Robust Low-Cost Water-Gas Shift Membrane Reactor for High-Purity Hydrogen Production from Coal-Derived Syngas

Zhijiang Li, James Torkelson and Neng Ye

Aspen Products Group, Inc.
186 Cedar Hill Street, Marlborough, MA 01752

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Project ID #: PDP 27

Overview

Timeline

- Start: June 1, 2005
- End: May 31, 2007
- ~40% Completed

Budget

- Total project funding
  - DOE: $498k (80%)
  - Contractor: $124.5k (20%)
- Funding received in FY06
  - $249k (DOE)
- Funding for FY07
  - $249k (DOE)

Barriers

- Membrane cost
- Catalyst durability
- Membrane durability

DOE Targets

- >30% cost reduction
- Tolerance to S, Cl, H_2O
- Equilibrium H_2 yield

Objectives

Overall Objectives

Develop a WGS membrane reactor for H_2 production from coal-derived syngas

- Lower cost, >30% cost reduction over conventional processes
- Robust, tolerant to sulfur and chlorides

FY2006 Objectives

- Develop a contaminant-tolerant, highly active WGS catalyst
- Develop a contaminant-tolerant H_2 selective membrane
- Design a 50 L/h WGS membrane reactor

FY2007 Objectives

- Construct and test the 50 L H_2/h reactor
- Scale up to 500 L H_2/h
- Modeling
- Perform an economic analysis

Approach

Shell-and-Tube Reactor Concept

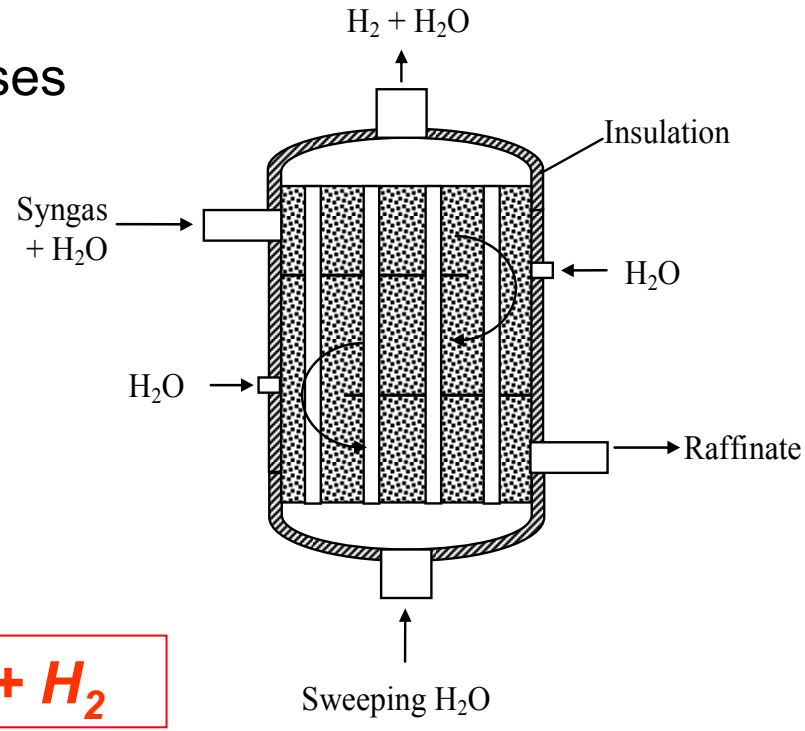
- Consists of a contaminant-tolerant WGS catalyst and H_2-selective membrane tubes
- Enhances H_2 production with simultaneous H_2 separation to break equilibrium limitation
- Simplifies downstream cleanup processes

Technical Challenges

- Catalyst tolerance to S, Cl
- Membrane tolerance to S, Cl, H_2O

Operating Conditions

- 300-500 ºC
- 300-500 psig on feed side



WGS Reaction: $CO + H_2O \Leftrightarrow CO_2 + H_2$

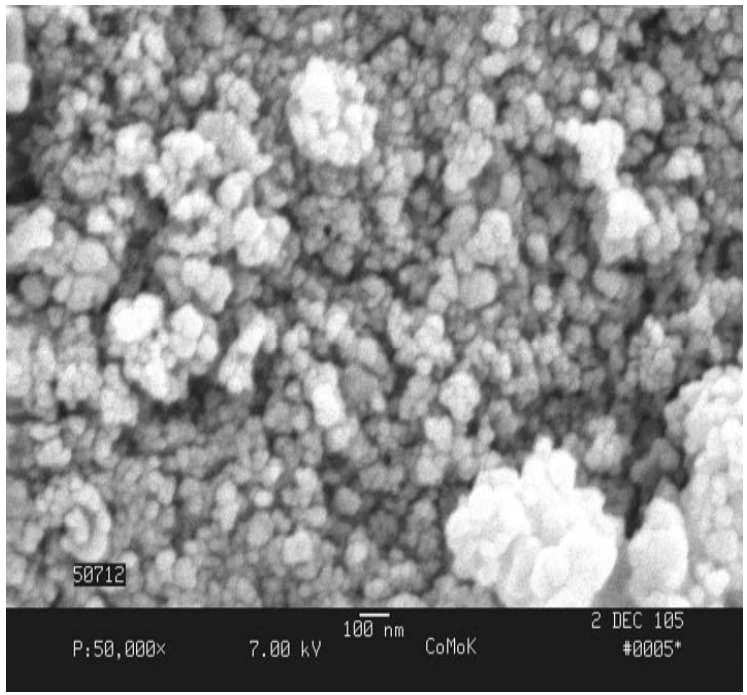
WGS Catalyst Preparation

Catalyst Development Approach

- Promoted transition metal catalysts
- Supported and un-supported
- Low material and fabrication costs
- High surface area
- Stable phases
- Grain size: ~50 nm

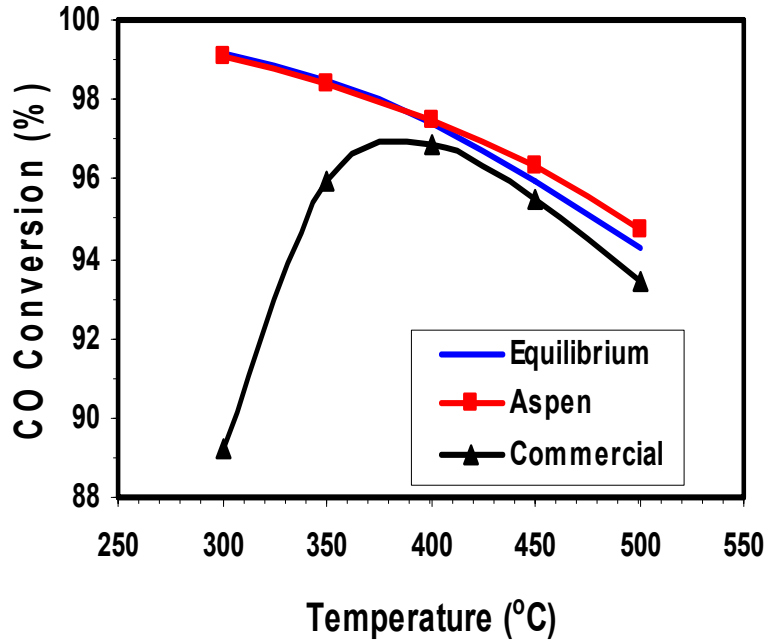
Catalyst Characterization

- Surface Area
- Pore size and volume
- Microstructure
- Crystalline Phases



WGS Catalyst Evaluation

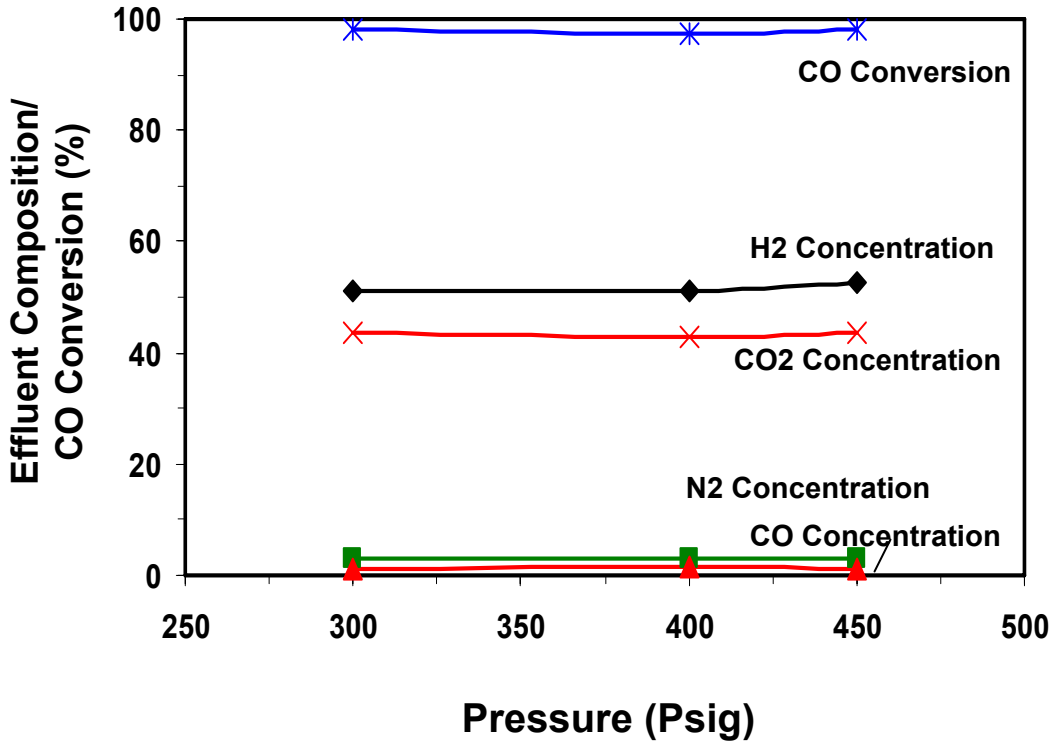
- Identified a most active WGS catalyst
- Determined related operating conditions
- Demonstrated
  - sulfur tolerance to 3000 ppm
  - higher activity than some leading commercial WGS catalysts
  - equilibrium H_2 yield



Operating Conditions:

Feed: 60% CO, 25% H_2, 10% CO_2, 5% N_2, 3000 ppm H_2S
H_2O/C: 4 (molar)
Pressure: 400 psig
Space Velocity: 3,000 1/h (dry-based)

WGS Catalyst Evaluation

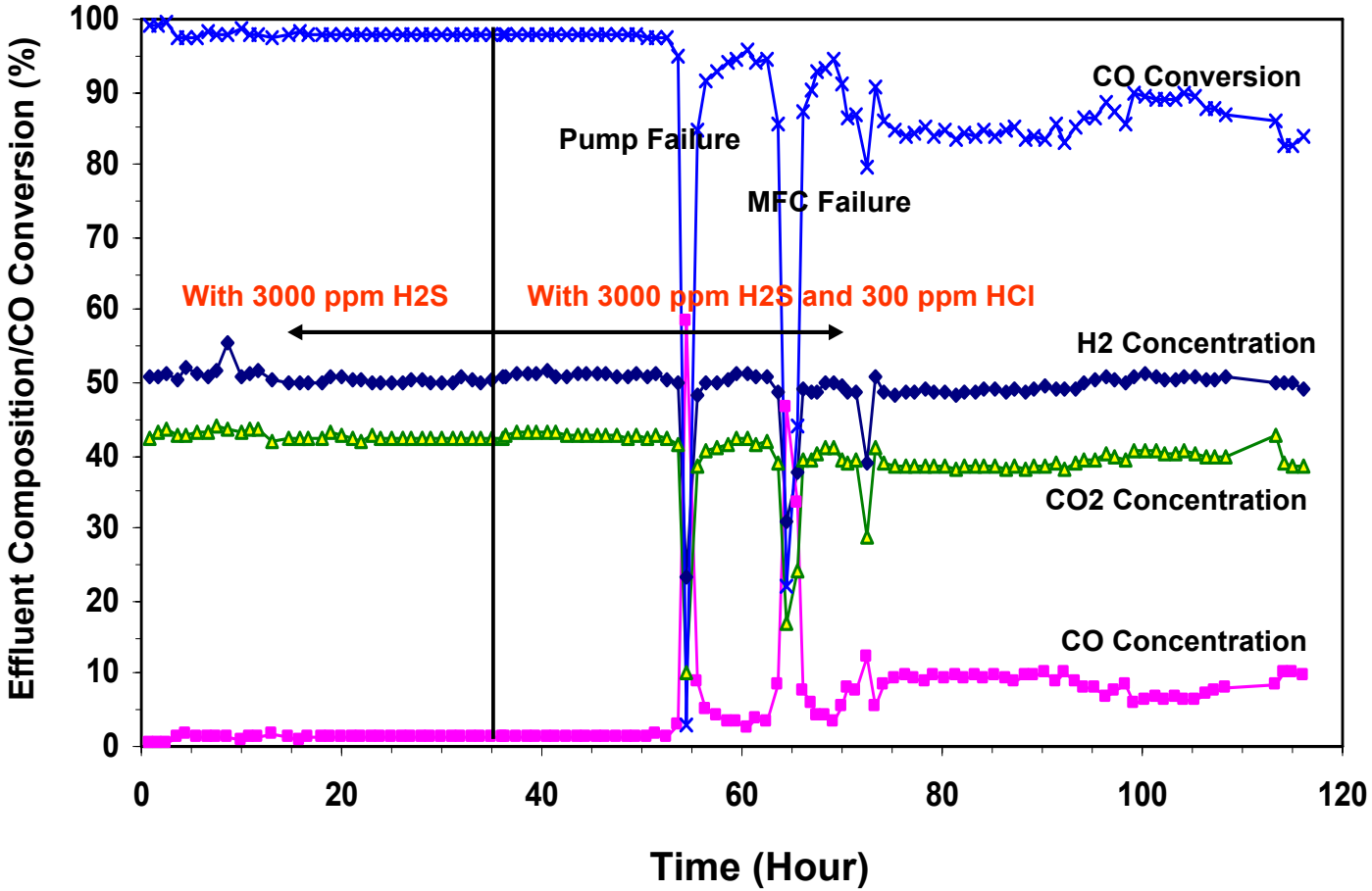


Conditions:

Feed: 60% CO,
25% H_2,
10% CO_2,
5% N_2,
3000 ppm H_2S
H_2O/C: 4 (molar)
Temperature: 400 °C
Pressure: 300-450 psig
Space Velocity: 3,000 1/h (dry-based)

Equilibrium conversion was achieved in the range from 300 to 500 psig.

WGS Catalyst Stability



Conditions:

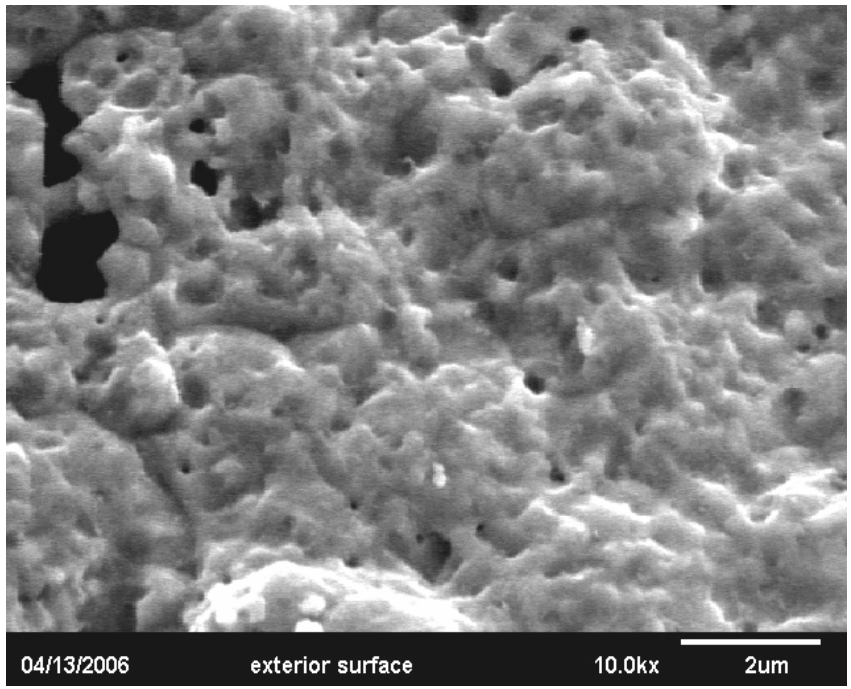
Feed: 60% CO,
25% H_2,
10% CO_2,
5% N_2,
3000 ppm H_2S
H_2O/C: 4 (molar)
Temperature: 400 °C
Pressure: 350-400 psig
Space Velocity: 3,000 1/h (dry-based)

The catalyst is stable in the presence of high concentrations of sulfur and HCl.

Membrane Preparation

Membrane Development Approach

- Dense membranes with surface modifications
- Surface modification to increase H_2 flux and stability
- Low material cost
  (<20% Pd-based membranes)

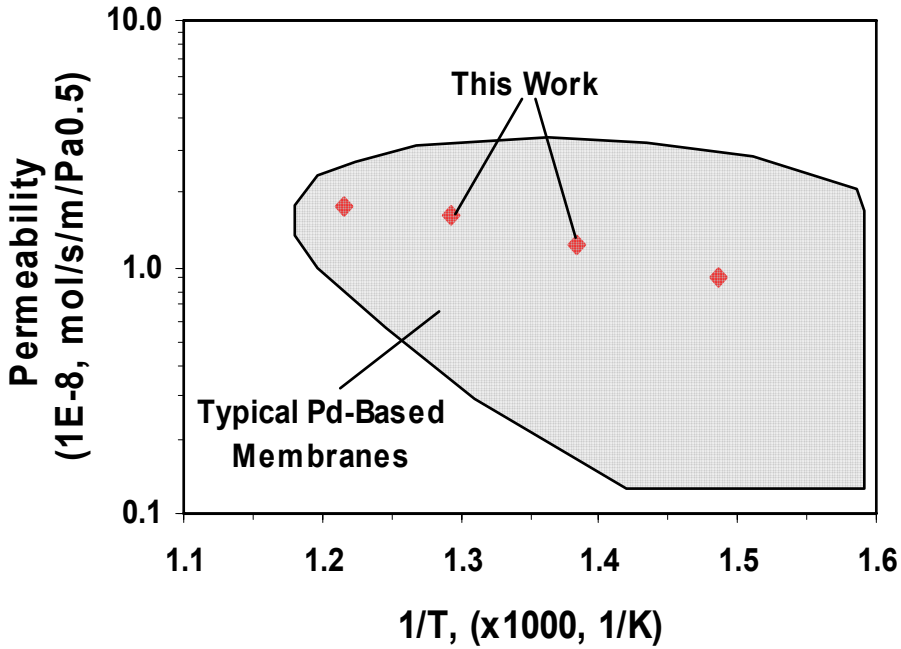


Membrane Characterization

- Microstructure
- Composition
- Crystalline Phases
- Defects

Membrane Evaluation

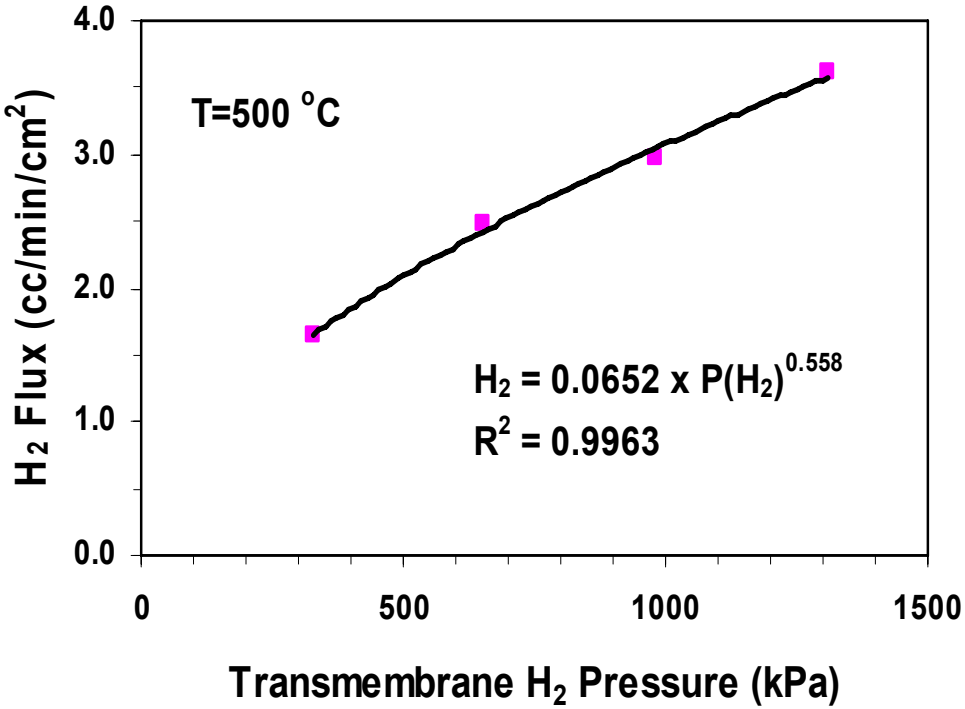
- Determined a suitable membrane thickness
  - High H_2 flux
  - Good mechanical strength
- Optimized operating conditions
- Demonstrated
  - Membranes permeable to only H_2, *i.e,* high to infinite H_2 selectivity
  - H_2 permeability comparable to that of Pd-based membranes
- Validated proposed approach to low-cost, high permeability membranes



Operating Conditions:

Feed: 95% H_2-5% He
Temperature: 350-550 °C
Pressure: 200 psig

Membrane Evaluation



Operating Conditions:

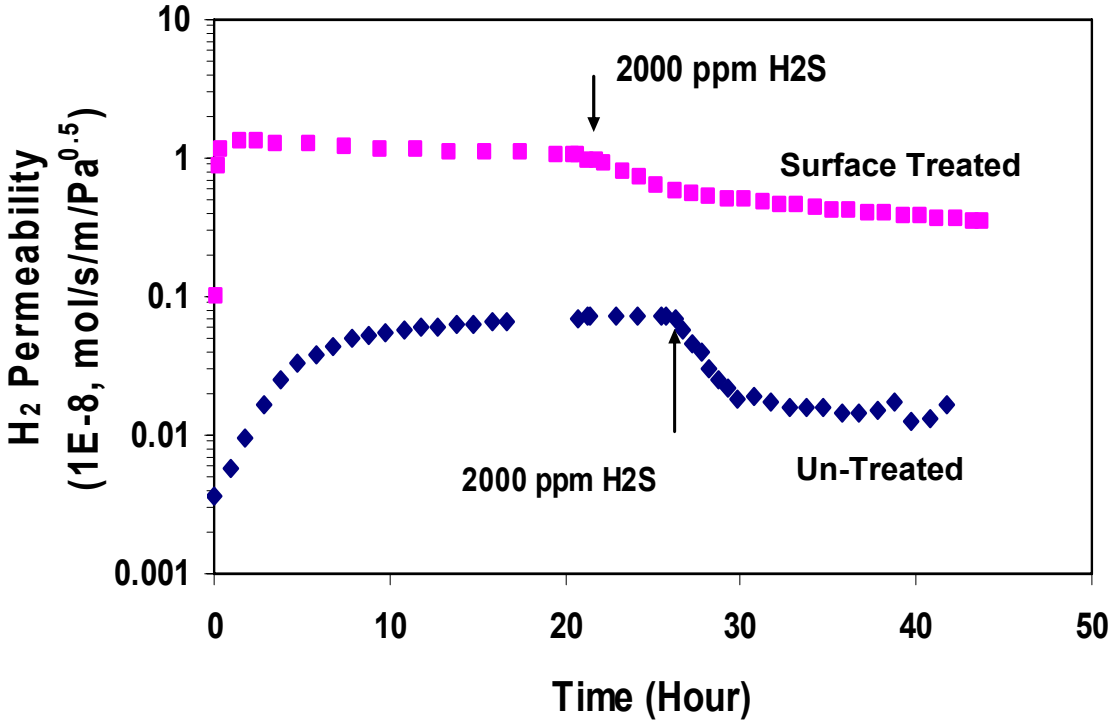
Feed: 95% H_2-5% He

Temperature: 500 °C

Pressure: 50-200 psig

- **High H_2 fluxes were obtained.**
- **H_2 flux is approximately proportional to square root of H_2 partial pressure.**

Membrane Tolerance to Sulfur



Operating Conditions:

Feed: 95% H_2-5% He

Temperature: 450 °C

Pressure: 200 psig

- **Surface treatment increases membrane H_2 permeability and stability.**
- **The membranes are tolerant to high concentrations of sulfur.**
- **Tolerance to Cl and H_2O is being investigated.**

Future Work

- **Membrane**
  - Optimization of membrane composition
- **50 L H_2/h Membrane Reactor**
  - Design
  - Preparation of longer Membranes
  - Construction
  - Testing
- **500 L H_2/h Membrane Reactor**
  - Design
  - Construction
  - Testing
- **Modeling**
- **Cost Analysis**

Summary

- **Successfully developed a low-cost, contaminant-tolerant, nanosized catalyst for WGS reaction of coal-derived syngas.**
- **Demonstrated that the catalyst**
  - is highly active. Equilibrium H_2 yield can be achieved at practical operating conditions.
  - is very stable in the presence of high concentrations of sulfur and chlorides.
  - can be operated in wide temperature and pressure ranges: 300-500 ºC and 300-500 psig.
- **Successfully developed a low-cost, sulfur-tolerant, H_2-selective membrane.**
- **Demonstrated that the membrane:**
  - is permeable to only H_2.
  - has comparable H_2 permeability to Pd-based membranes.
  - is tolerant to high concentrations of sulfur.
- **Optimized membrane thickness.**