Steam-stable silica-based membranes

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Published in:
PPM 2013 Abstracts

Publication date:
2013

Document Version
Early version, also known as pre-print

Link to publication from Aalborg University

Citation for published version (APA):
Boffa, V. (2013). Steam-stable silica-based membranes. In PPM 2013 Abstracts (pp. 223)
Designing steam-stable silica membranes

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Microporous silica membranes

Diagram showing a microporous silica membrane module with feed, permeate, retentate, and selective layer.

Chemical speciation:

- C_{3}H_{8}
- CH_{4}
- N_{2}
- H_{2}S
- CO_{2}
- H_{2}
- H_{2}O

A

Analysis:

- C_{3}H_{8}:
  - Value: 4.3
- CH_{4}:
  - Value: 3.8
- N_{2}:
- H_{2}S:
- CO_{2}:
- H_{2}:
- H_{2}O:
  - Value: 2.65
Upcoming technology platforms for green fuel production require the development of advanced molecular separation systems for recovering liquid biofuels, biomethane and hydrogen.

### Gas separation
- H₂ purification
- CO₂ sequestration
- Biogas upgrading

### Pervaporation
- Alcohol dehydration
- Separation of organic solvents
Ultramicroporous silica membranes

Nano Lett. 2012, 12, 1081–1086
Sol-gel
Sol-gel
**Hydrothermal treatment**

**HT1:** steam exposure ($P_{H2O} = 0.56$ bar) at $150 \, ^\circ C$ for 70 h;

**HT2:** steam exposure ($P_{H2O} = 0.56$ bar) at $200 \, ^\circ C$ for 70 h.

Nature of sol-gel derived silica membranes

High free energy:

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

Calorimetric analysis

Dried at 180 °C

Calcined at 700 °C

Calcined at 1250 °C
Nature of sol-gel derived silica membranes

High free energy:

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

Fabrication of hydrothermally stable microporous membranes

Strategies:

- Doped-silica membranes
- Non-SiO2 membranes
- Zeolite membranes
- Hybrid organic-inorganic silica membranes
<table>
<thead>
<tr>
<th>Modifier</th>
<th>Precursor</th>
<th>MSi molar ratio</th>
<th>Support</th>
<th>Deposition</th>
<th>Calcination T [°C]</th>
<th>H₂ Permeance ( \times 10^9 ) [mol Pa⁻¹ m⁻² s⁻¹]</th>
<th>Hydrothermal stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure silica</td>
<td>0</td>
<td>disk</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>Sol-gel</td>
<td>400-600</td>
<td>1700</td>
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<tr>
<td>Al₂O₃</td>
<td>Al(O-secBu)₃</td>
<td>0.02-0.065</td>
<td>tube</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>CVD</td>
<td>600</td>
<td>100-160</td>
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<tr>
<td>TiO₂</td>
<td>Ti(O-iPr)₄</td>
<td>0.03-0.2</td>
<td>tube</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>CVD</td>
<td>500-700</td>
<td>200-700</td>
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<tr>
<td>ZrO₂</td>
<td>Zr(O-ηBu)₄</td>
<td>0.11-1</td>
<td>tube</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>Sol-gel</td>
<td>570</td>
<td>40-300</td>
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<tr>
<td>Nb₂O₅</td>
<td>Nb(O-ηBu)s;</td>
<td>0.33</td>
<td>disk</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>Sol-gel</td>
<td>500</td>
<td>37</td>
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<tr>
<td>NiO/Co</td>
<td>Ni(NO₃)₂·6H₂O</td>
<td>0.25-1</td>
<td>tube</td>
<td>α-Al₂O₃/SiO₂-ZrO₂</td>
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<td>550-650</td>
<td>188</td>
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<tr>
<td>Co₃O₄</td>
<td>Co(NO₃)₂·6H₂O</td>
<td>0.25</td>
<td>tube</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>Sol-gel</td>
<td>600</td>
<td>6-10</td>
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<tr>
<td>C</td>
<td>HTAB</td>
<td></td>
<td>disk</td>
<td>α-Al₂O₃/γ-Al₂O₃</td>
<td>Sol-gel</td>
<td>500</td>
<td>48</td>
</tr>
</tbody>
</table>

V. Boffa, 2012, Fabrication of ultramicroporous silica membranes for pervaporation and gas-separation, in Molecules at Work (B. Pignataro ed.) Wiley-VCH, 177-205.
Synthesis of mesoporous MxOy-silica powders

Addition of CTAB as pore tailoring agent

Drying and calcination at 450 °C

Hydrothermal treatment

Drying

Characterization

In autoclave at 120 °C for 48 h

Characterization
• TiO₂ doping is suitable to stabilize silica membranes for applications, which require high membrane permeability.
• ZrO₂ and Nb₂O₅-doped silica layers can be used where membrane stability is more important than membrane permeability.
Our data indicate that Ti(IV), Zr(IV), and Nb(V) ions act as network formers: they increase $T_g$ and steam-resistance of porous silica structure, by enhancing its network connectivity.
Nb$_2$O$_5$-silica membrane

This membrane is not a simple sieve, it can separate molecules also on the basis of their chemical properties.

Inorganic nanoporous membranes

1) Uhlhorn et al. 1992
“Synthesis of ceramic membranes”, J. Mater. Sci. 27 (527).

Defect free-membranes

Sol-gel science and technology

1980 1990 2000 2010
Inorganic nanoporous membranes

1. J. Sekulic et al. 2002 Microporous silica and doped silica membrane for alcohol dehydration by pervaporation, Desalination 148 (19).


Hybrid materials

- Organic backbone
- Amino functional groups

Stable membranes

Timeline:
- 1980
- 1990
- 2000
- 2010
Inorganic nanoporous membranes

Doped materials


Stable membranes

Defect-free membranes

Functional membranes

1980 1990 2000 2010
Conclusions

“Fabrication and application of inorganic membranes relies on the development of new functional and ultrastable materials”
Acknowledgements

Aalborg University
• Prof. Yuanzheng Yue

Turin University
• Dr. Giuliana Magnacca

Danish National Advanced Technology Foundation