High Purity Hydrogen from Coal-Derived Syngas

Jim Torkelson, Neng Ye, Zhijiang Li and Mark Fokema
Aspen Products Group, Inc.
May 15, 2007
Overview

Timeline
• Start: June 2005
• End: May 2008
• 75% Complete

Budget
• Total project funding
  – DOE: $498k
  – Contractor: $125k
• Funding received in FY06
  – $231k
• Funding for FY07
  – $201k

Barriers
• Hydrogen from Coal – Research, Development & Demonstration Program
  – WGS Reaction Barriers
    • D. Impurity Intolerance/Catalyst Durability
  – Hydrogen Separation Barriers
    • I. Poisoning of Catalytic Surfaces
    • Q. Impurities in Hydrogen from Coal
Overall Goal

Develop water gas shift (WGS) membrane reactor that cost-effectively produce pure hydrogen from coal-derived synthesis gas containing significant amounts of hydrogen sulfide and hydrogen chloride
• Replaces multiple process units (contaminant removal, high temperature shift, low temperature shift, pressure swing adsorption) with single catalytic membrane reactor
• High process efficiency realized by improving hydrogen yield at low steam to carbon ratios
• Produces high-pressure CO2-rich stream potentially suitable for sequestration
Objectives

- Develop sulfur- and chloride-tolerant, highly active WGS catalyst that is able to operate at low steam to carbon ratios
- Develop low-cost, contaminant-tolerant $\text{H}_2$-selective membrane
- Demonstrate an integrated WGS membrane reactor operating on simulated coal-derived syngas
- Analyze cost benefits of the demonstrated WGS membrane reactor technology
Approach

Develop water gas shift catalyst and H\textsubscript{2}-selective membrane that both operate at 300-500°C, at 300-500 psig and are tolerant of high concentrations of H\textsubscript{2}S and HCl

Catalyst

• MoS\textsubscript{2}-based catalyst with modifiers to promote impurity tolerance

Membrane

• Dense Ta-based membrane with surface modifications to promote H\textsubscript{2} dissociation/association reactions in the presence of S and Cl
WGS Catalyst Development

60% CO, 25% H₂, 10% CO₂, 5% N₂, 3000 ppm H₂S, H₂O/CO=4, 400 psig, GHSV=3000 h⁻¹

- Equilibrium yields realized with catalyst A3 at 300-500°C
- Tolerant to 3000 ppmv (dry gas) H₂S
WGS Catalyst Stability

Catalyst A3, 60% CO, 25% H₂, 10% CO₂, 5% N₂, H₂O/CO=4, 400°C, 400 psig, GHSV=3000 h⁻¹

- Stable in the presence of 3000 ppmv (dry gas) H₂S
- Mild reversible deactivation with 350 ppmv (dry gas) HCl
Membrane Design

• Developed substrate cleaning and coating technique
• Examined effects of substrate thickness, coating composition, coating thickness and annealing conditions on pure H₂ permeability
• Examined effects of H₂O, H₂S, CO, and CO₂ on membrane performance
Membrane $H_2$ Permeability

- $H_2$ permeability greater than dense Pd-based membranes
- High selectivity $\rightarrow$ $H_2$ purity $>99.9\%$
- Good mechanical strength - tested up to 550°C & 400 psi

Test Conditions
- 95% $H_2$ – 5% He
- 350-550°C
- 200 psig $H_2$

\[ \frac{1}{T/\text{K}} \text{ vs } H_2\text{ Permeability (mol/s/m/Pa}^{0.5}) \]

References:
Membrane Sulfur Tolerance

Test Conditions
425°C
150 psig H₂

- Membrane tolerant of high concentration of H₂S
- 14% reduction in permeability upon exposure to 2000 ppm H₂S
Membrane Moisture Tolerance

Test Conditions
425°C
150 psig H₂

- Membrane tolerant of high concentration of steam
- 22% reduction in permeability upon exposure to 33% H₂O
Future Work

FY 2007
- Quantify performance and stability of membrane in contaminant-laden syngas
- Examine membrane microstructure in order to relate permeability to structure and synthetic parameters
- Fabricate and demonstrate integrated water gas shift membrane reactor

FY 2008
- Conduct cost analysis
Summary

Water Gas Shift
• Contaminant-tolerant water gas shift catalyst development and testing completed
• Equilibrium yields demonstrated at practical operating conditions
• Catalyst maintains high activity over wide temperature range (300-500°C)
• Excellent catalyst durability in the presence of 3000 ppm H₂S and 350 ppm HCl observed over 220 hours

H₂-Permeable Membrane
• Dense metal membranes with high H₂ permeability and H₂ selectivity demonstrated
• Membrane H₂ permeability greater than that of Pd-based membranes
• Membrane maintains high permeability in the presence of 2000 ppm H₂S and 33% H₂O
# Hydrogen From Coal Program Goals

## Water Gas Shift Catalyst

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>Current Status</th>
<th>Targets</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Form</td>
<td>Pellets</td>
<td>Advanced configurations – TBD</td>
<td>Pellets</td>
</tr>
<tr>
<td>Active Metal</td>
<td>Cu/Zn or Fe/Cr or Co/Mo</td>
<td>Advanced configurations – TBD</td>
<td>Mo</td>
</tr>
<tr>
<td>Feed Temperature (°C)</td>
<td>200-300</td>
<td>&gt;250</td>
<td>&gt;400</td>
</tr>
<tr>
<td>Feed Pressure (psia)</td>
<td>450-1150</td>
<td>&gt;450</td>
<td>&gt;750</td>
</tr>
<tr>
<td>Approach to Equilibrium (°C)</td>
<td>8-10</td>
<td>&lt;6</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Min. H₂O/CO Ratio</td>
<td>2.6</td>
<td>&lt;2.6</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Sulfur Tolerance (ppm₉)</td>
<td>varies</td>
<td>&gt;20</td>
<td>&gt;100</td>
</tr>
<tr>
<td>COS Conversion</td>
<td>varies</td>
<td>Partial</td>
<td>Total</td>
</tr>
<tr>
<td>Chloride Tolerance (ppm₉)</td>
<td>varies</td>
<td>&gt;3</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Durability (y)</td>
<td>3-7</td>
<td>&gt;7</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Catalyst Cost ($/lb)</td>
<td>~5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

From “2006 Hydrogen from Coal Program RD&D Plan”
Hydrogen From Coal Program Goals

Hydrogen Separation

<table>
<thead>
<tr>
<th>Performance Criteria</th>
<th>Current Status</th>
<th>Targets</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux (scfh/ft²)</td>
<td>20-100</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>300-600</td>
<td>400-700</td>
<td>350-550</td>
</tr>
<tr>
<td>S Tolerance (ppmv)</td>
<td>Yes</td>
<td>~20</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Cost ($/ft²)</td>
<td>150-200</td>
<td>150</td>
<td>2000</td>
</tr>
<tr>
<td>WGS Activity</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>ΔP Capability (psig)</td>
<td>100</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>CO Tolerance</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>H₂ Purity (%)</td>
<td>90-98</td>
<td>95</td>
<td>&gt;99.99</td>
</tr>
<tr>
<td>Durability (y)</td>
<td>-</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

From “2005 Hydrogen from Coal Program RD&D Plan” & “2006 Hydrogen from Coal Program RD&D Plan”
Acknowledgement

This material is based upon work supported by the Department of Energy under Award Number DE-FC26-05NT42452.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.