DOE Hydrogen Program

High Purity Hydrogen from Coal-Derived Syngas

Jim Torkelson, Neng Ye, Zhijiang Li and Mark Fokema

Aspen Products Group, Inc.

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Project ID: PDP 21

ASPEN PRODUCTS GROUP, INC.

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 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_2-selective membrane that both operate at 300-500°C, at 300-500 psig and are tolerant of high concentrations of H_2S and HCl

Catalyst

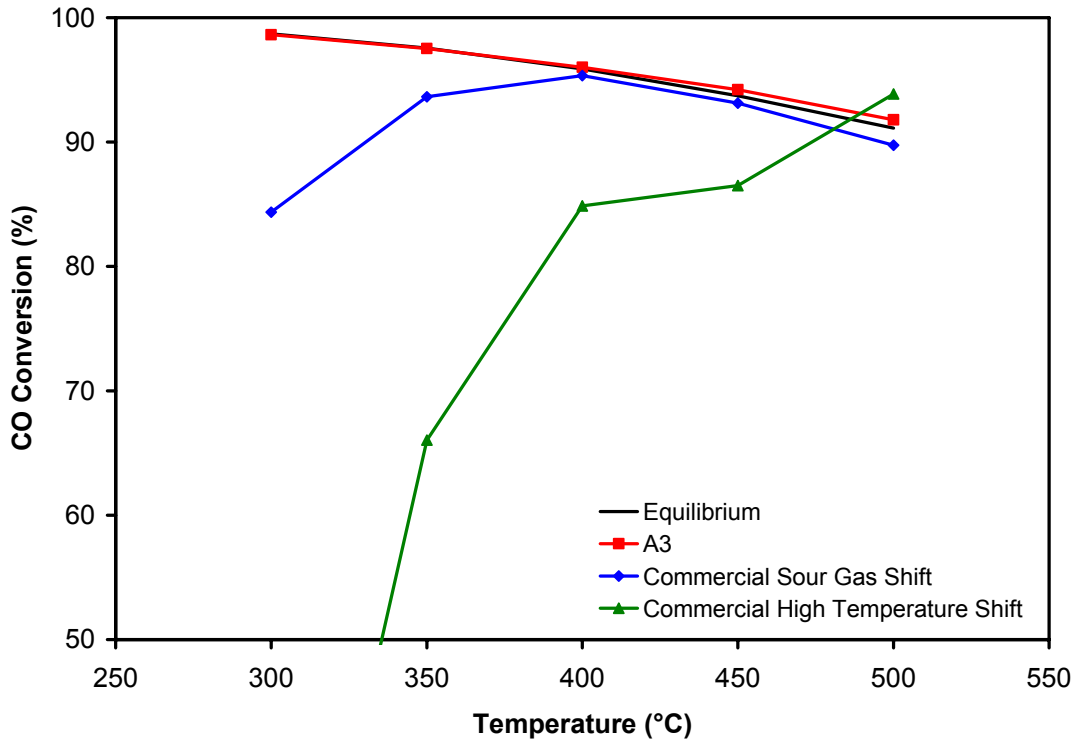
- MoS_2-based catalyst with modifiers to promote impurity tolerance

Membrane

- Dense Ta-based membrane with surface modifications to promote H_2 dissociation/association reactions in the presence of S and Cl

WGS Catalyst Development

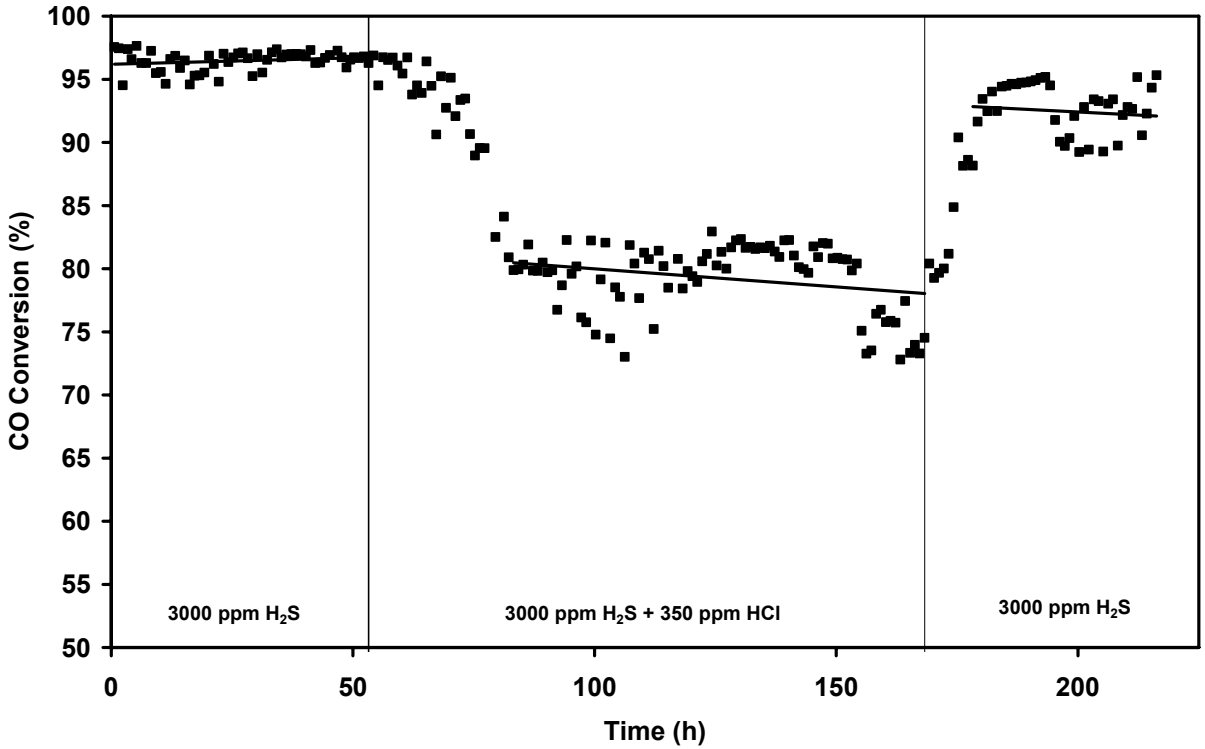
60% CO, 25% H_2, 10% CO_2, 5% N_2, 3000 ppm H_2S, H_2O/CO=4, 400 psig, GHSV=3000 h^{-1}



- Equilibrium yields realized with catalyst A3 at 300-500°C
- Tolerant to 3000 ppm_v (dry gas) H_2S

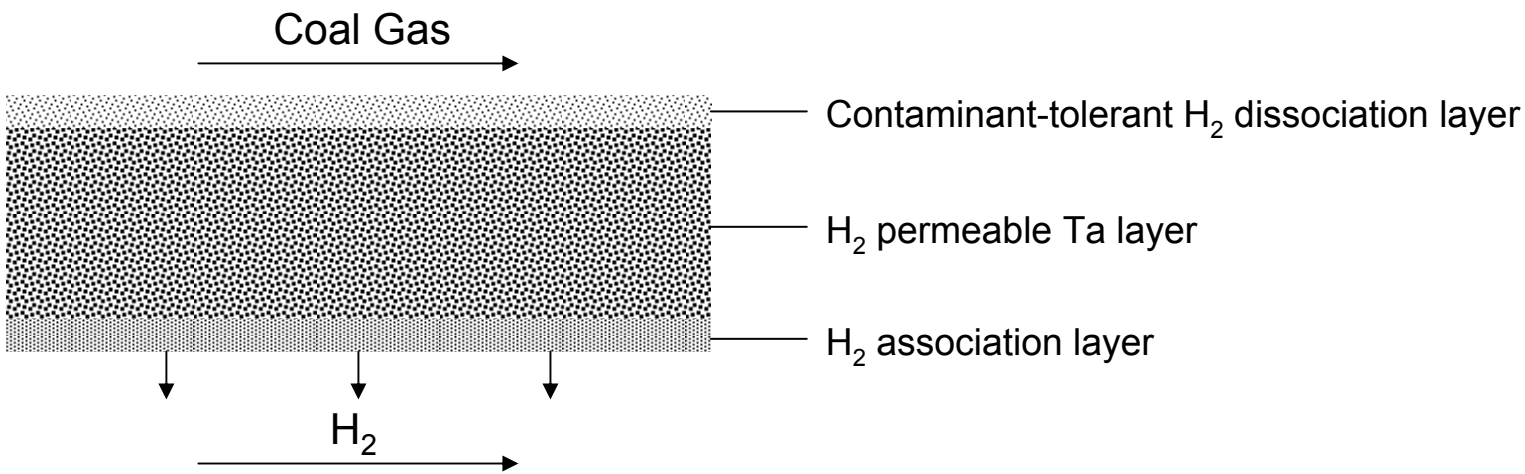
WGS Catalyst Stability

Catalyst A3, 60% CO, 25% H_2, 10% CO_2, 5% N_2, H_2O/CO=4, 400°C, 400 psig, GHSV=3000 h^{-1}



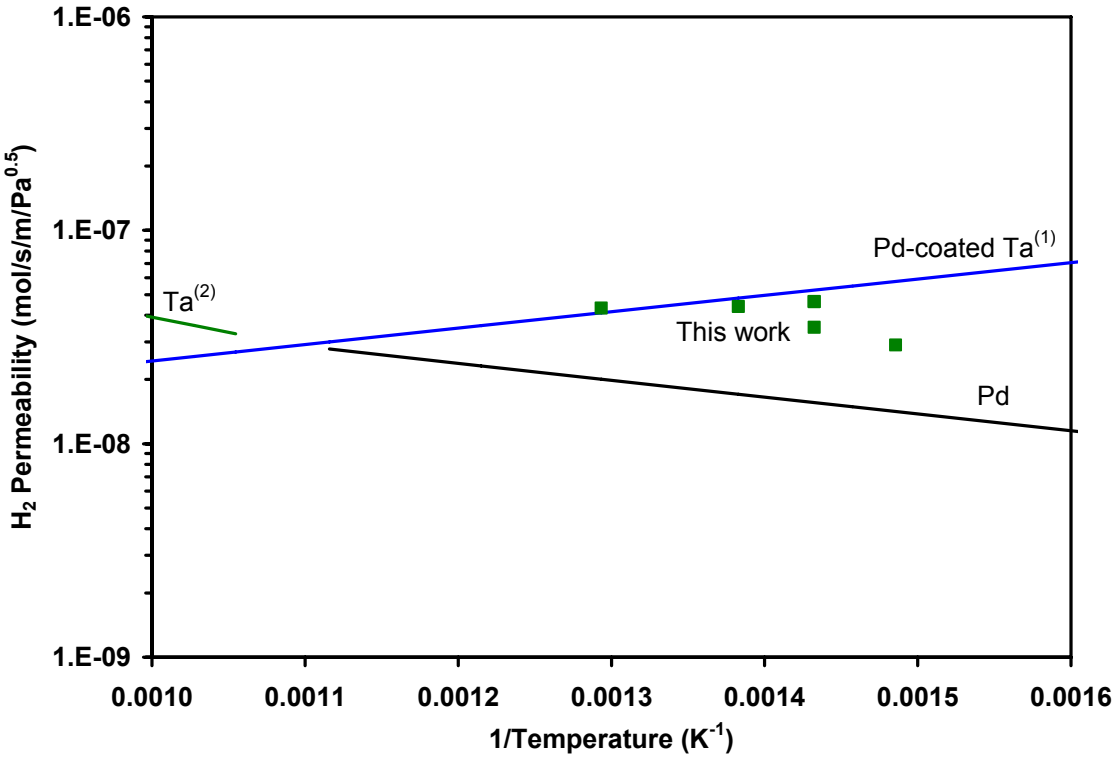
- Stable in the presence of 3000 ppm_v (dry gas) H_2S
- Mild reversible deactivation with 350 ppm_v (dry gas) HCl

Membrane Design



- Developed substrate cleaning and coating technique
- Examined effects of substrate thickness, coating composition, coating thickness and annealing conditions on pure H_2 permeability
- Examined effects of H_2O, H_2S, CO, and CO_2 on membrane performance

Membrane H_2 Permeability

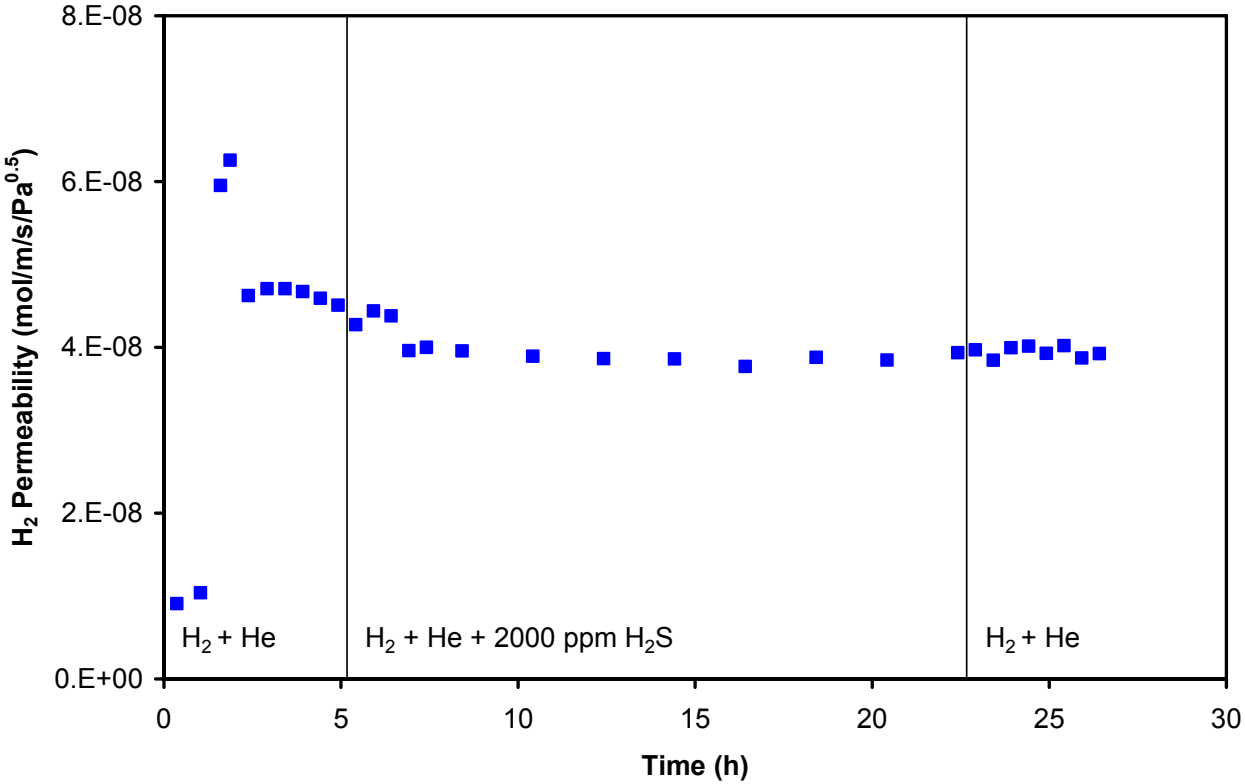


Test Conditions
95% H_2 – 5% He
350-550°C
200 psig H_2

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

[1] Rothenberger *et al.*, *J. Membr. Sci.*, 218, 19 (2003)
[2] Makrides *et al.*, Contract DA-49-189-AMC-136(d) (1965)

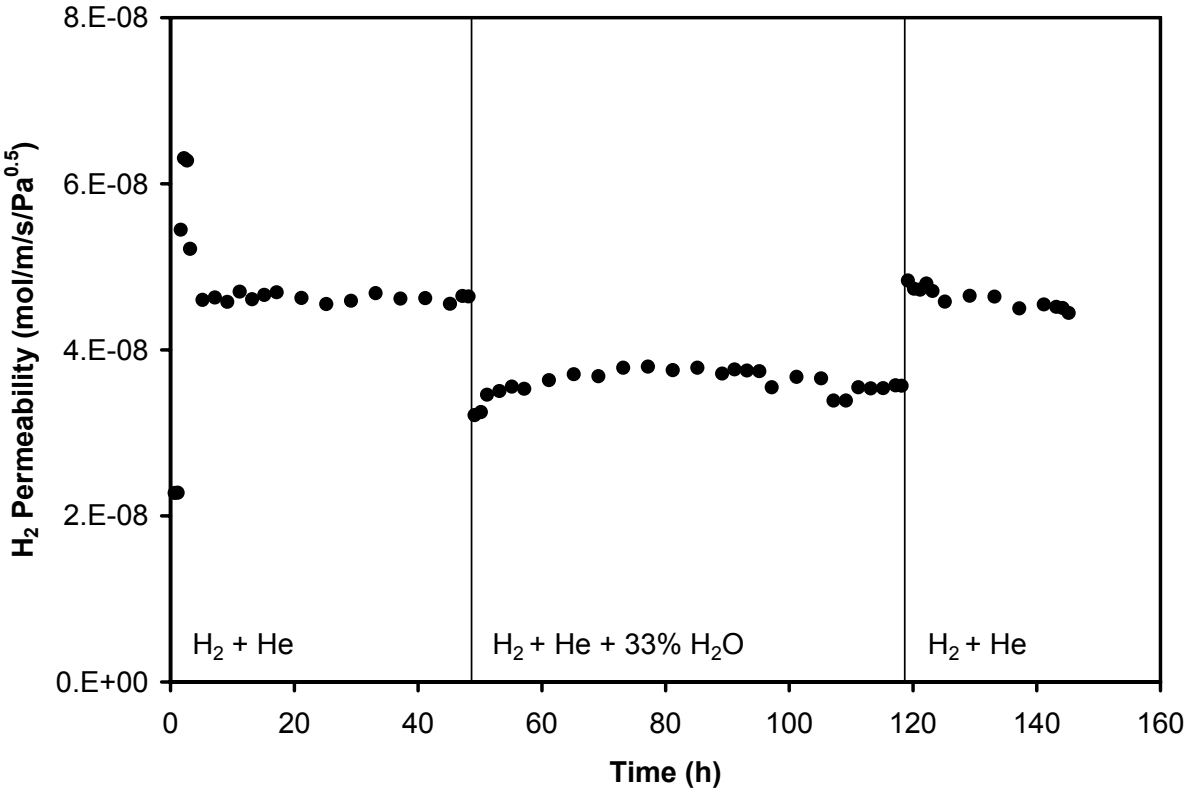
Membrane Sulfur Tolerance



Test Conditions
425°C
150 psig H_2

- Membrane tolerant of high concentration of H_2S
- 14% reduction in permeability upon exposure to 2000 ppm H_2S

Membrane Moisture Tolerance



Test Conditions
425°C
150 psig H_2

- Membrane tolerant of high concentration of steam
- 22% reduction in permeability upon exposure to 33% H_2O

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 H_2S and 350 ppm HCl observed over 220 hours

H_2-Permeable Membrane

- Dense metal membranes with high H_2 permeability and H_2 selectivity demonstrated
- Membrane H_2 permeability greater than that of Pd-based membranes
- Membrane maintains high permeability in the presence of 2000 ppm H_2S and 33% H_2O

Hydrogen From Coal Program Goals

Water Gas Shift Catalyst

Performance Criteria	Current Status	Targets		This Work
		2010	2015	
Catalyst Form	Pellets	Advanced configurations – TBD		Pellets
Active Metal	Cu/Zn or Fe/Cr or Co/Mo	Advanced configurations – TBD		Mo
Feed Temperature (°C)	200-300	>250	>400	>250
Feed Pressure (psia)	450-1150	>450	>750	415
Approach to Equilibrium (°C)	8-10	<6	<4	<4
Min. H_2O/CO Ratio	2.6	<2.6	<2	<2
Sulfur Tolerance (ppm_v)	varies	>20	>100	3000
COS Conversion	varies	Partial	Total	-
Chloride Tolerance (ppm_v)	varies	>3	>100	350
Durability (y)	3-7	>7	>10	-
Catalyst Cost ($/lb)	~5	<5	<5	-

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

Hydrogen From Coal Program Goals

Hydrogen Separation

Performance Criteria	Current Status			Targets			This Work
	Microporous	Cermet	Dense Ceramic	2007	2010	2015	
Flux (scfh/ft^2)	20-100	~300	2	100	200	300	20
Temperature (°C)	300-600	300-400	900	400-700	300-600	250-500	350-550
S Tolerance (ppm$_v$)	Yes	~20	-	-	20	>100	2000
Cost ($/ft^2)	150-200	<200	-	150	100	<100	-
WGS Activity	No	-	-	Yes	Yes	Yes	Yes
ΔP Capability (psig)	100	1000	-	100	400	800	400
CO Tolerance	Yes	Yes	-	Yes	Yes	Yes	-
H_2 Purity (%)	90-98	>99.999	-	95	99.5	99.99	>99.9
Durability (y)	-	0.9	-	1	3	5	-

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

Acknowledgement

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