

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

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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, H₂O
- Equilibrium H₂ yield

Objectives

Overall Objectives

- Develop a WGS membrane reactor for H₂ 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 H₂ selective membrane
- Design a 50 L/h WGS membrane reactor

FY2007 Objectives

- Construct and test the 50 L H₂/h reactor
- Scale up to 500 L H₂/h
- Modeling
- Perform an economic analysis

Approach

Shell-and-Tube Reactor Concept

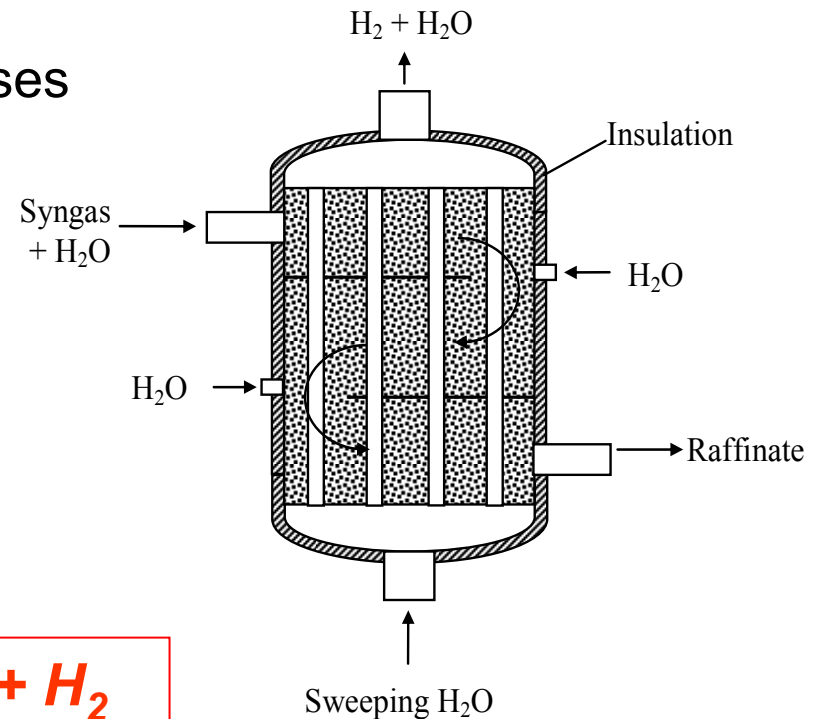
- Consists of a contaminant-tolerant WGS catalyst and H₂-selective membrane tubes
- Enhances H₂ production with simultaneous H₂ separation to break equilibrium limitation
- Simplifies downstream cleanup processes

Technical Challenges

- Catalyst tolerance to S, Cl
- Membrane tolerance to S, Cl, H₂O

Operating Conditions

- 300-500 °C
- 300-500 psig on feed side



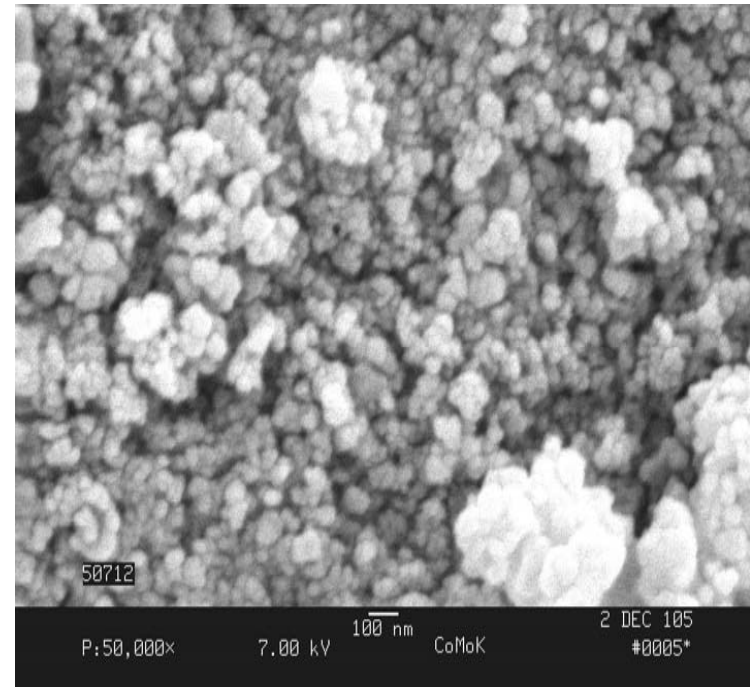
WGS Catalyst Preparation

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

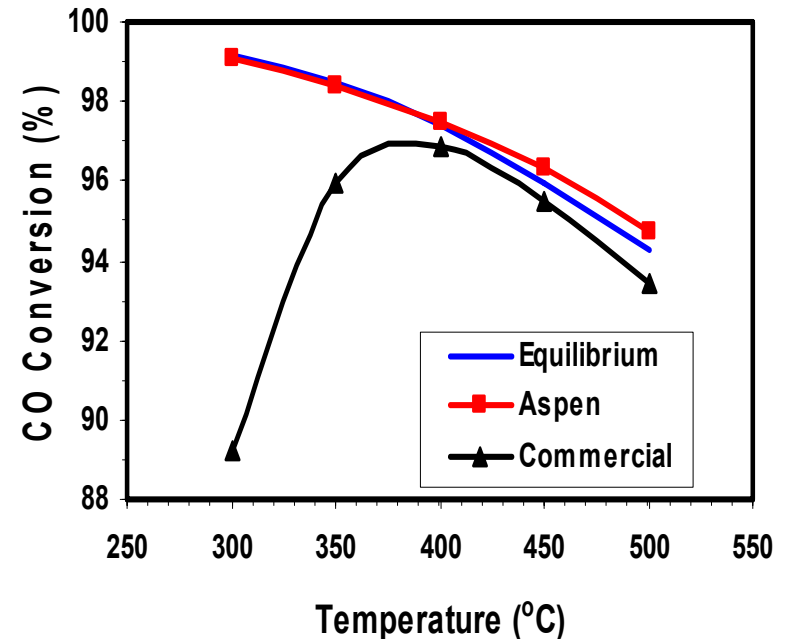
Catalyst Characterization

- 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 H₂ yield



Operating Conditions:

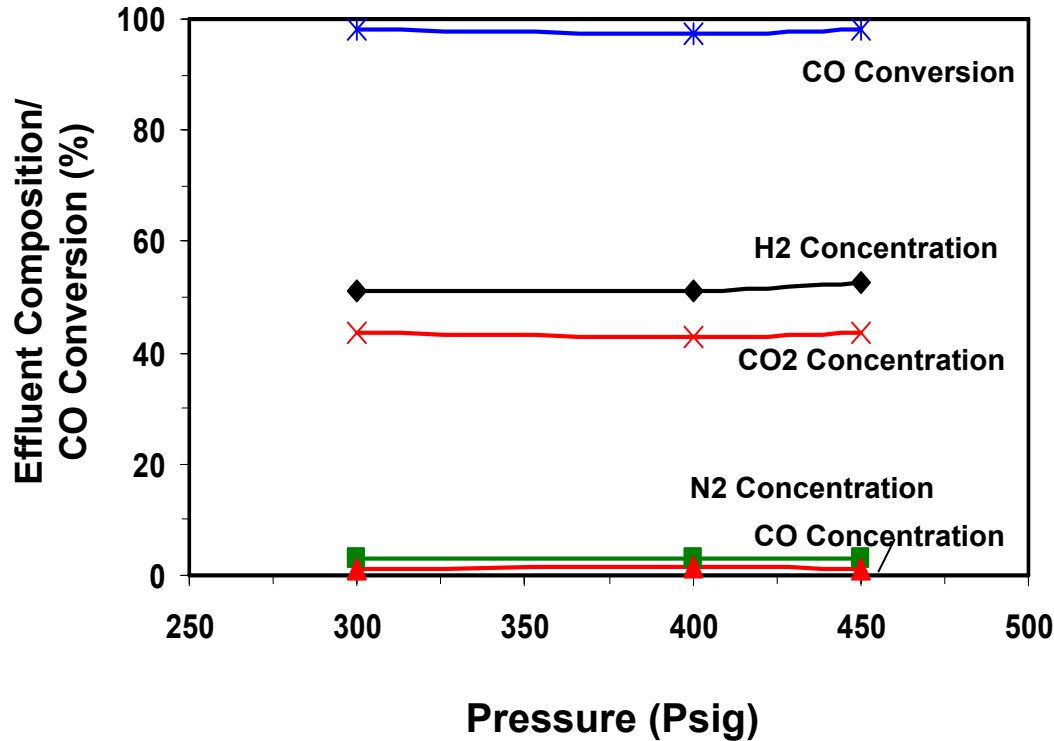
Feed: 60% CO, 25% H₂, 10% CO₂, 5% N₂,
3000 ppm H₂S

H₂O/C: 4 (molar)

Pressure: 400 psig

Space Velocity: 3,000 1/h (dry-based)

WGS Catalyst Evaluation

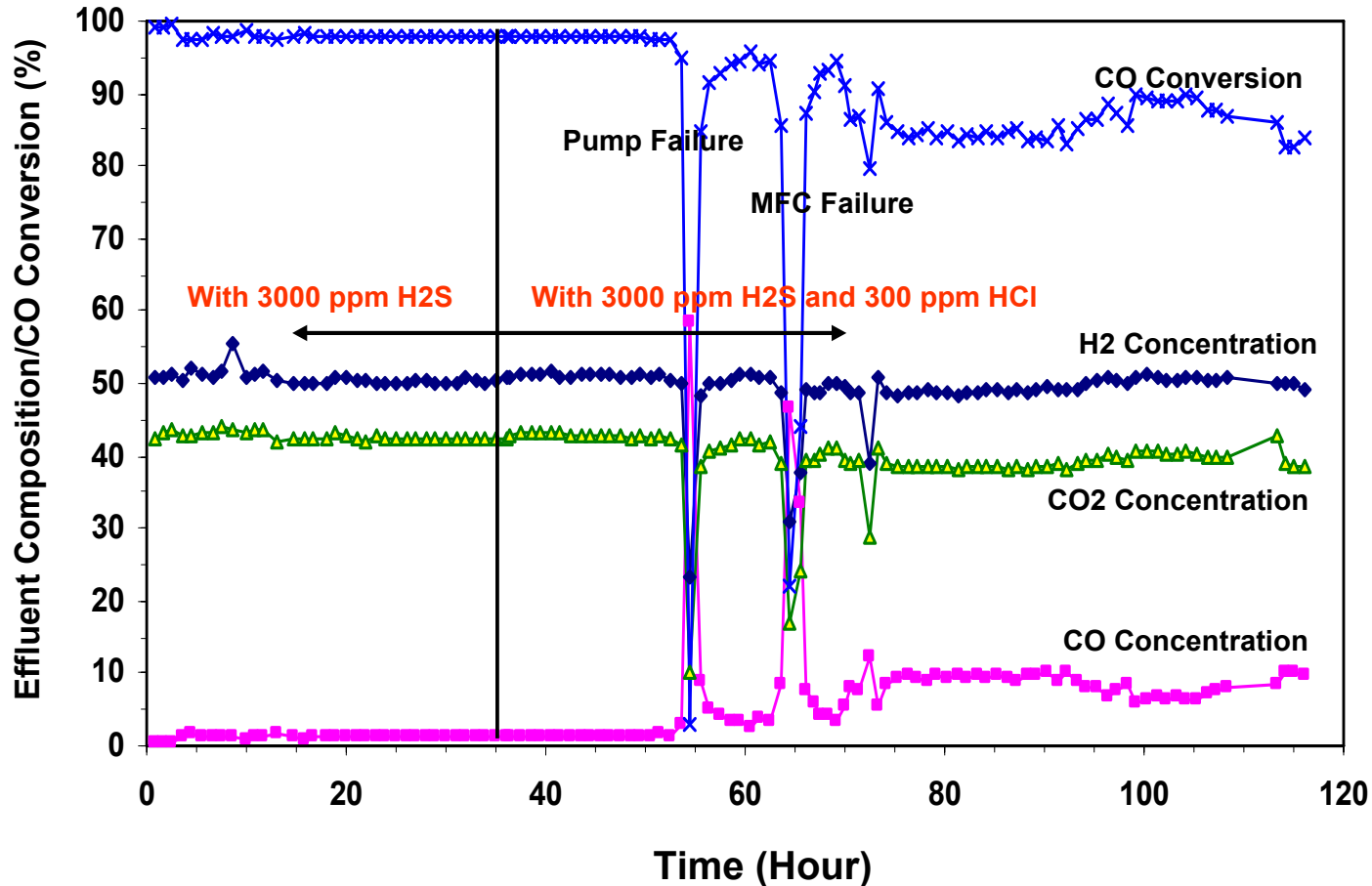


Conditions:

Feed: 60% CO,
25% H₂,
10% CO₂,
5% N₂,
3000 ppm H₂S
H₂O/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% H₂,
10% CO₂,
5% N₂,

3000 ppm H₂S

H₂O/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.

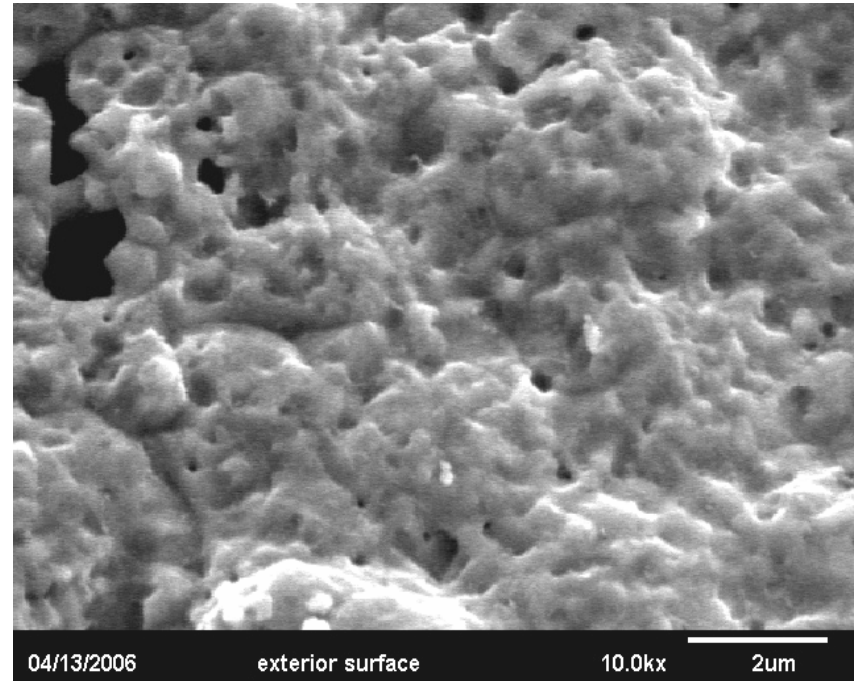
Membrane Preparation

Membrane Development Approach

- Dense membranes with surface modifications
- Surface modification to increase H₂ flux and stability
- Low material cost
($<20\%$ Pd-based membranes)

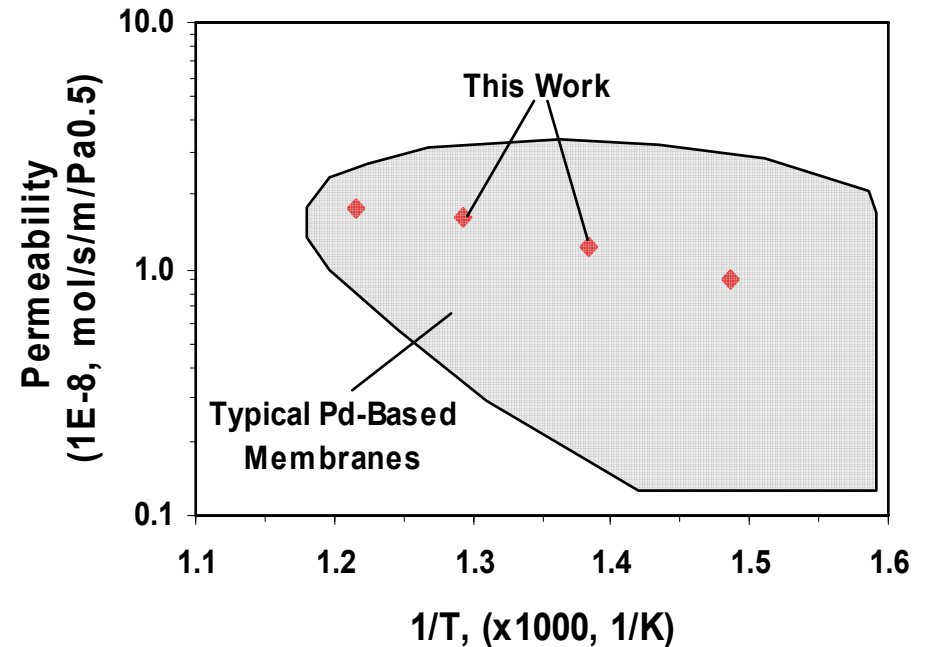
Membrane Characterization

- Microstructure
- Composition
- Crystalline Phases
- Defects



Membrane Evaluation

- Determined a suitable membrane thickness
 - High H₂ flux
 - Good mechanical strength
- Optimized operating conditions
- Demonstrated
 - Membranes permeable to only H₂, *i.e.*, high to infinite H₂ selectivity
 - H₂ permeability comparable to that of Pd-based membranes
- Validated proposed approach to low-cost, high permeability membranes



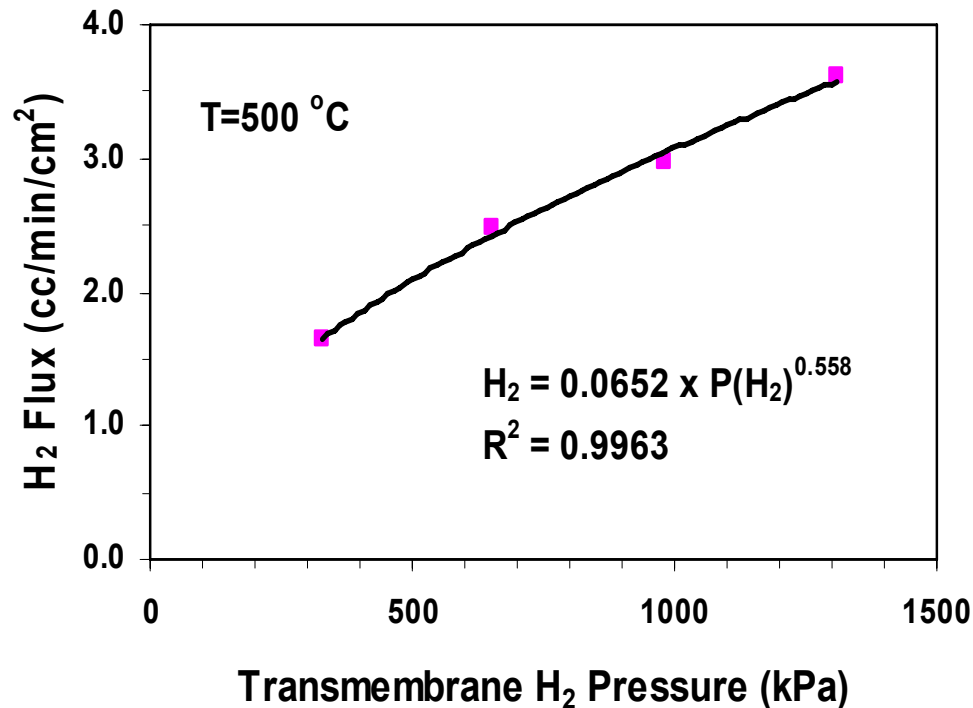
Operating Conditions:

Feed: 95% H₂-5% He

Temperature: 350-550 °C

Pressure: 200 psig

Membrane Evaluation



Operating Conditions:

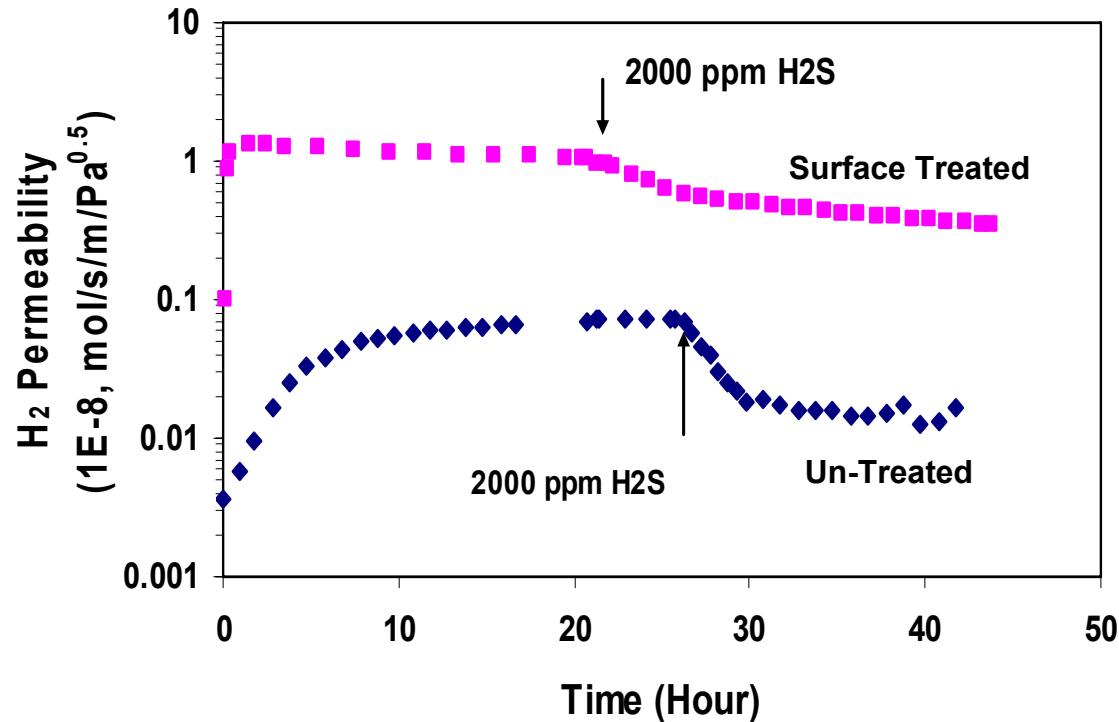
Feed: 95% H₂-5% He

Temperature: 500 °C

Pressure: 50-200 psig

- High H₂ fluxes were obtained.
- H₂ flux is approximately proportional to square root of H₂ partial pressure.

Membrane Tolerance to Sulfur



Operating Conditions:

Feed: 95% H₂-5% He

Temperature: 450 °C

Pressure: 200 psig

- Surface treatment increases membrane H₂ permeability and stability.
- The membranes are tolerant to high concentrations of sulfur.
- Tolerance to Cl and H₂O is being investigated.

Future Work

- **Membrane**
 - Optimization of membrane composition
- **50 L H₂/h Membrane Reactor**
 - Design
 - Preparation of longer Membranes
 - Construction
 - Testing
- **500 L H₂/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 °C 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.**