Steam-stable silica-based membranes

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Designing steam-stable silica membranes

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Microporous silica membranes

Feed

C\textsubscript{3}H\textsubscript{8} \quad CH\textsubscript{4} \quad N\textsubscript{2} \quad H\textsubscript{2}S \quad CO\textsubscript{2} \quad H\textsubscript{2} \quad H\textsubscript{2}O

4.3 \quad 3.8 \quad \downarrow \quad \downarrow \quad 2.65

Permeate side

selective layer

retentate side
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>M/ Si molar ratio</th>
<th>Geometry</th>
<th>Material</th>
<th>Deposition</th>
<th>Calcination [°C]</th>
<th>H$_2$ 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>$\alpha$-Al$_2$O$_3$/$\gamma$-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>Reference silica membrane</td>
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<td></td>
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<td></td>
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<td></td>
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<tr>
<td>modified membranes</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>Al(O-secBu)$_3$</td>
<td>0.02-0.065</td>
<td>tube</td>
<td>$\alpha$-Al$_2$O$_3$/$\gamma$-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-$i$Pr)$_4$</td>
<td>0.03-0.2</td>
<td>tube</td>
<td>$\alpha$-Al$_2$O$_3$/$\gamma$-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-$n$Bu)$_4$</td>
<td>0.11-1</td>
<td>tube</td>
<td>$\alpha$-Al$_2$O$_3$/$\gamma$-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-$n$Bu)$_5$</td>
<td>0.33</td>
<td>disk</td>
<td>$\alpha$-Al$_2$O$_3$/$\gamma$-Al$_2$O$_3$</td>
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<td>500</td>
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<td>NiO/Ni</td>
<td>Ni(NO$_3$)$_2$·6H$_2$O</td>
<td>0.25-1</td>
<td>tube</td>
<td>$\alpha$-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>$\alpha$-Al$_2$O$_3$/$\gamma$-Al$_2$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>
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<td>$\alpha$-Al$_2$O$_3$/$\gamma$-Al$_2$O$_3$</td>
<td>Sol-gel</td>
<td>500</td>
<td>48</td>
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</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

- Synthesis of MxOy-silica sols
- 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

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


Inorganic nanoporous membranes

Doped materials


Stable membranes | Defect-free membranes | Functional membranes

Permeance [mol·Pa$^{-1}$·m$^{-2}$·s$^{-1}$]

- He
- H$_2$
- N$_2$
- CH$_4$
- CO$_2$
- SF$_6$

Kinetic diameter [nm]
Conclusions

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