

Zeolite Membrane Reactor for Water-Gas-Shift Reaction for Hydrogen Production

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Project ID: PD073

Overview

Timeline

- Project start date:
July 1, 2005
- Project end date:
October 31, 2011
- Percent complete: **90%**

Budget

- Total project funding
 - DOE **\$1,999,727**
 - Contractor: **\$501,310**
- Funding for FY9: **\$0**
- Funding for FY10: **\$50,000**

Barriers

Barrier addressed: Cost reduction of distributed hydrogen production from natural gas and renewable liquids through improvement of reforming and separation efficiencies

Partners

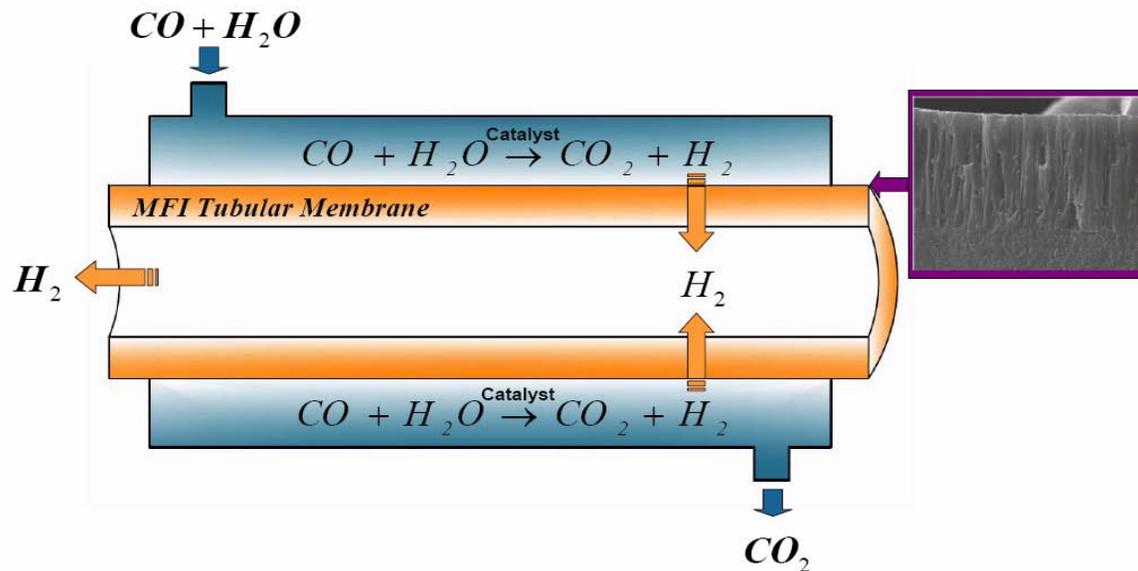
- University of Cincinnati
- Arizona State University
- Ohio State University

Relevance – Project Objectives

Fundamental study for the development of chemically and thermally stable zeolite membrane reactor for water-gas-shift reaction for hydrogen production

- *Synthesis and Characterization of Chemically and Thermally Stable Silicalite Membranes*
- *Experimental and Theoretical Study on Gas Permeation and Separation Properties of the Silicalite Membranes*
- *Hydrothermal Synthesis of Tubular Silicalite Membranes and Gas Separation Study*
- *Experimental and Modeling Study of Membrane Reactor for Water-Gas-Shift Reaction*

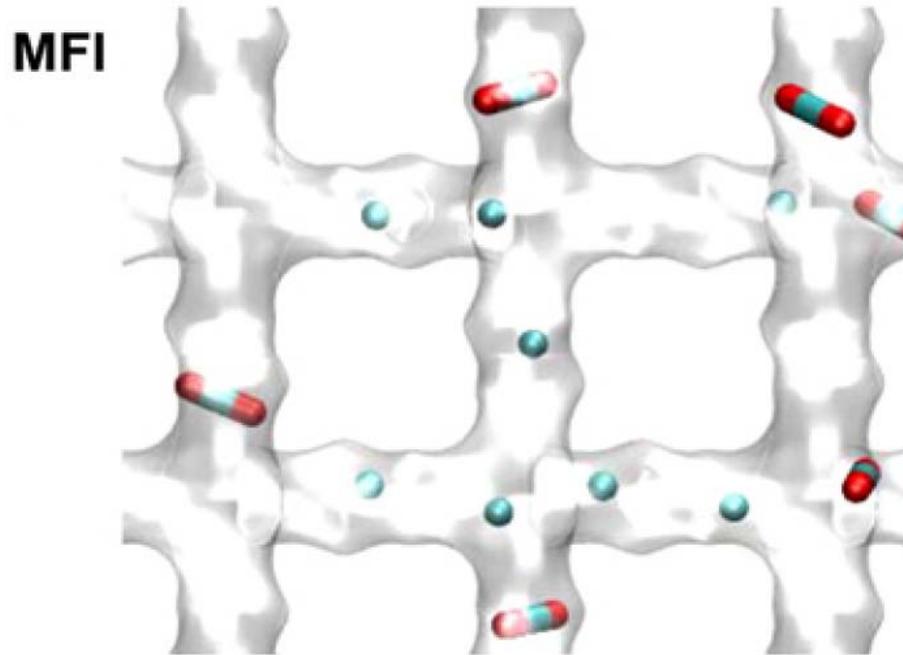
Approach – Zeolite Membrane Reactor for Water-Gas Shift Reaction



Zeolite Membrane Requirements:

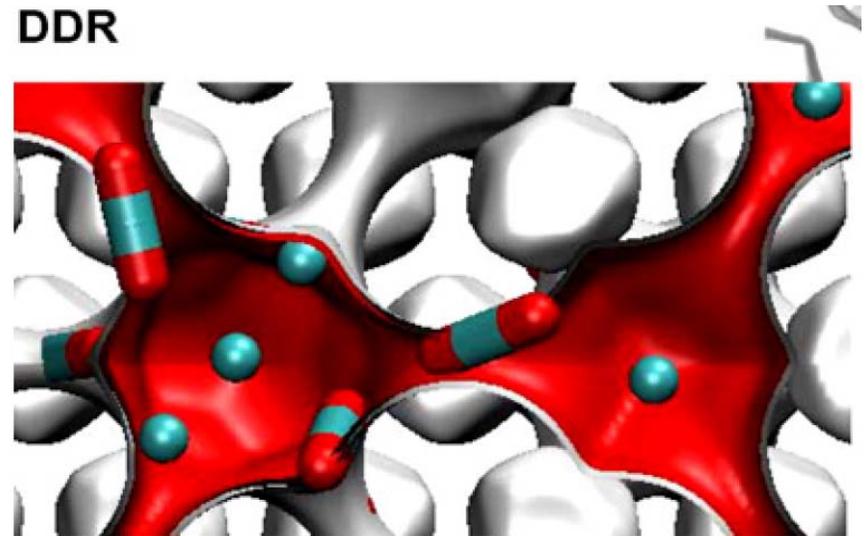
- Operate at 350-550°C
- Chemically stable in H_2S , thermally stable at $\sim 400^\circ C$
- Hydrogen permeance $\sim 5 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$
- Hydrogen selectivity ~ 50
- Two product streams: H_2 ($>94\%$ purity) and CO_2 (>97 purity)

Approach – Chemical Stable Microporous MFI (Silicalite) and DDR-type Zeolite Membranes



Intersecting channels

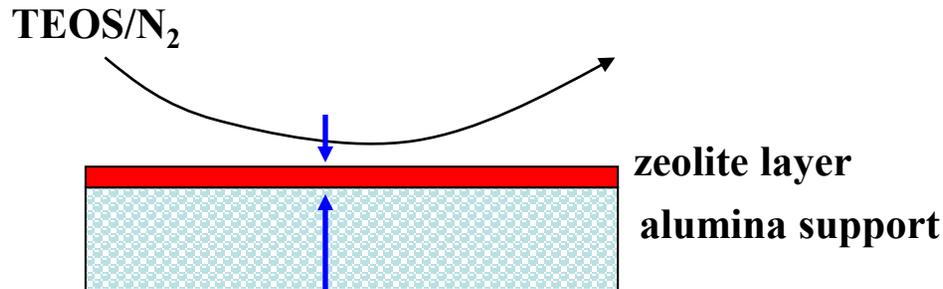
*MFI (Silicalite): 10-T-Ring
intersecting channels of 5.1-5.6 Å
in size*



Cages separated by narrow windows

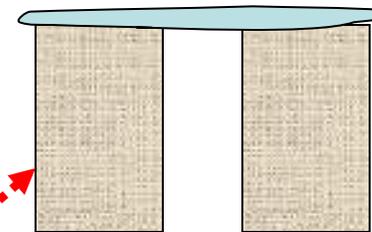
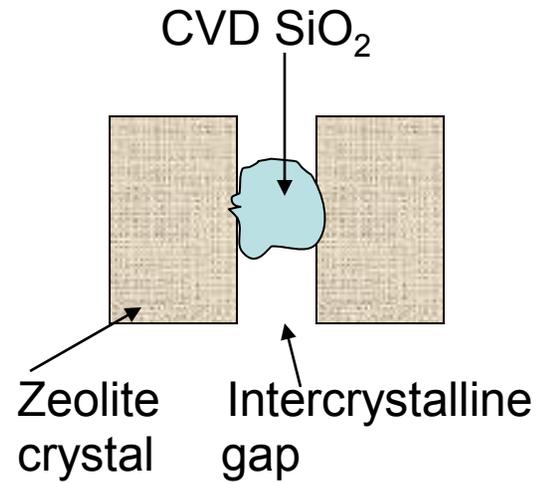
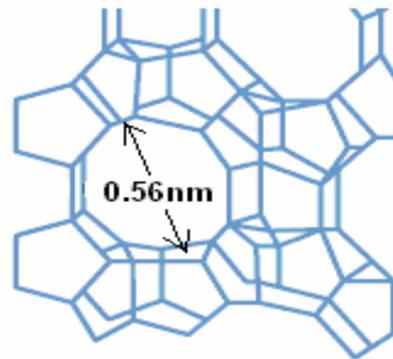
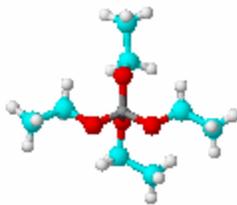
*8-T-Ring, Windows of 3.6-4.4 Å
in size
(studied as a reference)*

Approach – Counter-diffusion CVD of Silica for Improving Membrane Quality



- CVD reaction temp: 550°C,
- Bubbling temp: room temp.

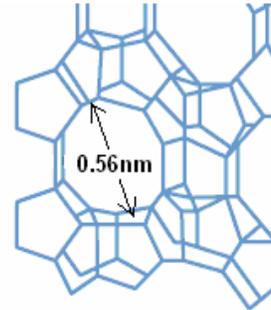
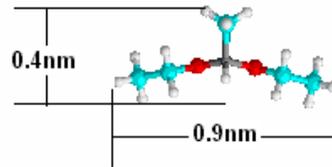
TEOS
0.95 nm



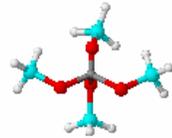
Hydrothermal stability test shows this is less likely the result of CVD

Approach – CVD Narrowing Zeolitic Pores to Further Improve Selectivity

**methyldiethoxysilane
(MDES)**



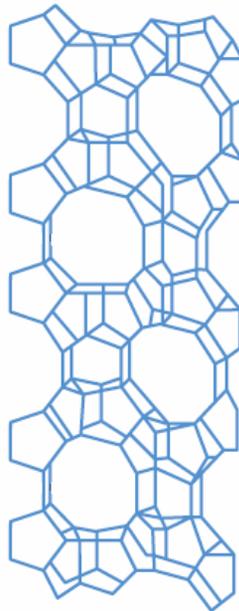
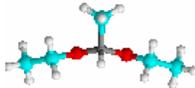
**TMOS
0.89nm**



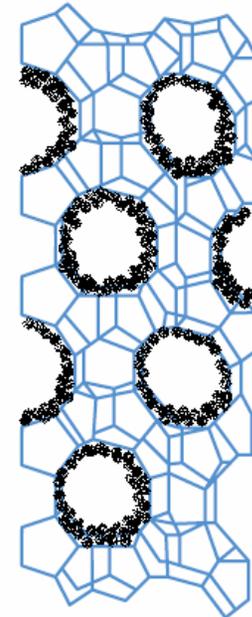
**TEOS
0.95nm**



**MDES
0.4 × 0.9nm**



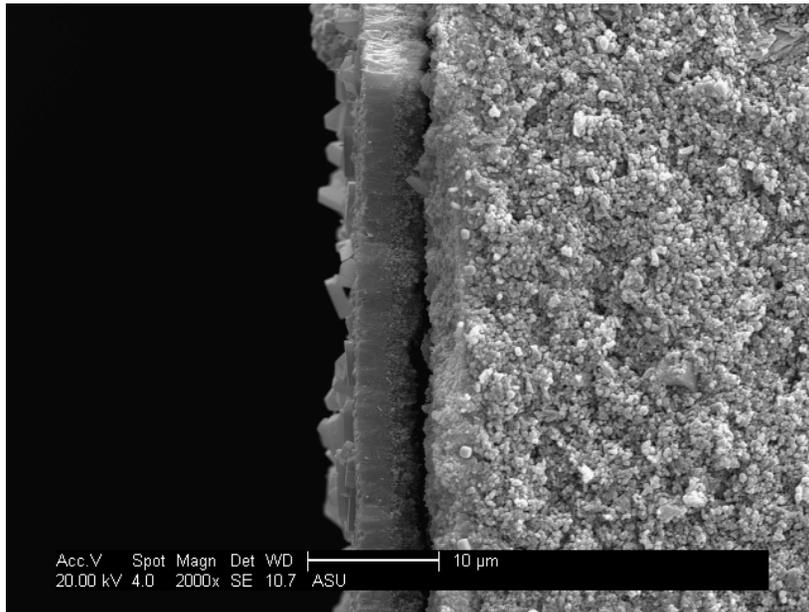
**On stream
CVD**



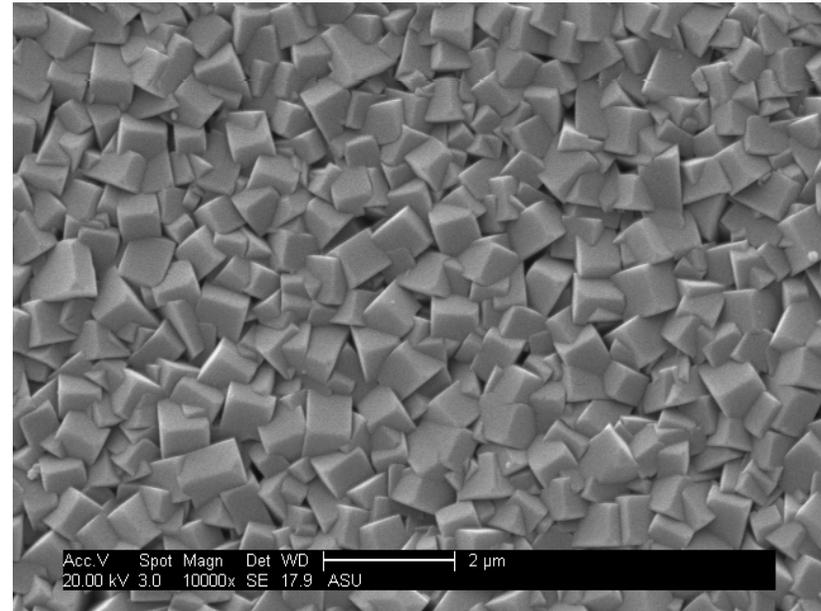
Previous Technical Accomplishments (Milestones Achieved)

- Obtain disk-shaped silicalite membranes on the desired intermediate layers with H_2/CO_2 separation factor over 10 and H_2 permeance larger than 1×10^{-7} mol/m².s.Pa.
- Develop methods to fabricate tubular membrane support with desired intermediate layers.
- Obtain a new WGS catalyst with activity and selectivity comparable to the best available commercial catalyst but with improved chemical stability in SO_2 and H_2S containing WGS reaction stream at temperatures higher than 500°C.
- Develop a membrane module and sealing system for tubular membrane reactor that can be operated in the WGS conditions for at least 1 month.
- Develop micro-wave synthesis method to prepare tubular silicalite membranes with H_2/CO_2 perm-selectivity over 10 and H_2 permeance larger than 4×10^{-7} mol/m².s.Pa.
- Obtain CVD modified tubular silicalite membranes with H_2/CO_2 separation factor over 120 and H_2 permeance larger than 2.0×10^{-7} mol/m².s.Pa.

Technical Accomplishment – Synthesis of High Quality MFI-type Zeolite Membranes

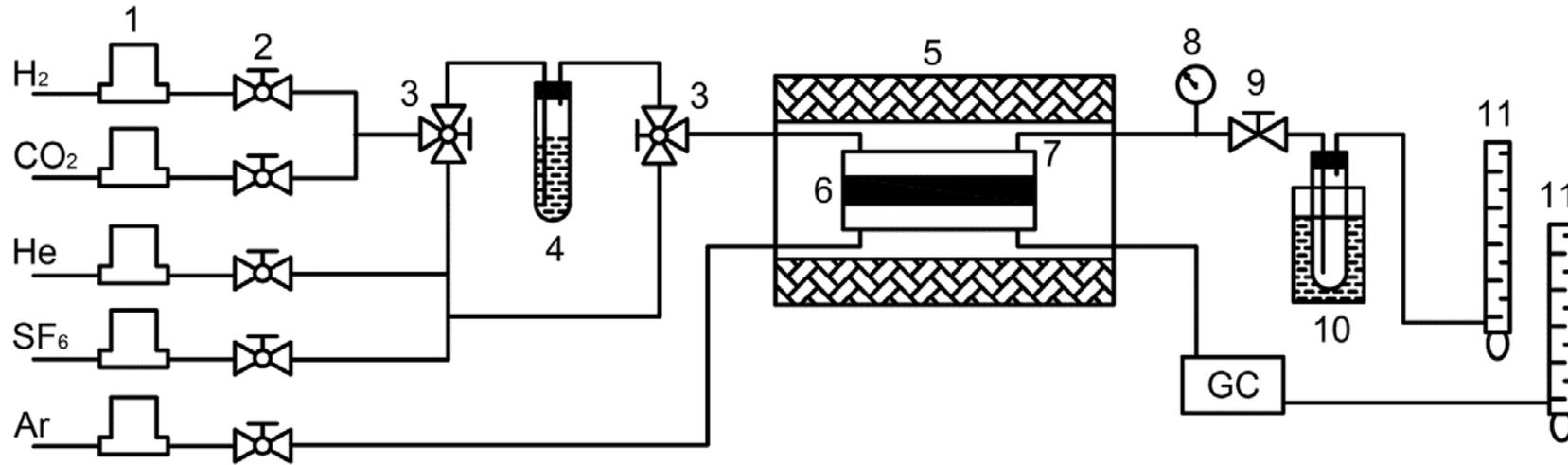


Zeolite layer (~5 µm) α -alumina layer



- Synthesized by a template-free secondary growth method to minimize intercrystalline gaps
- Post-CVD modification with TEOS to repair the defects
- Zeolite membranes can be prepared by microwave method
- Zeolite membranes can be grown on YSZ intermediate layer to improve chemical stability

Technical Accomplishment – Gas Permeation/Separation Study

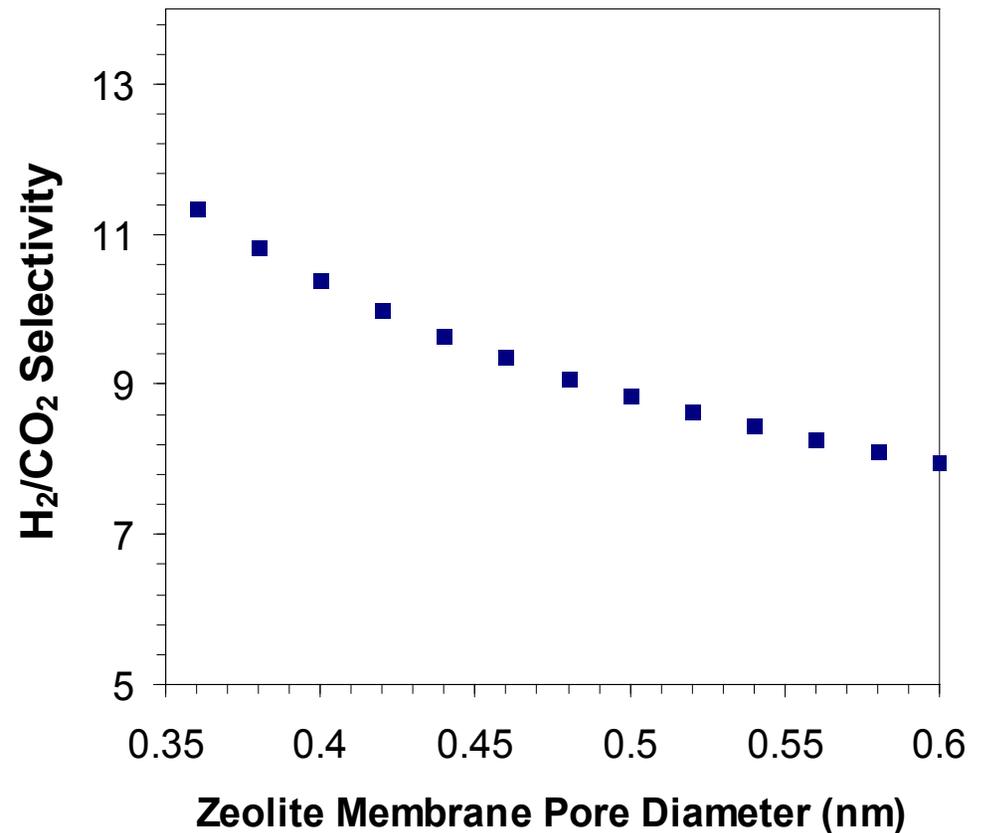
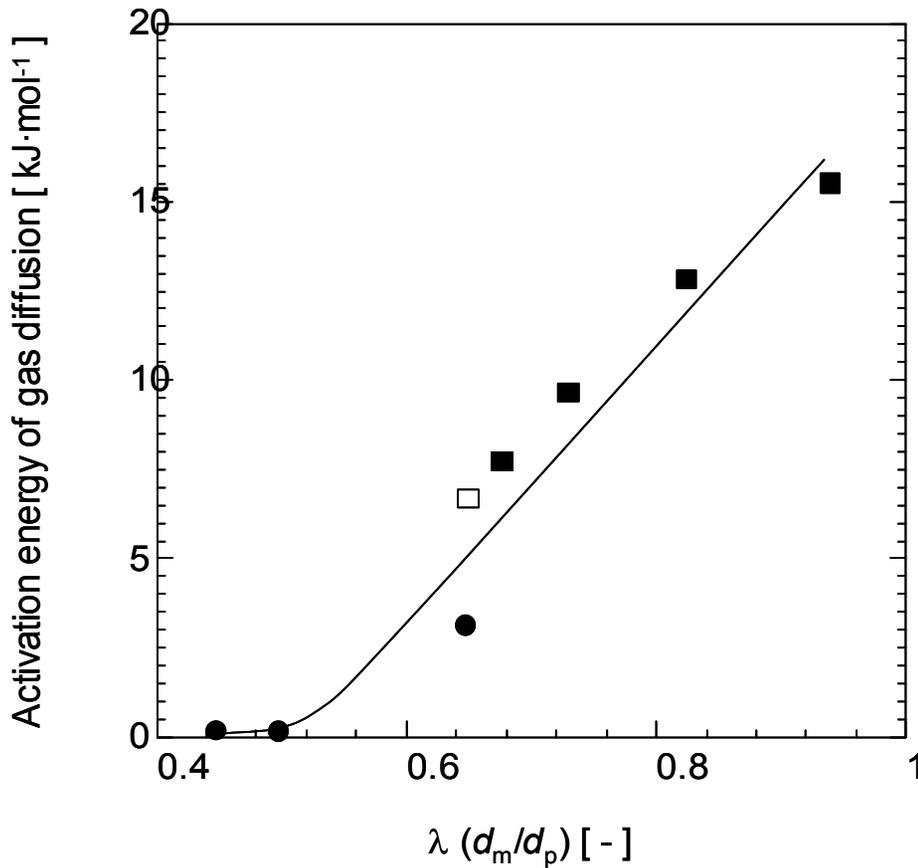


- 1. Mass flow controller
- 2. 2-way ball valve
- 3. 3-way ball valve
- 4. Bubbler
- 5. Box furnace
- 6. MFI membrane
- 7. Permeation cell
- 8. Pressure gauge
- 9. Needle valve
- 10. Cold trap
- 11. Bubbler flow meter

	He	H ₂	CO ₂	CO
Kinetic Diameter, d_m (nm)	0.26	0.289	0.33	0.376
L-J Length, σ_m (nm)	0.255	0.283	0.394	0.369
Molecular Weight, Mw (g/mol)	4	2	44	28

Technical Accomplishment – Limited Separation Ability of Defect-Free Microporous Zeolite Membranes

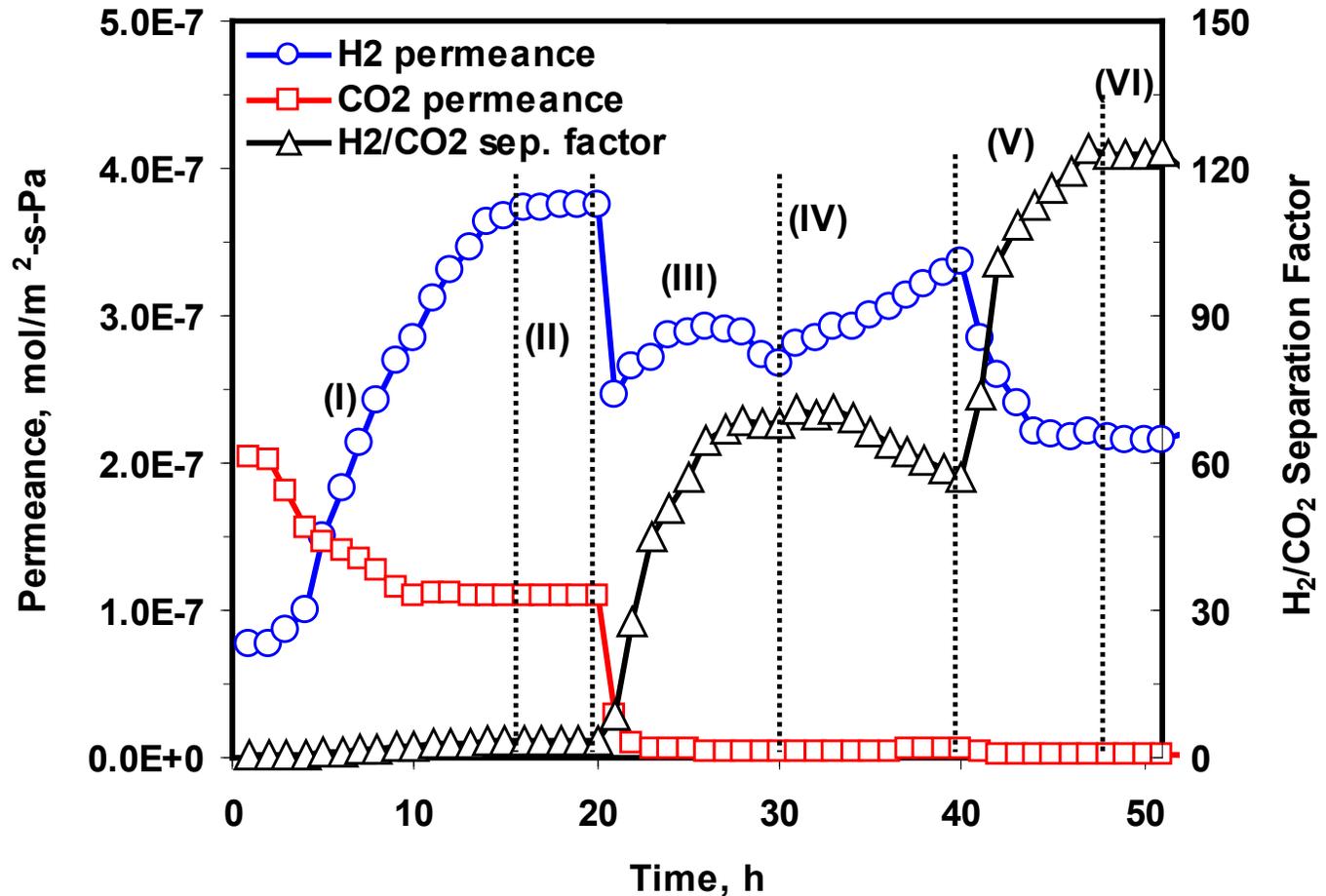
$$F_i = \left[\frac{\phi \alpha}{L z} \right] \left[\frac{8}{\pi R M_{w,i} T} \right]^{1/2} \exp\left(\frac{-E_{d,i}}{RT}\right) \quad \alpha_{H_2/CO_2} = \left(\frac{M_{w,CO_2}}{M_{w,H_2}} \right)^{1/2} \exp\left(\frac{E_{d(CO_2)} - E_{d(H_2)}}{RT}\right)$$



The maximum H₂/CO₂ selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.

Technical Accomplishment – CVD for Reduction of Zeolitic Pores and Improvement of H₂/CO₂ Separation Factor

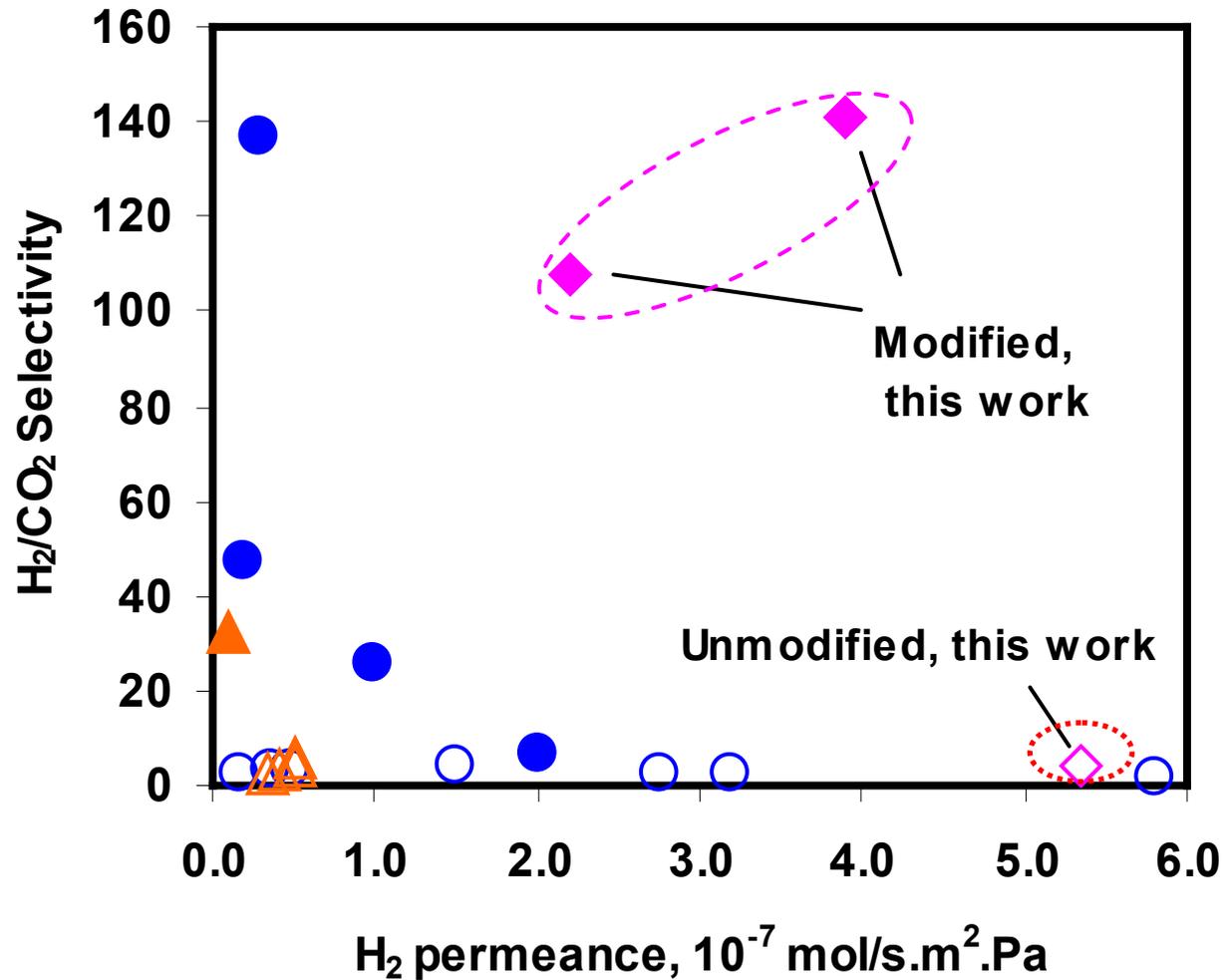
On-stream monitoring of H₂/CO₂ separation performance during the CCD modification on α -alumina-supported MFI membrane



H₂/CO₂ selectivity of MFI type zeolite membrane can be effectively improved by CVD of MDES via controlled catalytic cracking deposition (CCD) in selective sites in zeolite pores

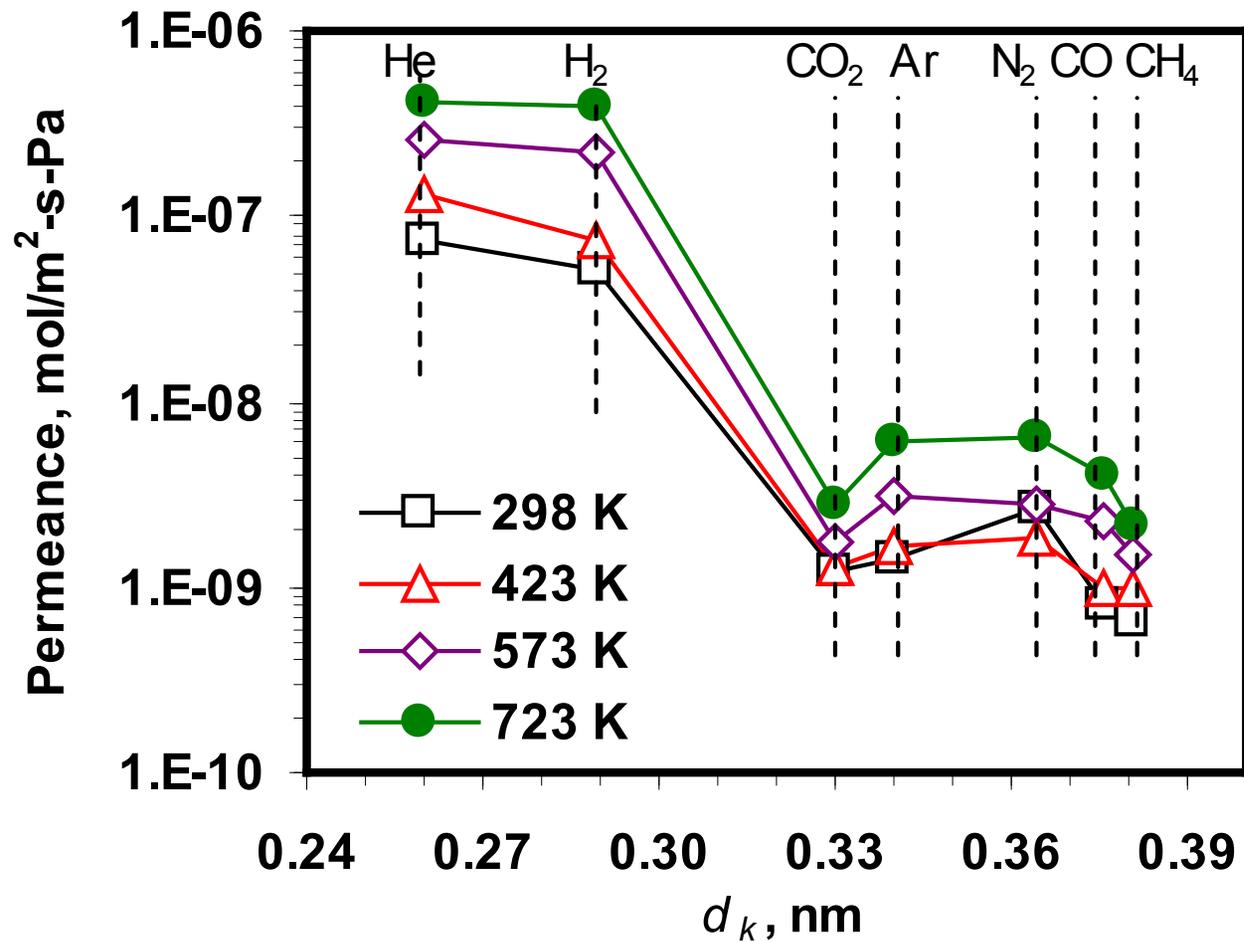
Technical Accomplishment – Zeolite Membrane with High H₂/CO₂ Perm-Selectivity

Comparison of the CVD-modified zeolite membrane with literature membrane performance for H₂/CO₂ separation



H₂/CO₂ perm-selectivity of 140 and H₂ permeance about 4x10⁻⁷ mol/s.m².Pa at 450°C was obtained for the CVD modified membranes

Technical Accomplishment – Single Gas Permeance of a CVD Modified Membrane at different Temperatures



CVD modified zeolite membrane exhibits molecular sieving properties

Technical Accomplishment – High Quality Tubular Supports Developed

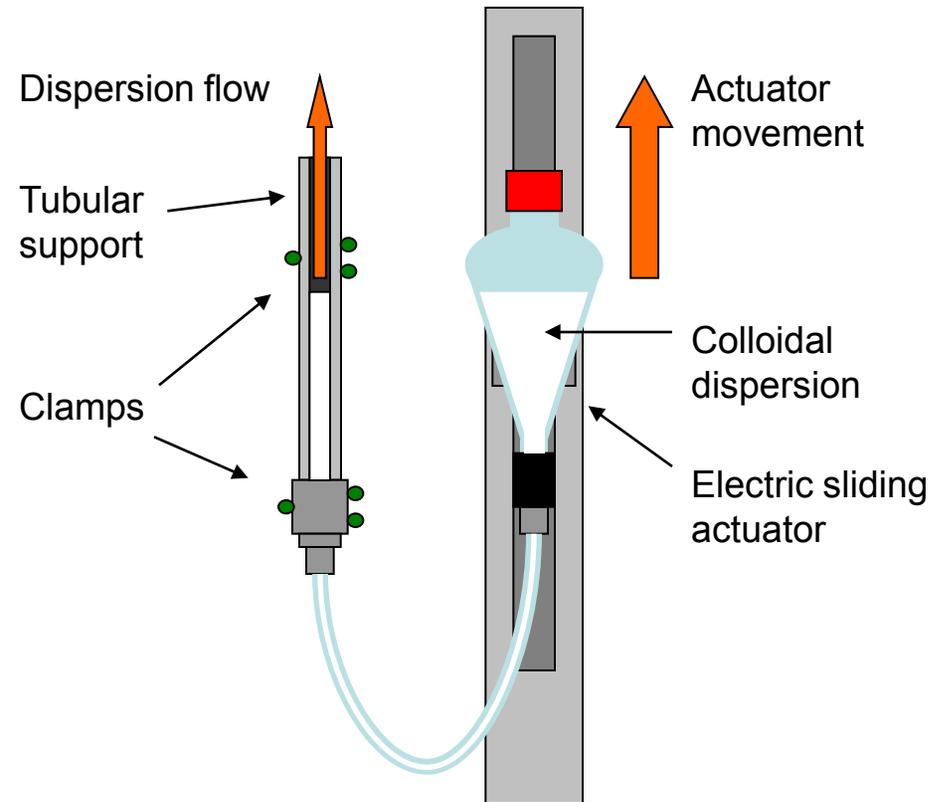
- Application of intermediate layers onto tubular supports by flow coating

- AKP30 coating:

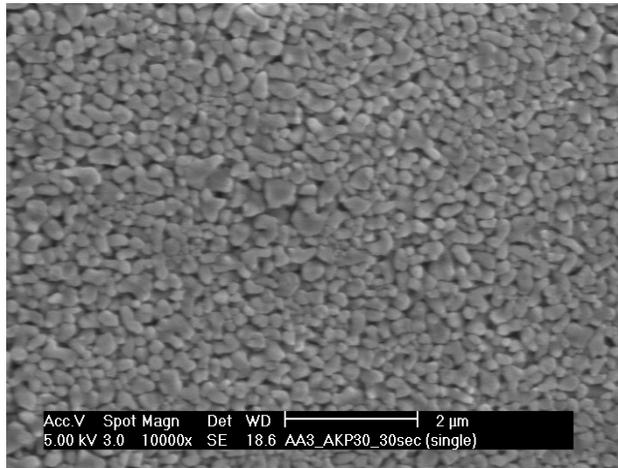
8 wt% AKP30 coating (w/ 0.1 wt% Darvan 821A, 1.2 wt% PVP) onto AA3 α -Al₂O₃ (provided by MetaMateria Partners) and Pall α -Al₂O₃ ($\phi_p=0.8 \mu\text{m}$) supports

- γ -Al₂O₃ deposition:

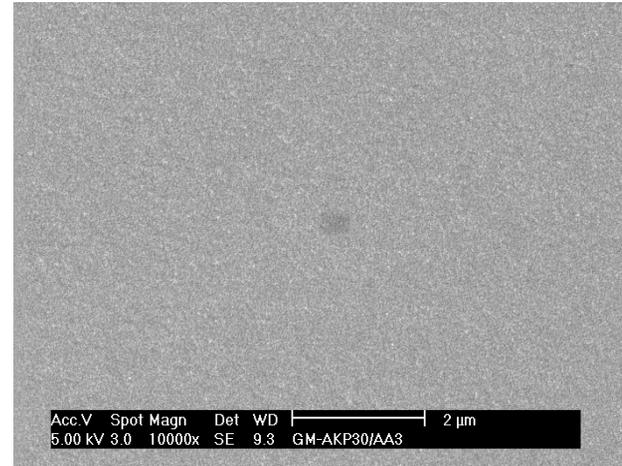
γ -Al₂O₃ deposition onto AKP30-AA3 supports with Böhmiet sol [AlO(OH)] mixed with PVA (3:2 by vol.)



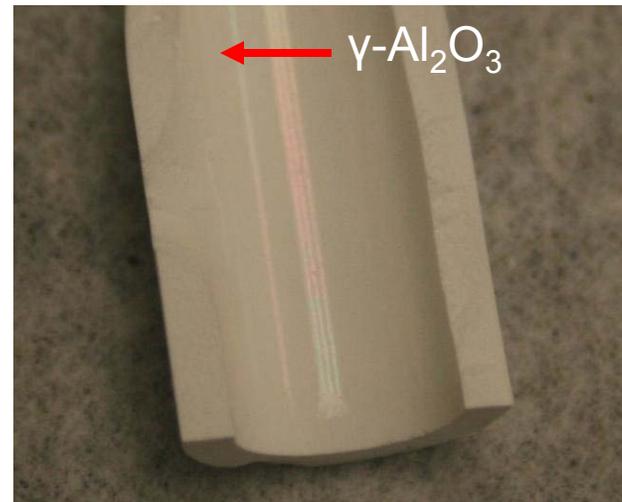
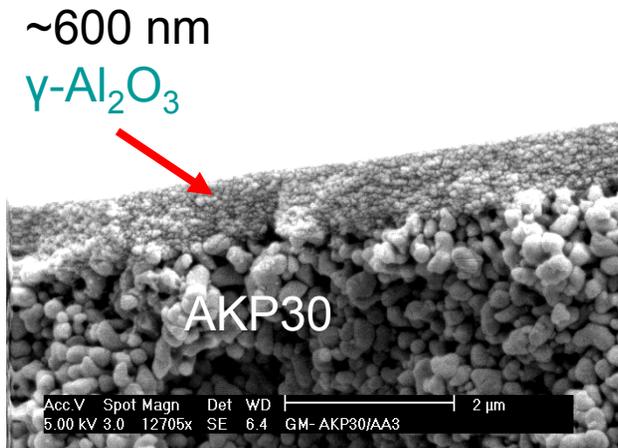
Technical Accomplishment – High Quality Tubular Supports Developed (Cont'd)



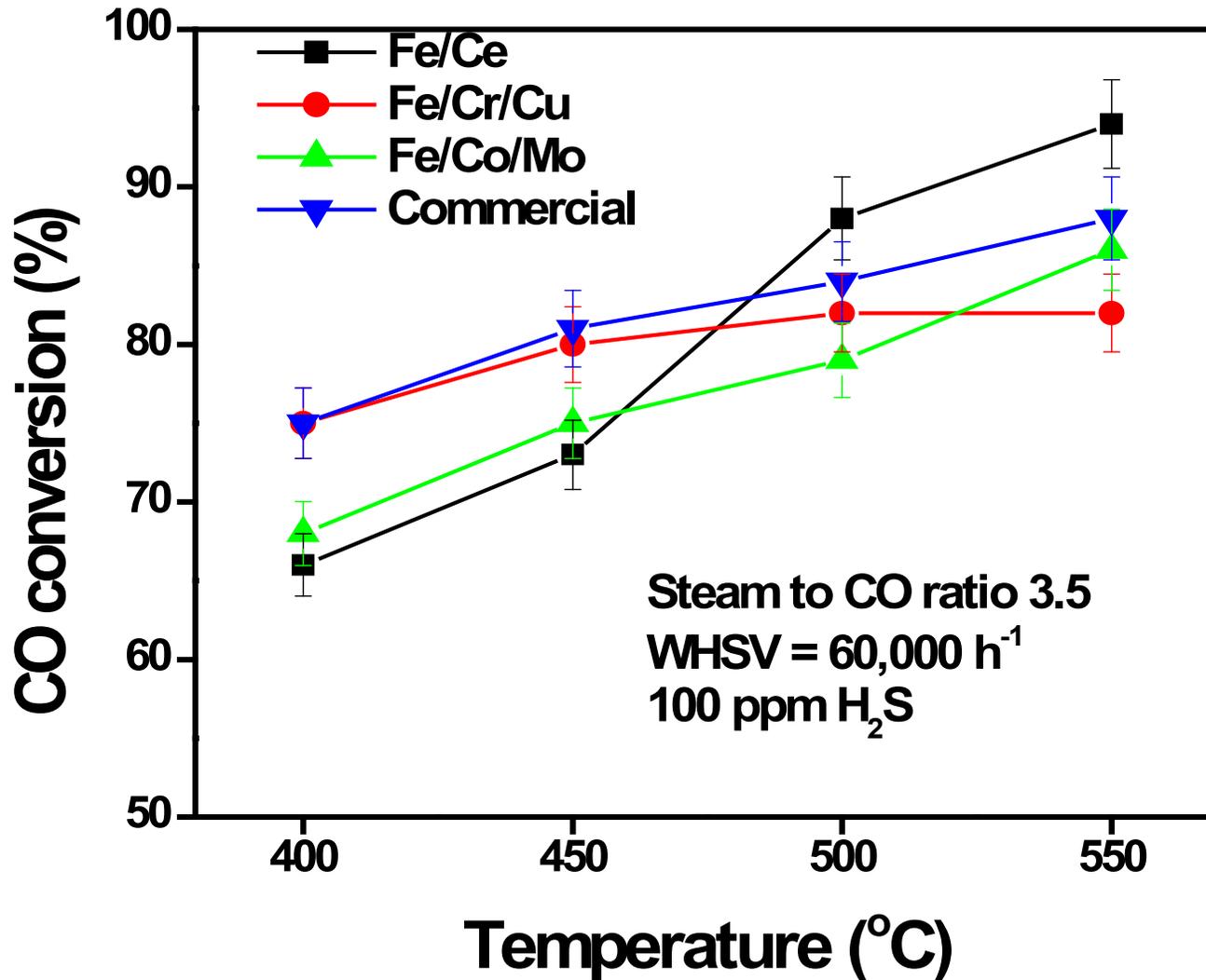
AKP30-AA3 (surface)



$\gamma\text{-Al}_2\text{O}_3\text{-AKP30-AA3}$ (surface)

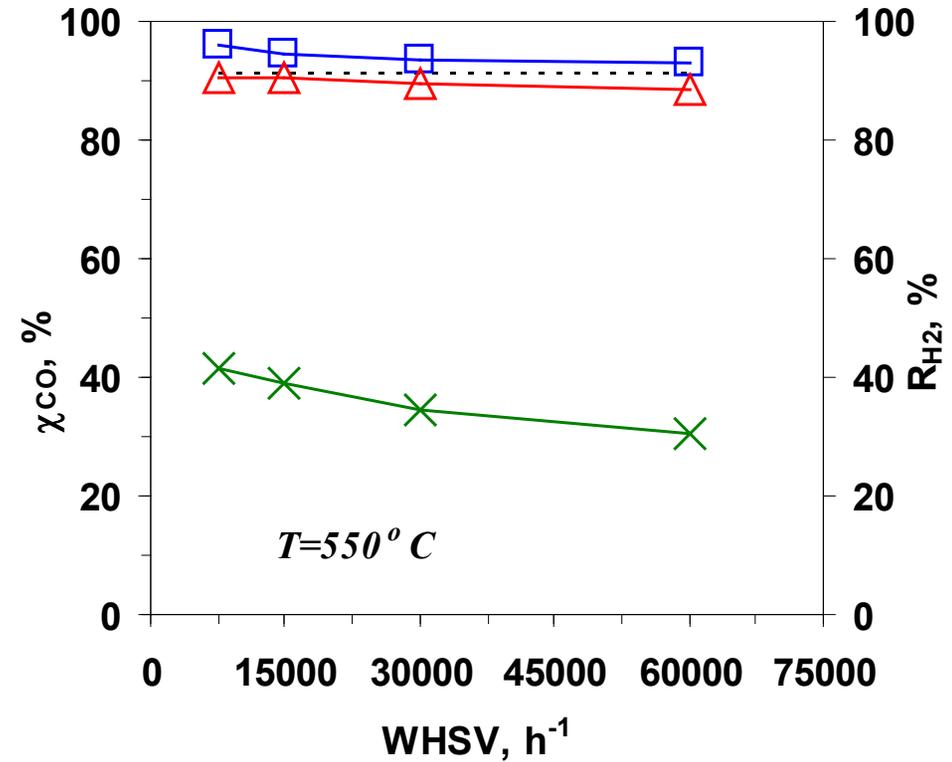
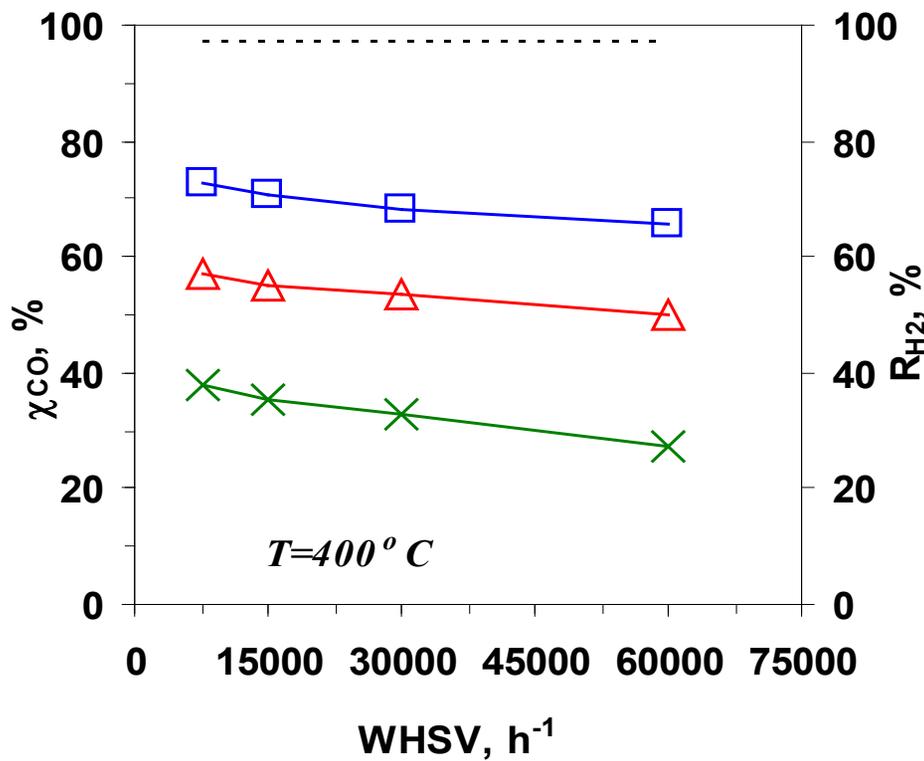


Technical Accomplishment – Sulfur Resistant, High Temperature WGS Catalyst Developed



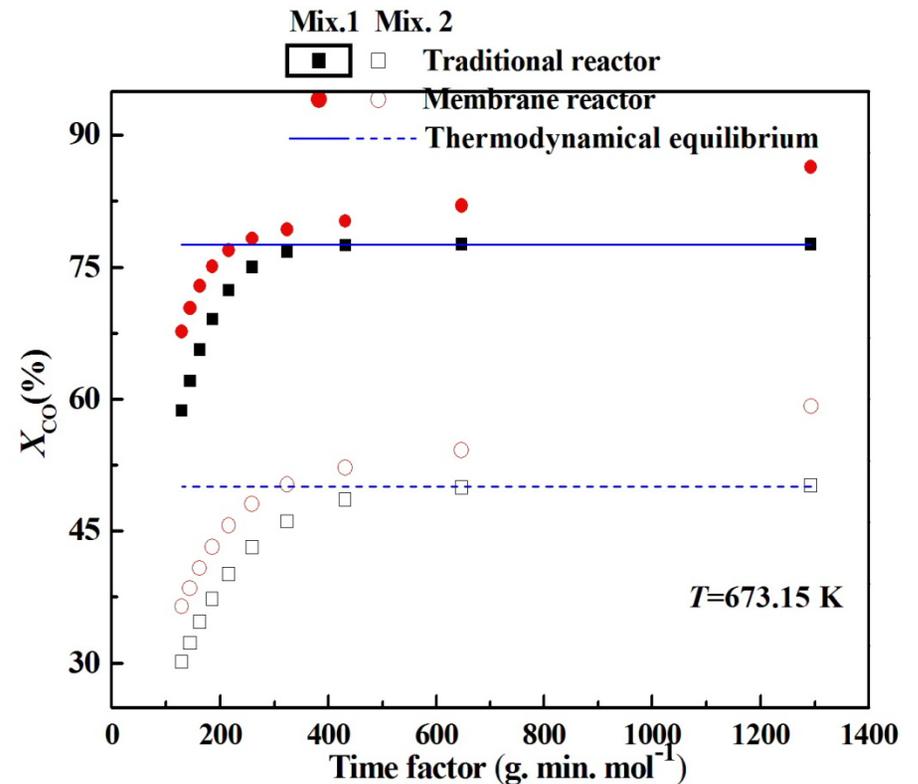
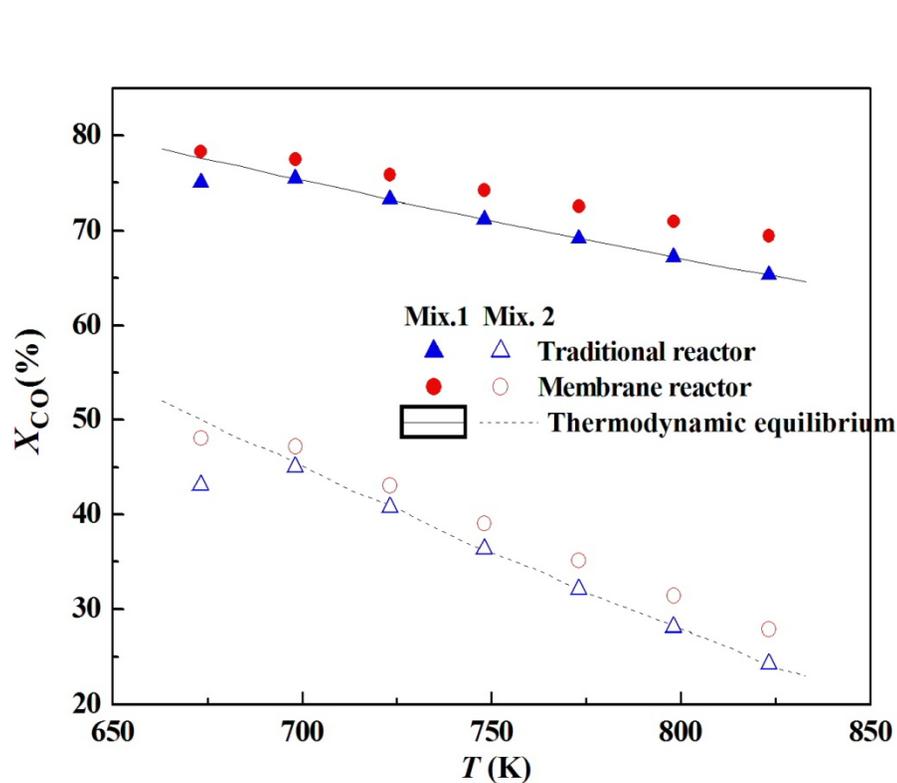
Activity comparison of the developed catalysts with a commercial catalyst at different WGS temperatures

Technical Accomplishment – Water Gas Shift Reaction in a CVD Modified Tubular Membrane Reactor



Effect of WHSV on CO-conversion and hydrogen recovery for a fixed $R_{H_2O/CO}$ of 3.5: (---) Equilibrium conversion ($\chi_{CO,e}$); (\square) Conversion in membrane reactor (χ_{CO}); (Δ) Conversion in traditional reactor (χ_{CO}); (\times) H₂ recovery.

Technical Accomplishment – Modeling of Water Gas Shift Reaction



Feed molar composition of the tube side	Mixture 1	Mixture 2
CO(%)	50	20
H ₂ O(%)	50	20
CO ₂ (%)	0	10
H ₂ (%)	0	50

Collaboration

- Within DoE H₂ Program
 - Arizona State University (membrane synthesis and WGS reaction)
 - University of Cincinnati (membrane modification and catalyst development)
 - Ohio State University (membrane support and module development)
- Outside of DoE H₂ Program
 - NGK Co. (Japan) (synthesis of DDR membranes)
 - Sintef Research (Norway) (CO₂ permselective membrane)
 - University of Victoria (Australia) (zeolite membrane synthesis)
 - Ecotality Inc. (US) (hydrogen storage technology)

ASU/NGK joint publication: M. Kanezashi, J. O'Brien- Abraham, Y.S. Lin and K. Suzuki, "Gas permeation through DDR-type zeolite membranes at high temperatures," *AIChE J.*, 54(6), 1478-1486(2008)

Propose Future Work for FY10

1. Fabrication of high quality membrane supports for growing silicalite membranes (OSU)
 - a) *Disk and tubular support with zirconia intermediate layer*
2. Synthesis of high quality silicalite membranes by secondary growth and CVD modification (UC, ASU)
 - a) *H_2/CO_2 selectivity > 100, H_2 permeance > 5×10^{-7} mol/m².s.Pa*
 - b) *Silicalite membranes on zirconia support with improved chemical stability*
3. Separation and stability study of silicalite membranes (ASU, UC)
 - a) *Measuring single and mixture gas permeability and selectivity in larger temperature (200-500 °C) and pressure (1-10 atm) range.*
 - b) *Studying stability of the membranes in WGS gas stream conditions (with steam) for up to 1 month.*

Propose Future Work for FY10

4. Stability and kinetic study of new WGS catalyst (UC)
 - a) *Long term stability study in sulfur containing gas (about 1 month)*

5. WGS reaction on silicalite membrane reactor (ASU, UC)
 - a) *Modeling WGS reaction in zeolite membrane reactor with known permeation and kinetic data*
 - b) *Improving membrane reactor system including setup (operatable up to 20 atm and 550°C) and membrane module*
 - c) *Optimization of the performance of WGS reaction in the silicalite membrane reactor*
 - d) *Studying stability of the membrane reactor for WGS reaction under optimum conditions.*

6. *Cost analysis of zeolite membrane reactor for WGS*

Summary

- **Relevance:**

Help to develop processes for cost-effective production of hydrogen from natural gas and renewable liquids

- **Approach:**

Study fundamental issues related to synthesis and separation properties of high quality, stable zeolite membranes, and develop the zeolite membrane reactor for water-gas-shift reaction and hydrogen separation

- **Technical Accomplishment and Progress:**

Improved understanding of synthesis and gas transport mechanism in zeolite membranes, developed and studied methods and techniques to prepare zeolite membranes with high H₂ permeance ($>2 \times 10^{-7}$ mol/m².s.Pa) and selectivity (>120) suitable for WGS membrane reactor application, and catalysts with improved properties for WGS reaction; improved WGS conversion with zeolite membrane reactor demonstrated.

- **Proposed Future Research:**

Prepare high performance zeolite membranes and catalyst and study WGS reaction in zeolite membrane reactors.