Pd-based membranes for high temperature hydrogen separation

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Agenda

- Mechanism of H₂ permeation
- Supported Pd-based membranes
- H₂ permeation

- Ceramic metallic support
- Ultra thin Pd-Ag < 2 µm
- Sulphur poisoning
- Pd Support Strong interaction

Low temperature < 300°C
Medium temperature 300-500°C
High temperature 300-500°C

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**H₂ permeation in Pd membranes**

*Ultra-thin membranes*

- Surface interference
- H₂ splitting

**Adsorption**

**Splitting**

**Diffusion**

**Recombination**

**Desorption**

Resistance of support
Methods of preparation of supported Pd membranes

**CVD**

- Vacuum
- **Pd acetate**

**Electroless plating**

- Support
- Seeds on support
- **Pd membrana**

**PVD**
### Characteristics of the porous support

**Surface properties**
- ✓ Small pore size
- ✓ Narrow pore size distribution
- ✓ Smooth surface
- ✓ Low resistance to gas permeation
- ✓ Mechanically strong
- ✓ No reaction with Pd layer

<table>
<thead>
<tr>
<th>Ceramic support</th>
<th>Metallic support</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Good surface properties</td>
<td>✓ Mechanically strong</td>
</tr>
<tr>
<td>✓</td>
<td>✓ No problems with sealing</td>
</tr>
<tr>
<td>✓</td>
<td>✓ Easy to connect to metallic reactors</td>
</tr>
<tr>
<td>X</td>
<td>X Not good surface properties</td>
</tr>
<tr>
<td>X</td>
<td>X Difficult to connect to metallic reactors</td>
</tr>
<tr>
<td>X</td>
<td>X Sealing</td>
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</table>

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Graphite sealings

Leak zone

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Low temperature (< 300 °C) H₂ permeation

Pd-Ag membranes

\[ \alpha-\beta \text{ transition Pd-H} \]


Pore filled Pd membranes

Pacheco Tanaka et.al
Advanced Materials, 18, 630-632,(2006)
Long term permeation test of a 1.3 μm PdAg membrane

400 °C  1 bar

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**H₂ flux at various gas mixtures and pressures at 400°C**

Membrane thickness 1.30 um

**Effect of dilution H₂ and N₂**

At H₂ /N₂ 60/40
Replacing some N₂ with CO

\[
J = \left( \frac{DS}{l} \right) e^{-\frac{(E_a/RT)(P^m_0 - P^m_1)}{P^m_{ret,avg} 0.5 - P^m_{perm} 0.5 (Pa)^{0.5}}}
\]

Effect of the pore size of the support

Smaller pore, thinner membrane

600 °C 100 kPa

H₂ permeance $7.8 \times 10^{-6}$ mol s$^{-1}$m$^{-2}$ Pa$^{-1}$

H₂/N₂ Selectivity 4700
Water gas shift reaction (WGS) (400 °C)

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2
\]

Strong -Interaction between Pd and TiO\textsubscript{2} (formation of PdTi alloy)

Fernandez et al., Int J. Hydrogen Energy 2015 (40) 3506-3519

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Five Pd-Ag membranes module WGS membrane reactor

Temperature 400 °C
\(P_{\text{permeate}}\) 1 bar, \(P_{\text{retentate}}\) 2 bar
Feed 10NL/min pure \(\text{H}_2\)

Catalyst: 2\% \(\text{Pt/Al}_2\text{O}_3\) 180 µm 88 g
\(\text{Al}_2\text{O}_3\) filler 160 µm 866 g

Helmi et al., Molecules 2016, 21, 376

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Metallic supported Pd-Ag membranes

Long term permeation test at 400 °C

- H₂ permeance 400 °C: \(0.9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}\)
- H₂/N₂ ideal selectivity 400 °C: \(>150,000\) for \(>200\) h
Metallic supported Pd-Ag membranes

Long term permeation test at more than 500 °C

- At >500 °C and after >800 h, \( \text{H}_2/\text{N}_2 \) ideal selectivity dropped to from 223000 to 2650
Effect of the addition of Au in a Pd-Ag alloy membrane

**H₂ flux in function of temperature**

**Activation energy**

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SEM images of the membranes after H2S test

Pd96.1Ag3.9  

Pd91.5 Ag4.7 Au3.8
Effect of the H2S in the hydrogen permeation on PdAg and PaAgAu membranes

Pd96.1Ag3.9/ Pd91.5 Ag4.7 Au3.8

JJ. Melendez et.al, journal of membrane science 542 (2017) 329-341

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Effect of the support on hydrogen permeation of Pd membranes at elevated temperature

α-alumina support

.. D.A. Pacheco Tanaka..., Chemistry Letters Vol.37, No.9 (2008)
α-alumina support

XPS spectra of the membrane surface

As deposited

After H₂ permeation
At 650 C

After H₂ permeation
At 850 C

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Hydrogen permeation flux versus operating time at \(650^\circ C\) with pressure differences of 100 kPa
Thank you for your attention

FOR MORE INFORMATION:
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