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%**

Barriers

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

Budget

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

Partners

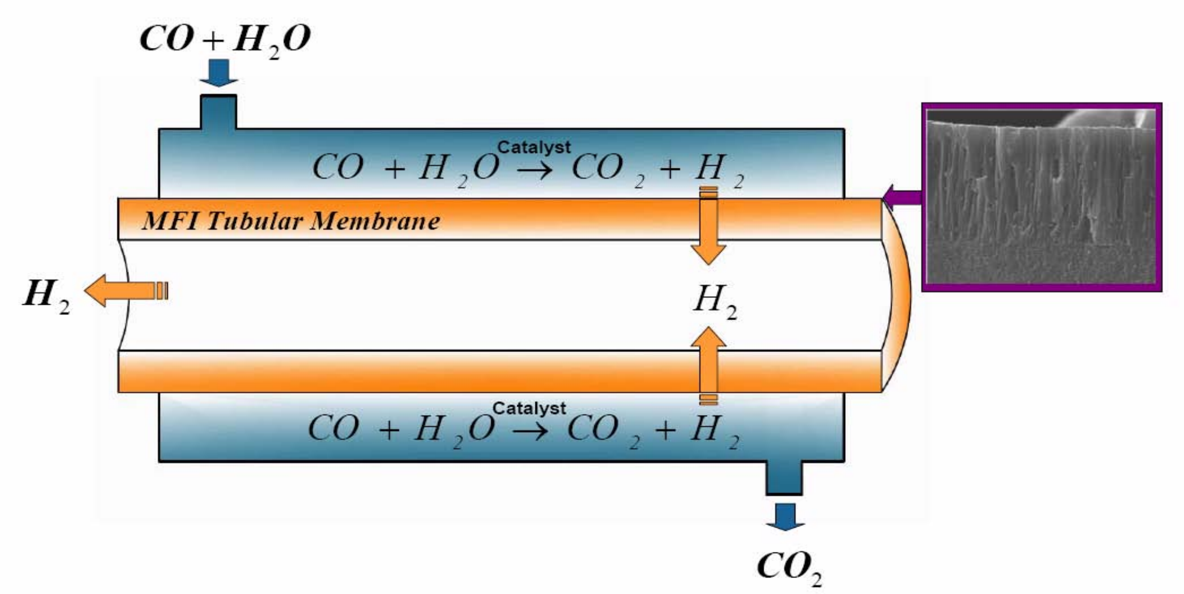
- University of Cincinnati
- Arizona State University
- Ohio State University

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*

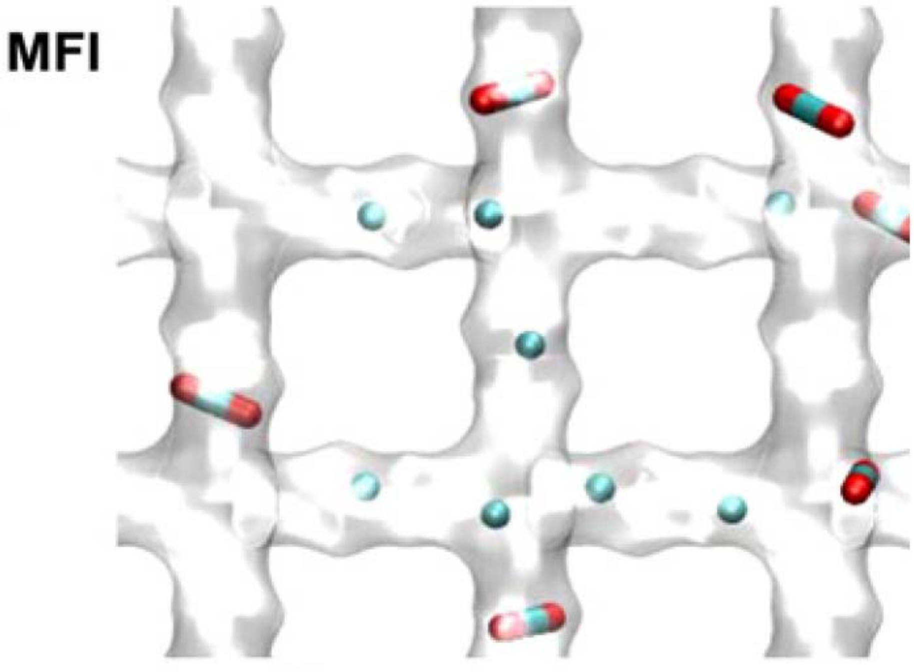
Approach – Zeolite Membrane Reactor for Water-Gas Shift Reaction

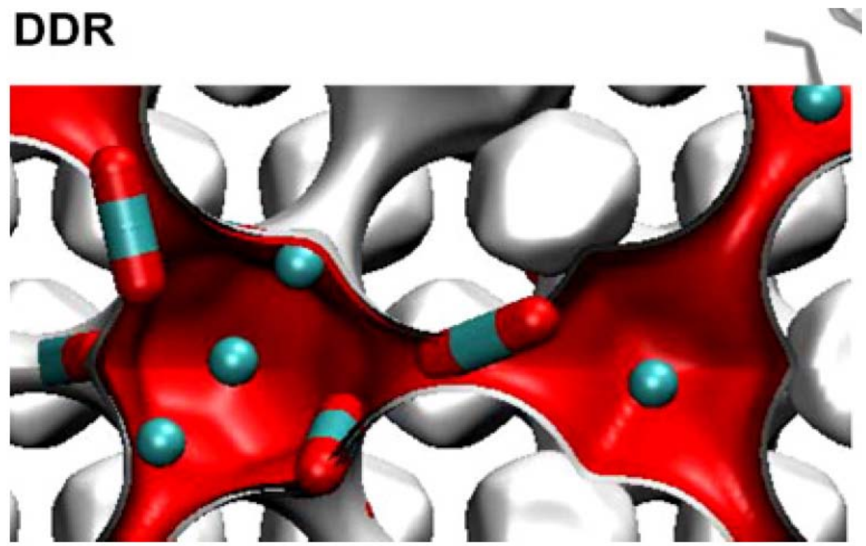


Zeolite Membrane Requirements:

- Operate at 350-550°C
- Chemically stable in H_2S, thermally stable at ~400°C
- Hydrogen permeance ~ 5×10^{-7} mol/m^2.s.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

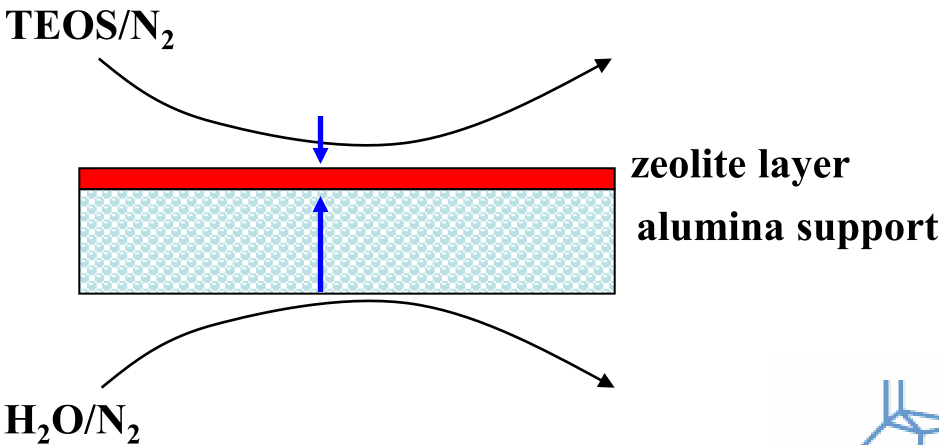
Cages separated by narrow windows

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

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

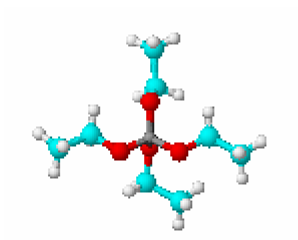
Figures from R. Krishna and J.M. van Baten, (2008)

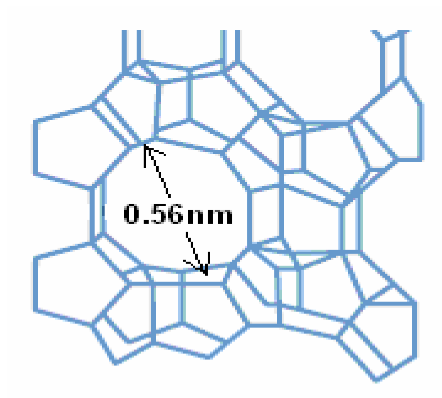
Approach – Counter-diffusion CVD of Silica for Improving Membrane Quality

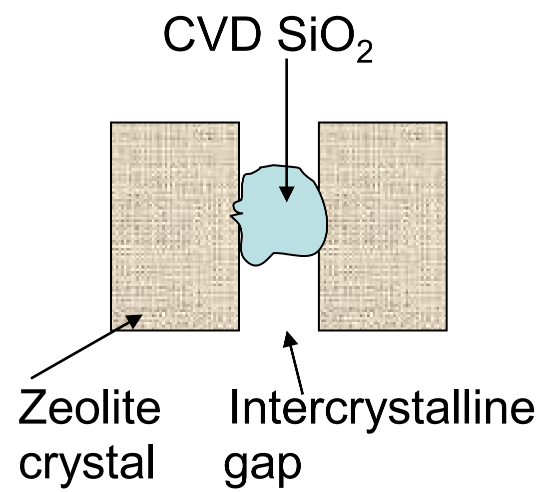


- CVD reaction temp: 550°C,
- Bubbling temp: room temp.

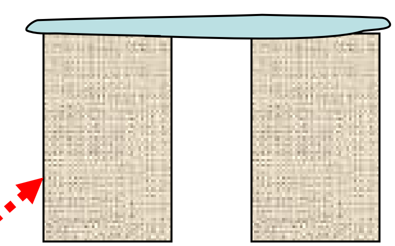
TEOS
0.95 nm





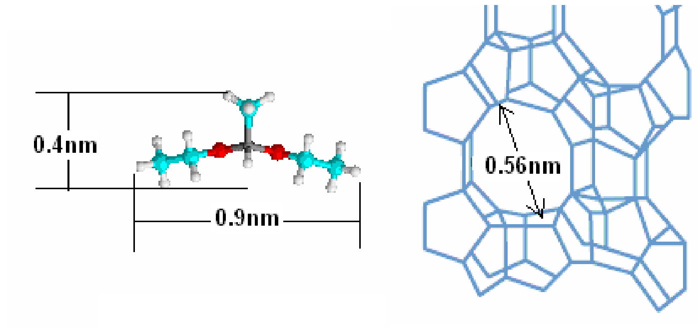


Hydrothermal stability test shows this is less likely the result of CVD



Approach – CVD Narrowing Zeolitic Pores to Further Improve Selectivity

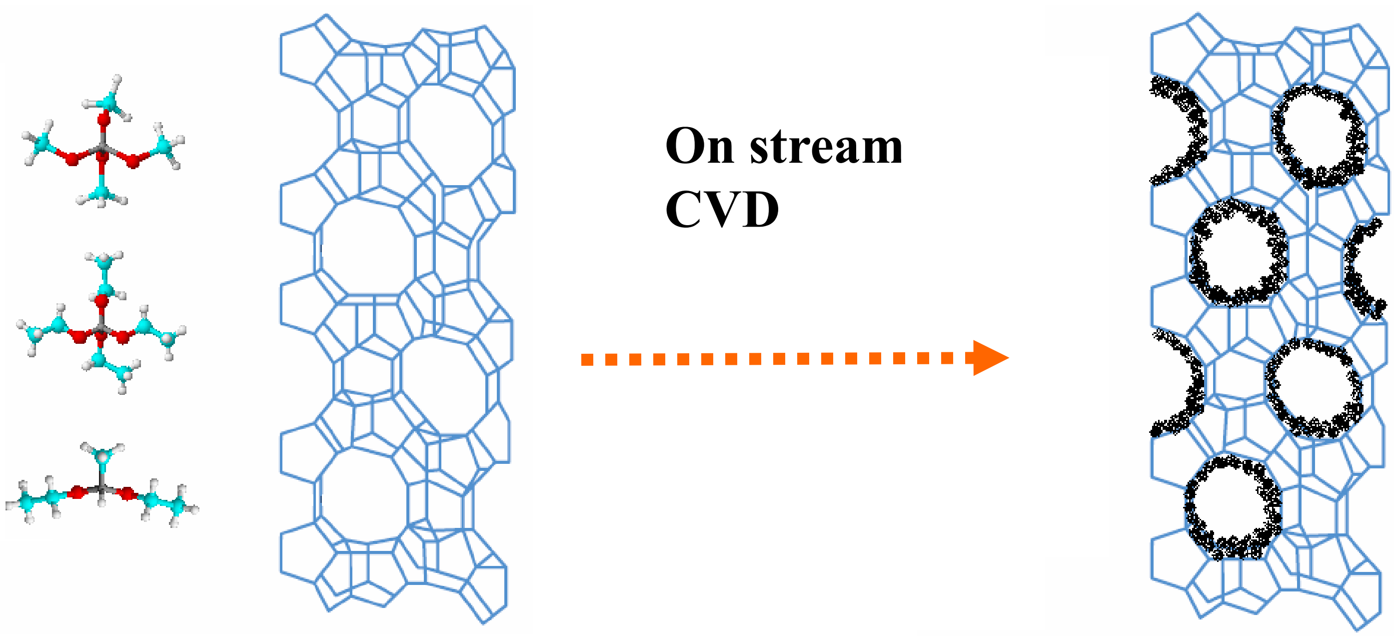
methyldiethoxysilane
(MDES)



TMOS
0.89nm

TEOS
0.95nm

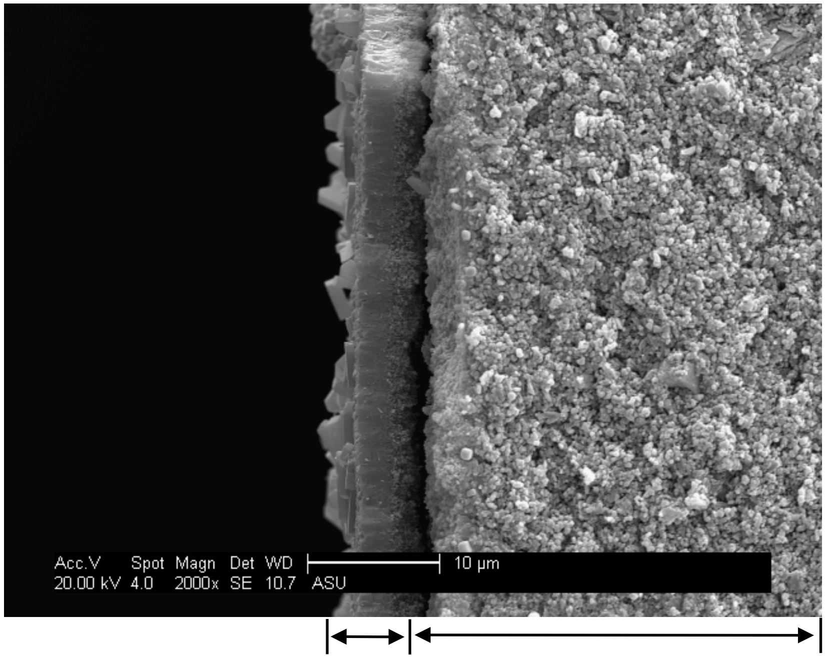
MDES
0.4 × 0.9nm



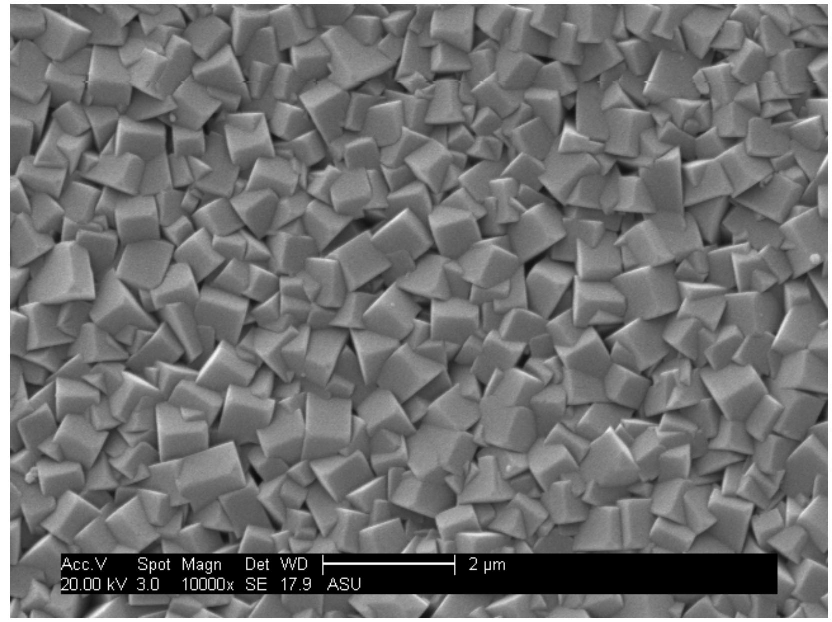
Previous Technical Accomplishments (Milestones Achieved)

- 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 $1x10^{-7}$ $mol/m^2.s.Pa$.
- 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^oC.
- 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 $4x10^{-7}$ $mol/m^2.s.Pa$.
- Obtain CVD modified tubular silicalite membranes with H_2/CO_2 separation factor over 120 and H_2 permeance larger than $2.0x10^{-7}$ $mol/m^2.s.Pa$.

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

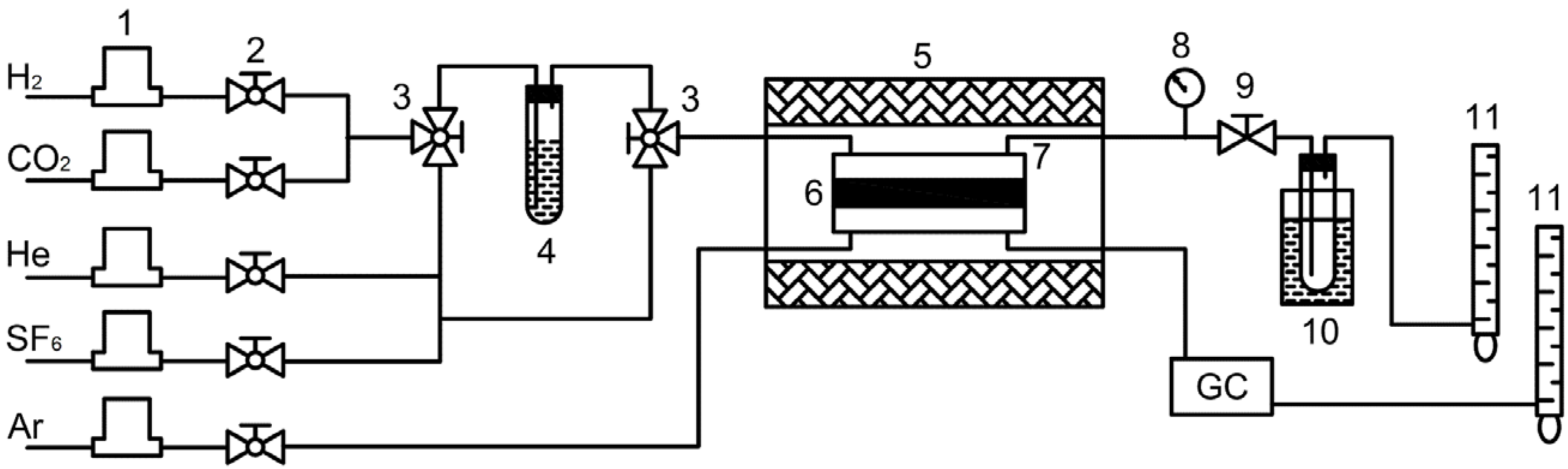


Zeolite layer (~5 μm) α-alumina layer



- 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

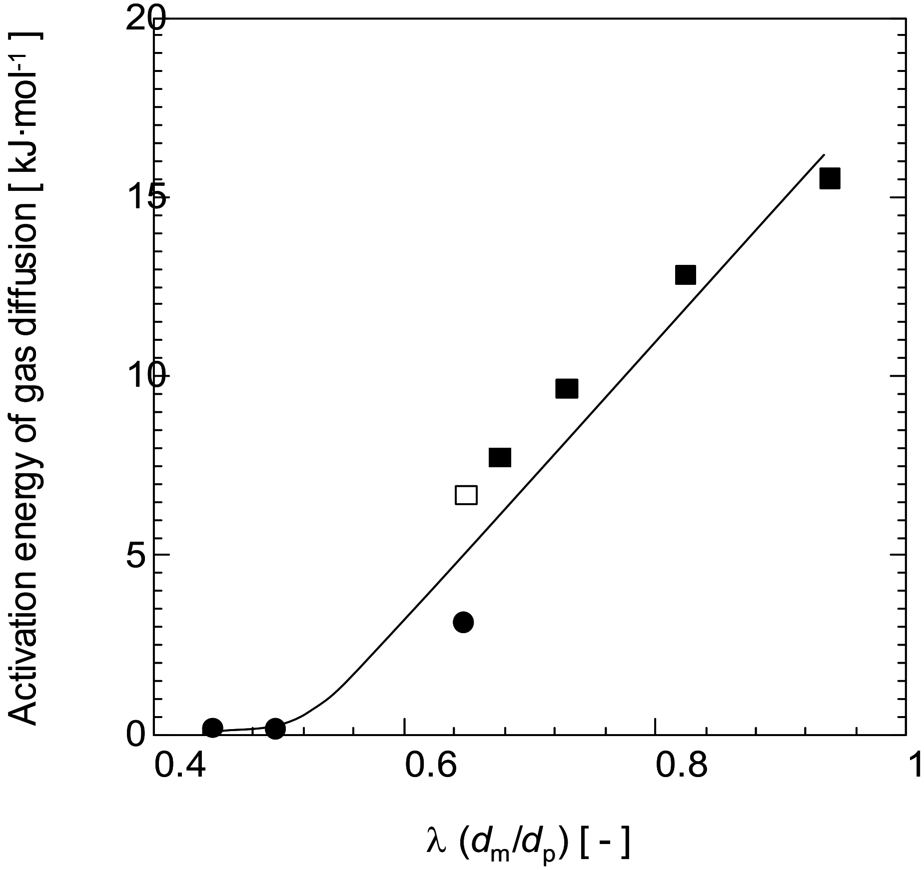


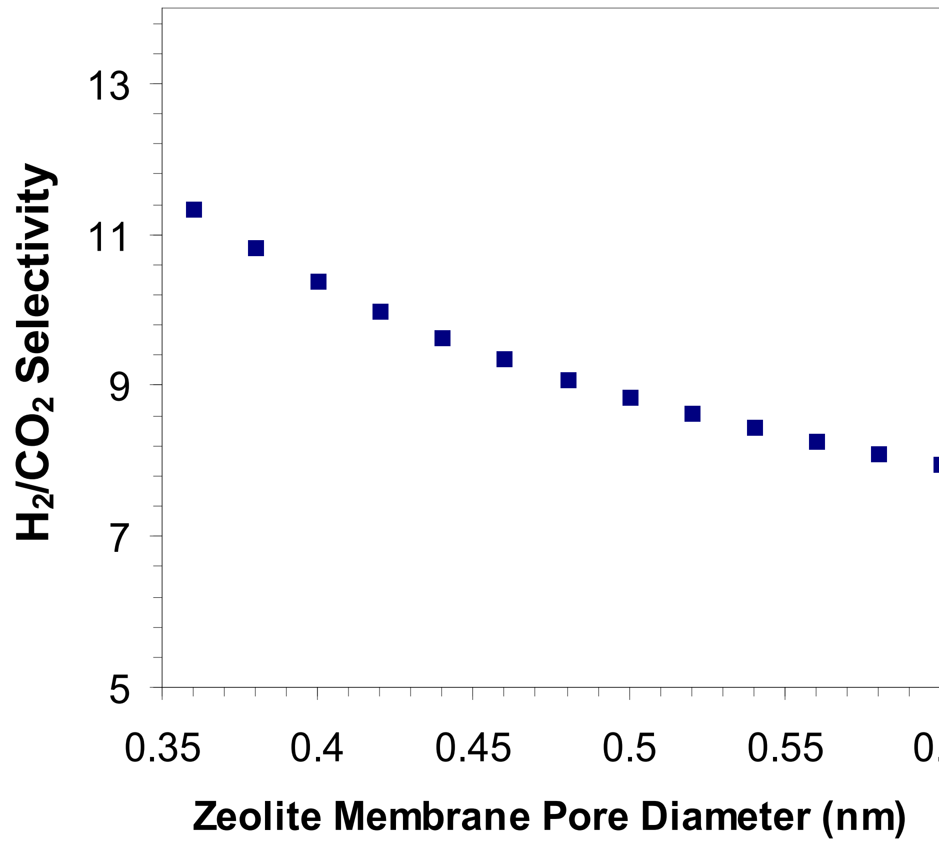
1. Mass flow controller
2. 2-way ball valve
3. 3-way ball valve
4. Bubbler
5. Box furnace
6. MFI membrane
7. Permeation cell
8. Pressure gauge
9. Needle valve
10. Cold trap
11. Bubbler flow meter

	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

$$F_i = [\frac{\phi}{L}\frac{\alpha}{z}][\frac{8}{\pi \ R \ M_{W,i} \ T}]^{1/2} \exp(\frac{-E_{d,i}}{RT}) \qquad \alpha_{H2/CO2} = (\frac{Mw_{CO2}}{Mw_{H2}})^{1/2} \exp(\frac{E_{d(CO2)} - E_{d(H2)}}{RT})$$

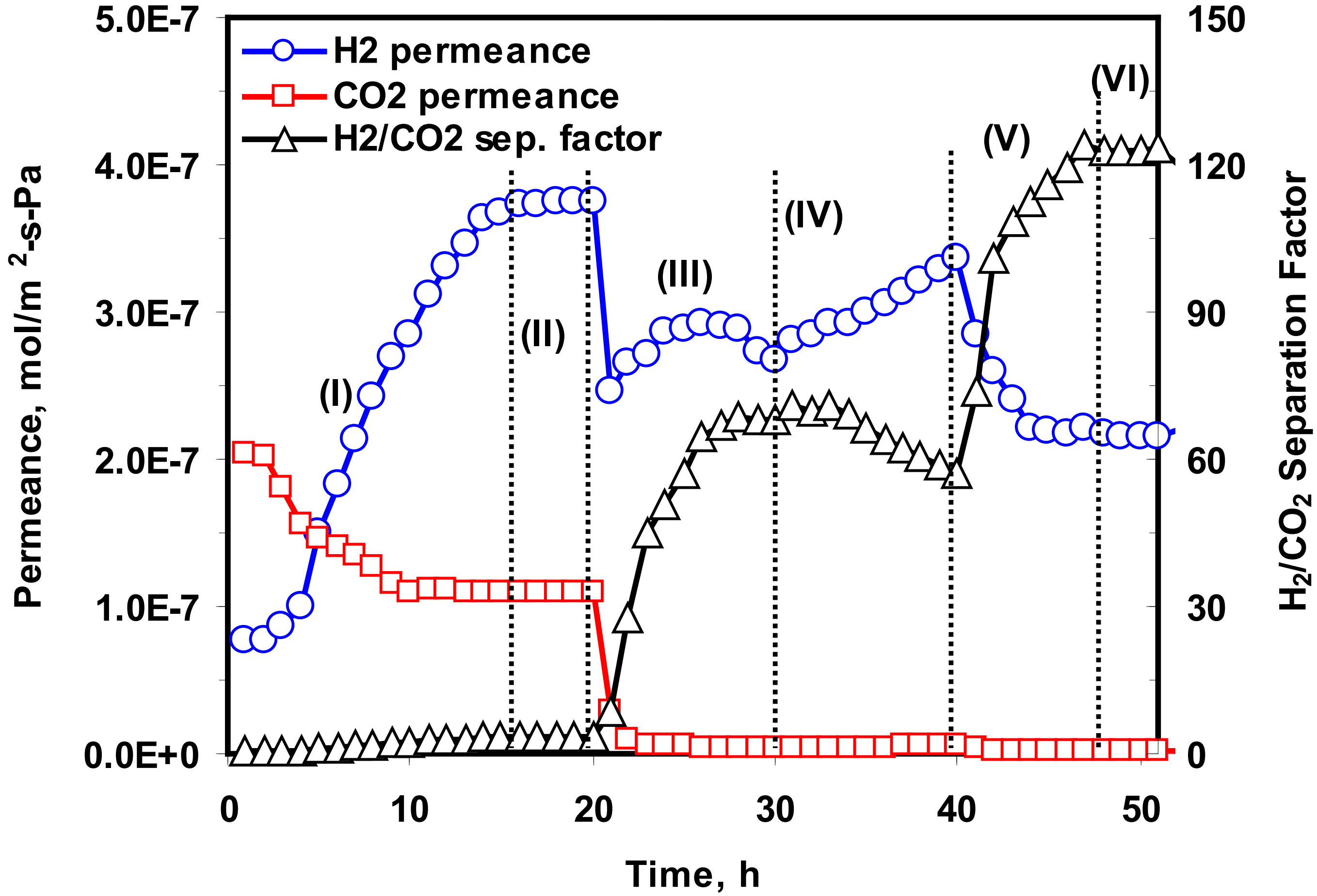




The maximum H_2/CO_2 selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.

Technical Accomplishment – CVD for Reduction of Zeolitic Pores and Improvement of H_2/CO_2 Separation Factor

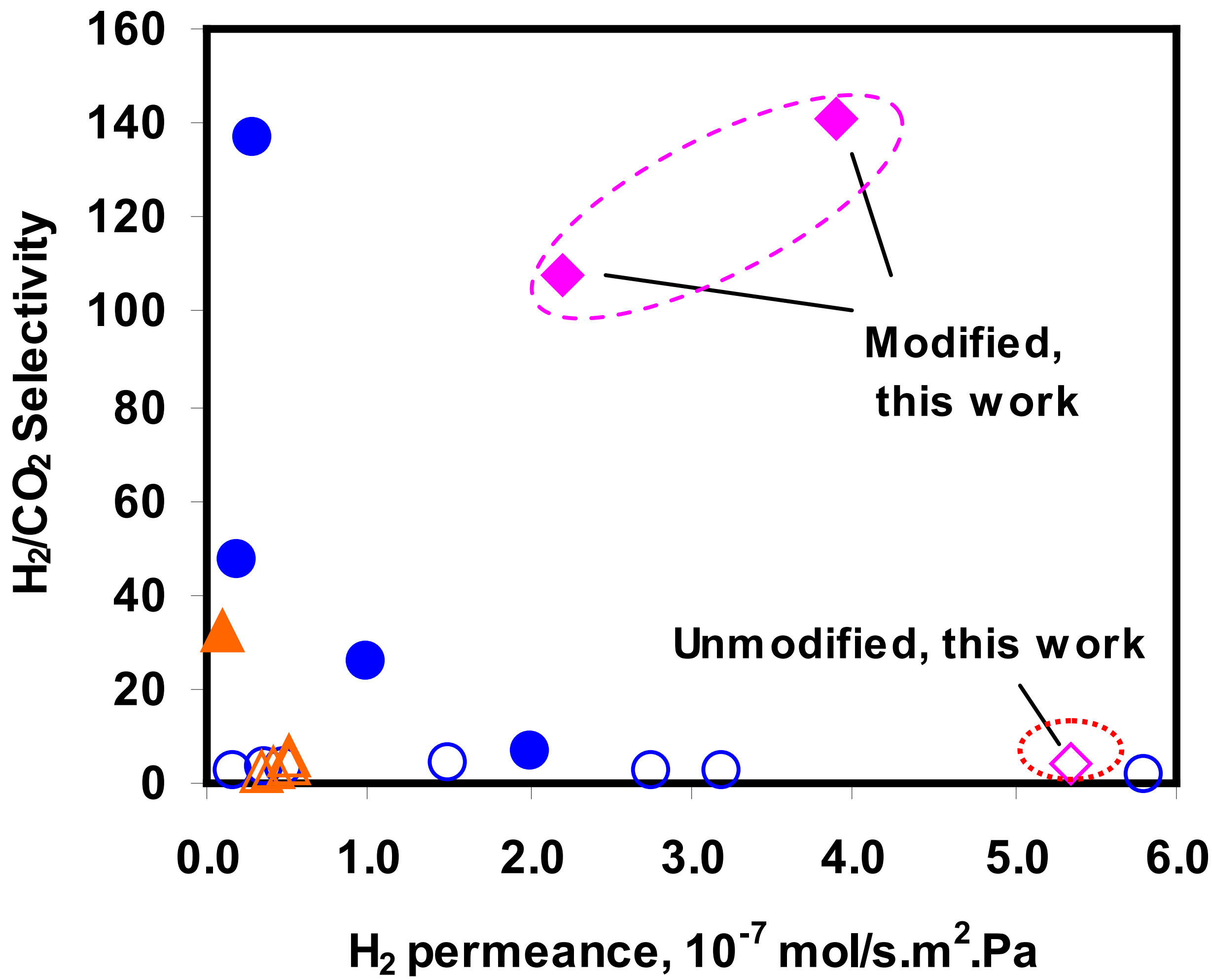
On-stream monitoring of H_2/CO_2 separation performance during the CCD modification on α-alumina-supported MFI membrane



H_2/CO_2 selectivity of MFI type zeoltie membrane can be effectively improved by CVD of MDES via controlled catalytic cracking deposition (CCD) in selective sites in zeolite pores

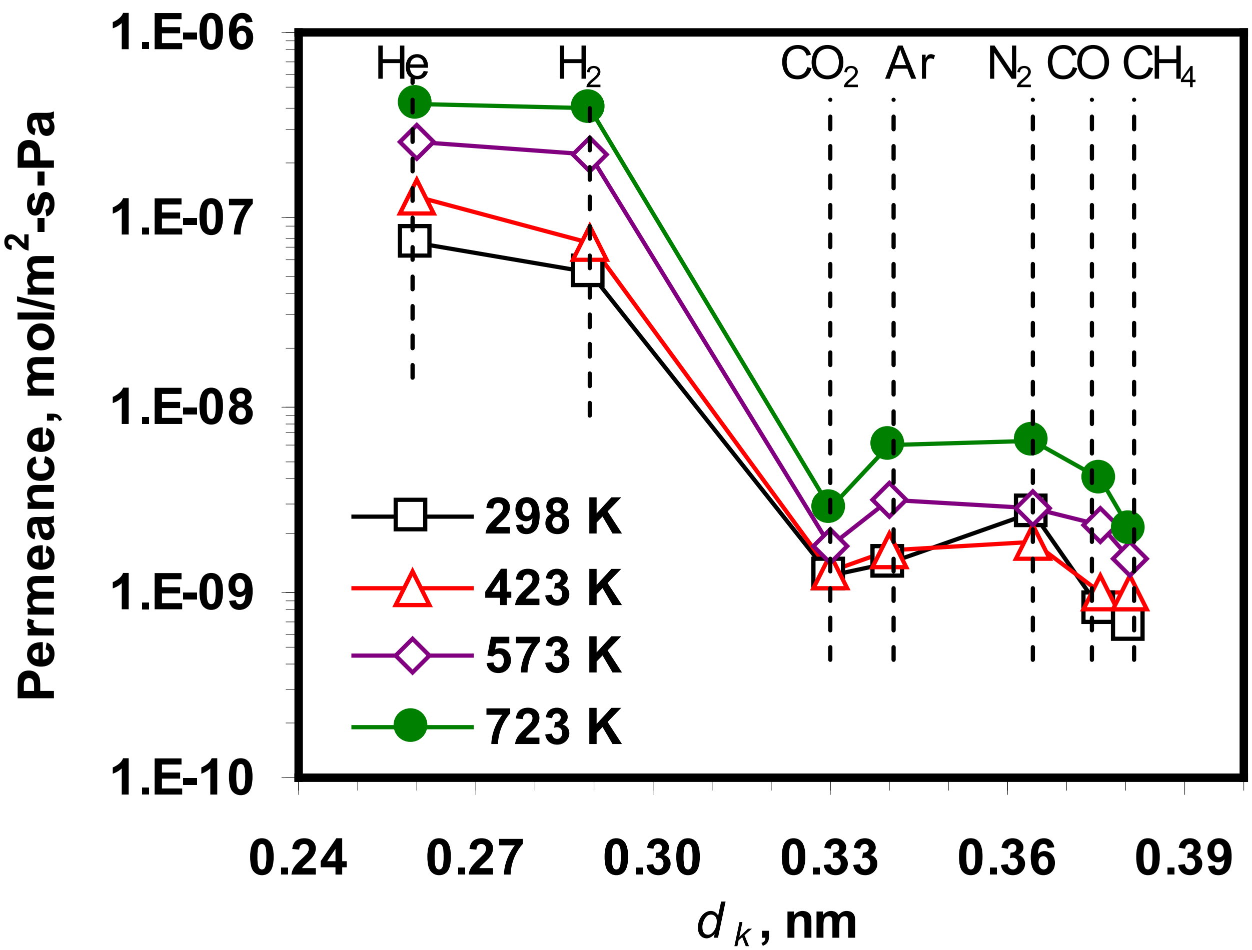
Technical Accomplishment – Zeolite Membrane with High H_2/CO_2 Perm-Selectivity

Comparison of the CVD-modified zeolite membrane with literature membrane performance for H_2/CO_2 separation



H_2/CO_2 perm-selectivity of 140 and H_2 permeance about 4×10^{-7} mol/s.m^2.Pa at 450°C was obtained for the CVD modified membranes

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



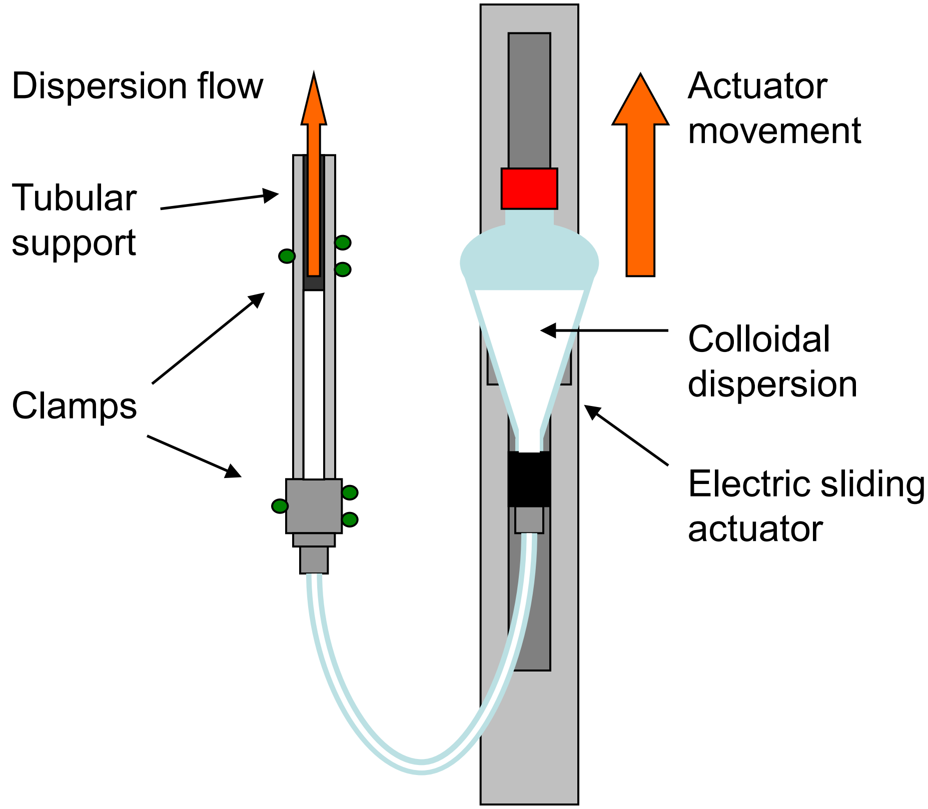
CVD modified zeolite membrane exhibits molecular sieving properties

Technical Accomplishment – High Quality Tubular Supports Developed

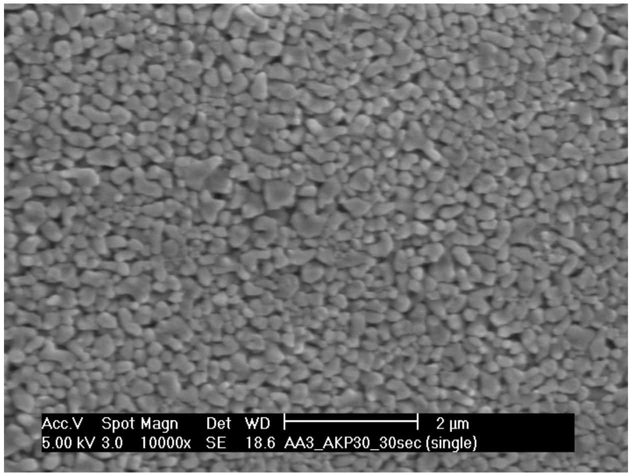
- Application of intermediate layers onto tubular supports by flow coating
  - AKP30 coating:

    8 wt% AKP30 coating (w/ 0.1 wt% Darvan 821A, 1.2 wt% PVP) onto AA3 α-Al_2O_3 (provided by MetaMateria Partners) and Pall α-Al_2O_3 ($Ø_p$=0.8 μm) supports
  - γ-Al_2O_3 deposition:

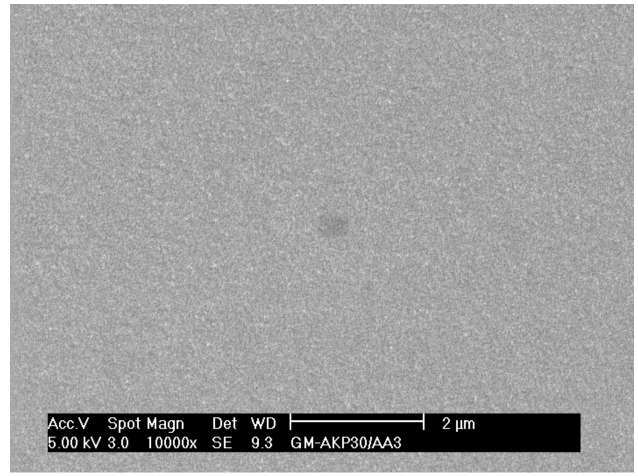
    γ-Al_2O_3 deposition onto AKP30-AA3 supports with Böhmiet sol [AlO(OH)] mixed with PVA (3:2 by vol.)



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

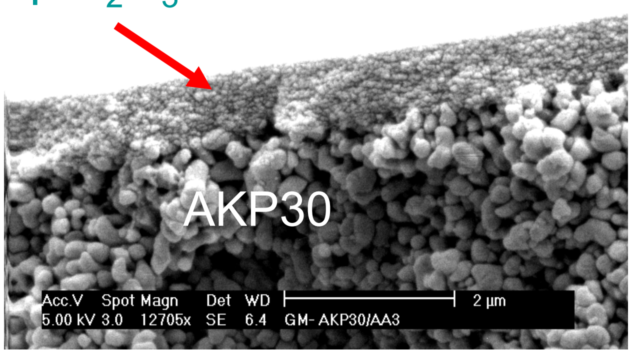


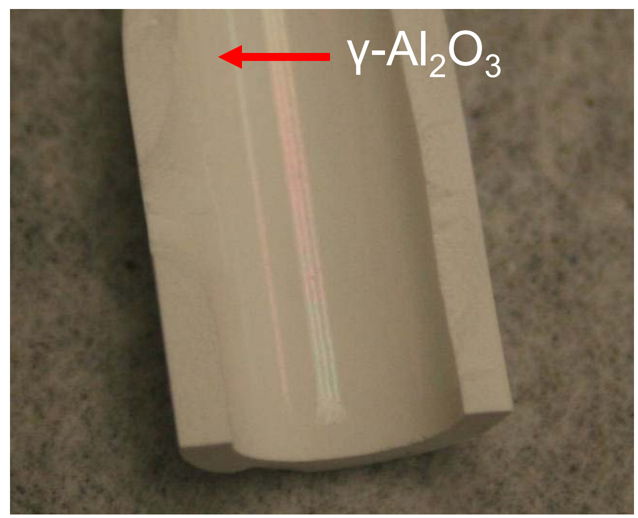
AKP30-AA3 (surface)



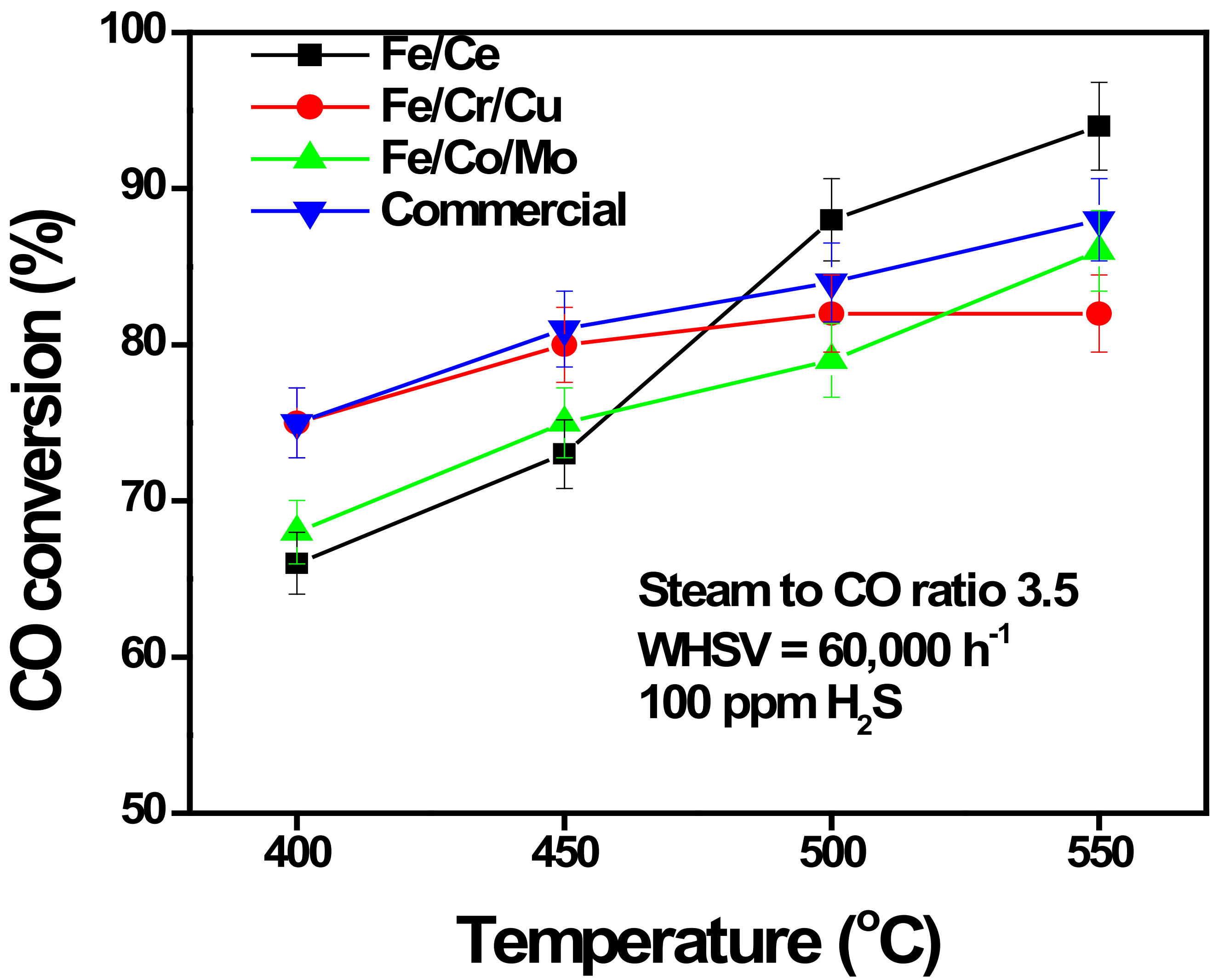
γ-Al_2O_3-AKP30-AA3 (surface)

~600 nm
γ-Al_2O_3



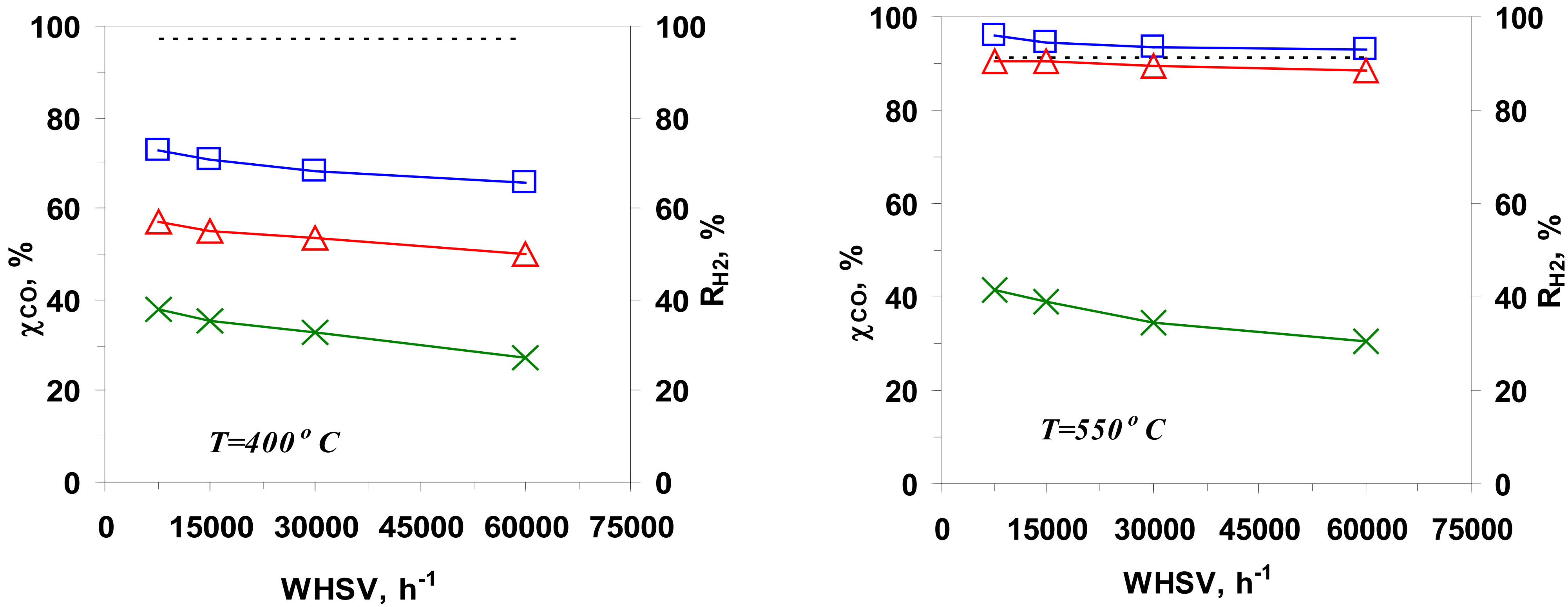


Technical Accomplishment – Sulfur Resistant, High Temperature WGS Catalyst Developed



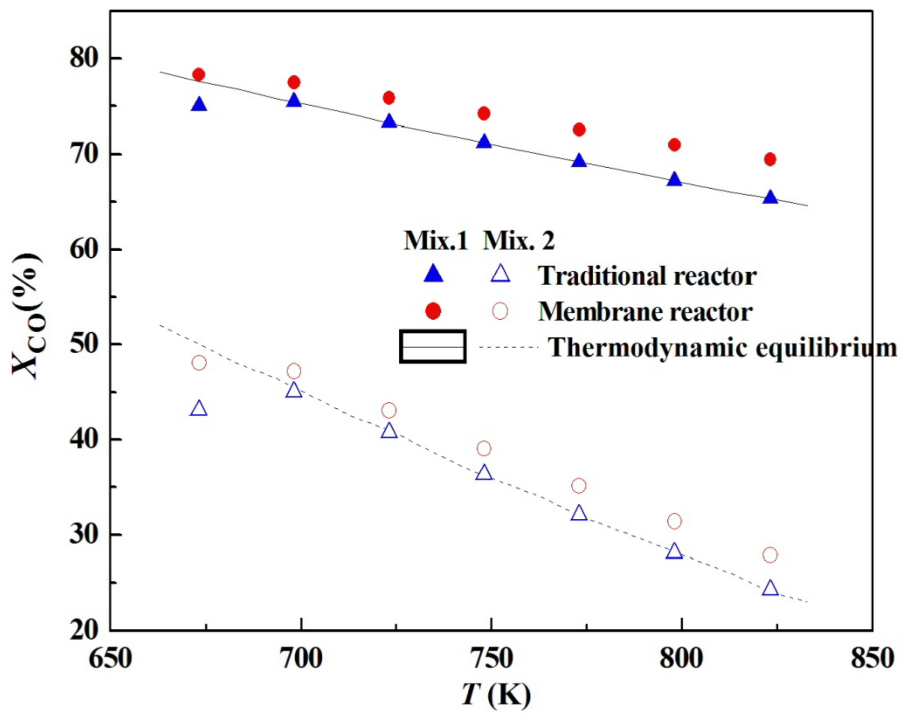
Activity comparison of the developed catalysts with a commercial catalyst at different WGS temperatures

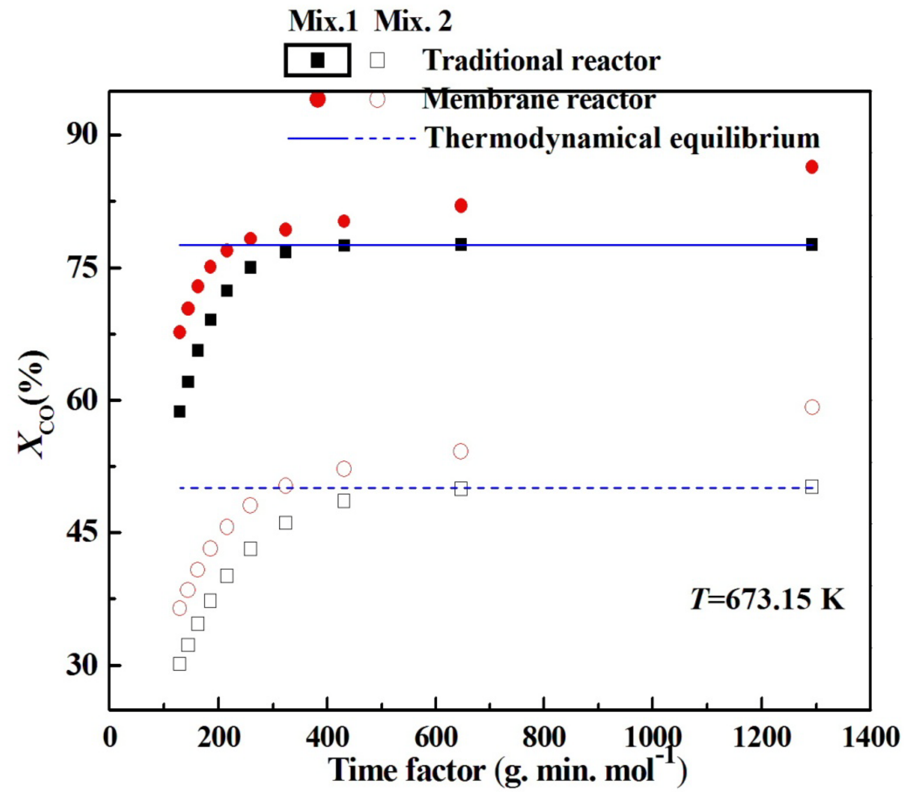
Technical Accomplishment – Water Gas Shift Reaction in a CVD Modified Tubular Membrane Reactor



Effect of WHSV on CO-conversion and hydrogen recovery for a fixed $R_{H2O/CO}$ of 3.5: (---) Equilibrium conversion ($\chi_{CO,e}$); (□) Conversion in membrane reactor (χ_{CO}); (Δ) Conversion in traditional reactor (χ_{CO}); (×) H_2 recovery.

Technical Accomplishment – Modeling of Water Gas Shift Reaction





Feed molar composition of the tube side	Mixture 1	Mixture 2
CO(%)	50	20
H_2O(%)	50	20
CO_2(%)	0	10
H_2(%)	0	50

Collaboration

- Within DoE H_2 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 H_2 Program
  - NGK Co. (Japan) (synthesis of DDR membranes)
  - Sintef Research (Norway) (CO_2 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 > $5x10^{-7}$ mol/m^2.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 ^{o}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^{o}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 H_2 permenace (>2×10^{-7} mol/m^2.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.