Steam-stable silica-based membranes

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Designing steam-stable silica membranes

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Microporous silica membranes

A

C$_3$H$_8$  CH$_4$  N$_2$  H$_2$S  CO$_2$  H$_2$  H$_2$O

4.3  3.8  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

![Graph showing permeance vs kinetic diameter for different gases]

- He
- H₂
- CO₂
- N₂
- CH₄

Permeance [mol Pa⁻¹ m⁻² s⁻¹]

Kineti diameter [nm]
Hydrothermal treatment

**HT1**: steam exposure ($P_{H_2O} = 0.56$ bar) at 150 °C for 70 h;

**HT2**: steam exposure ($P_{H_2O} = 0.56$ bar) at 200 °C for 70 h.

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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
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 Temp [°C]</th>
<th>H$_2$ Permeance [mol Pa 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-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>Sol-gel</td>
<td>400-600</td>
<td>1700</td>
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<td></td>
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<td>Al$_2$O$_3$</td>
<td>Al(O-secBu)$_3$</td>
<td>0.02-0.065</td>
<td>tube</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>CVD</td>
<td>600</td>
<td>100-160</td>
<td>+</td>
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<tr>
<td>TiO$_2$</td>
<td>Ti(O-iPr)$_4$</td>
<td>0.03-0.2</td>
<td>tube</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>CVD</td>
<td>500-700</td>
<td>200-700</td>
<td>+</td>
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<tr>
<td>ZrO$_2$</td>
<td>Zr(O-nBu)$_4$</td>
<td>0.11-1</td>
<td>tube</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>Sol-gel</td>
<td>570</td>
<td>40-300</td>
<td>+</td>
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<tr>
<td>Nb$_2$O$_5$</td>
<td>Nb(O-nBu)$_5$</td>
<td>0.33</td>
<td>disk</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>Sol-gel</td>
<td>500</td>
<td>37</td>
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<td>NiO/Ni</td>
<td>Ni(NO$_3$)$_2$·6H$_2$O</td>
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<td>tube</td>
<td>α-Al$_2$O$_3$/SiO$_2$-ZrO$_2$</td>
<td>Sol-gel</td>
<td>550-650</td>
<td>188</td>
<td>+</td>
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<tr>
<td>Co$_3$O$_4$</td>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>0.25</td>
<td>tube</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$O$_3$</td>
<td>Sol-gel</td>
<td>600</td>
<td>6-10</td>
<td>+</td>
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<tr>
<td>C</td>
<td>HTAB</td>
<td></td>
<td>disk</td>
<td>α-Al$_2$O$_3$/γ-Al$_2$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 in autoclave at 120 °C for 48 h

- Drying

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.
The graph shows the specific heat capacity ($C_p$) versus temperature ($\text{Temperature}$) in units of $[\text{J g}^{-1} \text{°C}^{-1}]$. There is a sharp increase in $C_p$ at a specific temperature, indicating a phase transition, possibly glass transition ($T_g$).
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.
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

- Doped materials
- 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”
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