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)

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Designing steam-stable silica membranes

Vittorio Boffa

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Microporous silica membranes
Upcoming technology platforms for green fuel production require the development of advanced molecular separation systems for recovering liquid biofuels, biomethane and hydrogen.

<table>
<thead>
<tr>
<th>Gas separation</th>
<th>Pervaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>• H₂ purification</td>
<td></td>
</tr>
<tr>
<td>• CO₂ sequestration</td>
<td></td>
</tr>
<tr>
<td>• Biogas upgrading</td>
<td></td>
</tr>
<tr>
<td>• Alcohol dehydration</td>
<td></td>
</tr>
<tr>
<td>• Separation of organic solvents</td>
<td></td>
</tr>
</tbody>
</table>

![Diagram of CO₂ sorption and H₂ production](image1)

![Image of CH₃CH₂OH and F-Cell car](image2)
Ultramicroporous silica membranes

Silica top layer

\(\gamma\)-Alumina

\(\alpha\)-Alumina

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

Permeance [mol Pa⁻¹ m⁻² s⁻¹]

- He
- H₂
- CO₂
- N₂
- CH₄

Kineti diameter [nm]

Log scale
Hydrothermal treatment

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

**HT2**: steam exposure ($P_{H2O} = 0.56$ bar) at 200 °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>Geometry</th>
<th>Material</th>
<th>Deposition</th>
<th>Calcination</th>
<th>$H_2$ Permeance</th>
<th>Hydrothermal stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T[°C]</td>
<td>$\text{mol Pa}^{-1} \text{m}^{-2} \text{s}^{-1}$</td>
<td>stability</td>
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<tr>
<td>Reference silica membrane</td>
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<td></td>
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<td>Pure silica</td>
<td>0</td>
<td>disk</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>Sol-gel</td>
<td>400-600</td>
<td>1700</td>
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<tr>
<td>modified membranes</td>
<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$\text{Al(O-secBu)}_3$</td>
<td>0.02-0.065</td>
<td>tube</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>CVD</td>
<td>600</td>
<td>100-160</td>
<td>+</td>
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<tr>
<td>$\text{TiO}_2$</td>
<td>$\text{Ti(O-iPr)}_4$</td>
<td>0.03-0.2</td>
<td>tube</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>CVD</td>
<td>500-700</td>
<td>200-700</td>
<td>+</td>
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<tr>
<td>$\text{ZrO}_2$</td>
<td>$\text{Zr(O-nBu)}_4$</td>
<td>0.11-1</td>
<td>tube</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>Sol-gel</td>
<td>570</td>
<td>40-300</td>
<td>+</td>
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<tr>
<td>$\text{Nb}_2\text{O}_5$</td>
<td>$\text{Nb(O-nBu)}_6$</td>
<td>0.33</td>
<td>disk</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>Sol-gel</td>
<td>500</td>
<td>37</td>
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<tr>
<td>$\text{NiO/Ni}$</td>
<td>$\text{Ni(NO}_3)_2\cdot 6\text{H}_2\text{O}$</td>
<td>0.25-1</td>
<td>tube</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\text{SiO}_2$-$\text{ZrO}_2$</td>
<td>Sol-gel</td>
<td>550-650</td>
<td>188</td>
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<tr>
<td>$\text{Co}_3\text{O}_4$</td>
<td>$\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$</td>
<td>0.25</td>
<td>tube</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</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>$\alpha$-$\text{Al}_2\text{O}_3/\gamma$-$\text{Al}_2\text{O}_3$</td>
<td>Sol-gel</td>
<td>500</td>
<td>48</td>
<td>+</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
• TiO$_2$ doping is suitable to stabilize silica membranes for applications, which require high membrane permeability.
• ZrO$_2$ and Nb$_2$O$_5$-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\textsubscript{2}O\textsubscript{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. Meter. 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

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