report on the development of organic/inorganic hybrid silica membranes with selectivities and fluxes, that are comparable with the silica based membranes in dehydration by pervaporation. Details of test results will be given in different dehydration applications up to 150°C including the dehydration of aprotic solvents. Further, results will be given on long term stability testing up to 150°C and up to 2 years of continuous operation in the dehydration of organic mixtures. The results show that a completely new class of hybrid materials is available that opens new markets for dehydration processes by pervaporation.

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Part of this work was supported with a grant from the Dutch Ministry of Economic Affairs via the EOS-LT (Long term energy research subsidy) programme, managed by SenterNovem.

References
Hydrothermal stable pervaporation membranes
Development of hybrid silica - HybSi®

Henk van Veen, Rob Kreiter, Marielle Rietkerk, Charles Engelen, Hessel Castricum, Andre ten Elshof, and Jaap Vente
Introduction

- 474 PJ/year Energy use in NL (petro)chemical (NL≈2400 PJ/year)
- Separation processes 190 PJ/year
- Low exergetic efficiency, so large energy saving potential

By 2015 potential energy savings in dehydration pervaporation:
- NL: 7 PJ/yr (2% of industrial energy consumption)
- World: 240 PJ/yr

By 2015 potential energy saving, /pervaporation:
Introduction

BUT

Pervaporation membrane stability is limited with respect to:
- (Hydro) thermal conditions
- Solvent resistance
- Acids
Pervaporation membrane materials: goals set

Test conditions dehydration of organics by pervaporation:
1. Temperature: 150°C.
2. Mixture 5 wt.% water in n-butanol.
4. Pressures and pressure differences up to 30 bar.

and the membrane process should meet the following industrial demands:
1. Water flux of 5 kg/m²h.
2. Selectivity of at least 360 (feed 5 wt.% water → permeate 95 wt.% water).
3. Run time of 3 years = average maintenance time of a process.
4. Change of flux and selectivity of less than 10% per year.
Steps in the membrane production

Sol synthesis
↓
Membrane coating
↓
Drying
↓
Firing
↓
Ceramic membrane layer
↓
Membrane characterisation

1. Extrusion
2. Suspension-coating
3. Sol-Gel coating
4. Membrane coating
Preparation of the membranes

Coat Vessel

“dry”

coat speed

wet

evaporation

coat vessel

septum

suspension

Tubes: 30 – 100 cm
Tubular microporous membranes

- Pores < 1 nm
- 4 nm pores
- 120 nm pores
- ZrO₂/TiO₂
- 1000 nm
Materials covered

Previous developments:
- SiO₂
- Methylated SiO₂

New leads:
- TiO₂
- ZrO₂
- Hybrid silica (HybSi®), organic bridges
Silica and Me-Silica long term pervaporation at 95°C

Feed = 5 wt.% water in nBuOH

Methylated silica solves problem of the flux decline, selectivity meets demands
Me-Silica long term pervaporation up to 165°C

Feed = 2.5 wt.% water in nBuOH
Membrane failure within weeks

Water flux and conc. in permeate vs. time

Chem.Comm.2004, 834-835
Pervaporation with titania membrane

Feed = 5 wt.% water in nBuOH
Strong flux decline in time

Microporous Titania
95°C - 5% H₂O in n-BuOH

Similar results for zirconia
Hybrid membranes from bisfunctional silica precursors

HybSi®

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

\[(\text{OC}_2\text{H}_5)_3 - \text{Si} - \text{CH}_2 - \text{CH}_2 - \text{Si} - (\text{OC}_2\text{H}_5)_3\]

(bis(triethoxysilyl)ethane, BTESE)

Patented in collaboration with Univ. of Twente and Univ. of Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer)

Hybrid membranes

1. Mix BTESE in EtOH
2. Mix MTES in EtOH
3. Mix Water, HNO₃, EtOH
4. Reflux at 60°C for 3 hrs
5. Mix
6. Coating and calcination

Images of BTESE and MTES structures are shown, along with an image of the hybrid membrane surface.
Hybrid membranes: different precursors for improved performance

Precursors:
Recipe 1 BTESE + MTES
Recipe 2 BTESE
Recipe 3 BTESM

MTES
\[ \text{EtO} \rightarrow \text{Si} \rightarrow \text{OEt} \]

BTESE
\[ \text{EtO} \rightarrow \text{Si} \rightarrow \text{Si} \rightarrow \text{EtO} \rightarrow \text{OEt} \]

BTESM
\[ \text{EtO} \rightarrow \text{Si} \rightarrow \text{Si} \rightarrow \text{OEt} \]
Performance hybrid membranes, 150°C

First membrane made
Recipe 1
Feed = 5 wt.% water in nBuOH
Lifetime > 650 days

Fluxes and water conc. in permeate vs. time

Life time state of the art methylated silica

J. Mater. Chem. 2008, 18, 2150-2158
Performance hybrid membranes, 150°C

Water flux vs. time

Recipe 2, S=1000
Recipe 1, S=1000
Recipe 1, S=100

Life time state-of-the-art MeSi

Feed = 5 wt.% water in nBuOH

Feed = 5 wt.% water in nBuOH

Performance hybrid membranes, 150°C

Water conc. in perm. vs. time

Recipe 1, S=1000
Recipe 2

Performance hybrid membranes, 190°C

Feed = 5 wt.% water in nBuOH
Recipe 2
On stream > 1 month, selectivity stable

 fluxes and water conc. in permeate vs. time

 Fluxes (g/m²·h)
 12000
 10000
 8000
 6000
 4000
 2000
 0

 Water in permeate [wt.%]
 100
 98
 96
 94
 92
 90
 88

 Time (days)
 0 10 20 30 40

 "Water flux"
 "Butanol flux"
 "Water in permeate"
Hybrid membranes application testing

Feed = 5 wt.% water in solvent
Recipe 1

Water flux and conc. in perm in different solvents

Water flux
Water conc. in permeate

Temperature =  55       70         85         95       70        55        70      120 °C

Solvents
MeOH  EtOH  PrOH  BuOH  MEK  THF  AcNi  NMP
Hybrid membranes application testing

Feed = 5 wt.% water in solvent

Water conc. in perm in different solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Recipe 1</th>
<th>Recipe 2</th>
<th>Recipe 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td></td>
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</tr>
<tr>
<td>EtOH</td>
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<td></td>
</tr>
<tr>
<td>PrOH</td>
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<td></td>
</tr>
<tr>
<td>BuOH</td>
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</tbody>
</table>

Temp. = 55 70 85 95 °C

Normalized permeance

Kelvin pore size (nm)
Acid stability

Feed: 5 wt.% water in \textit{n}-BuOH
0.005 – 0.5 wt.% HNO\textsubscript{3}
Recipe 2

Feed: 5 wt.% water in EtOH
0.1 wt% HAc
Recipe 3

Acid stability very promising

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Origins of hydrothermal stability hybrid silica - HybSi®

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

- High hydrothermal stability
- Wide range of organics possible
- Excellent performance in aggressive solvents
- Good acid stability
- Straightforward preparation, good reproducibility
Next steps

- **FOCUS: IMPLEMENTATION VIA PILOT DEMONSTRATION**
  - State of the art membrane
    - Further define application window pH, H₂O content, solvents
    - Create consortium for commercialisation of HybSi®: end user(s), membrane producer(s), system integrator(s), supplier(s) enabling parts.
    - Launching application(s).

- Further developments:
  - Reduce pore size: H₂O-EtOH, and hydrogen separation
  - Increase pore size: nanofiltration, MeOH from organics
  - Module geometry optimisation

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

\[
\text{Si} \quad \text{EtO} \quad \text{OEt} \quad \text{Si} \quad \text{EtO} \quad \text{OEt} \quad \text{EtO} \quad \text{OEt} \quad \text{EtO}
\]
Questions?

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