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

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Project PD_06_Lin

Overview

Timeline

- Project start date:
  July 1, 2005
- Project end date:
  August 30, 2010
- Percent complete: **60%**

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 received in FY08: **$459,553**
- Funding for FY9: **$0**

Partners

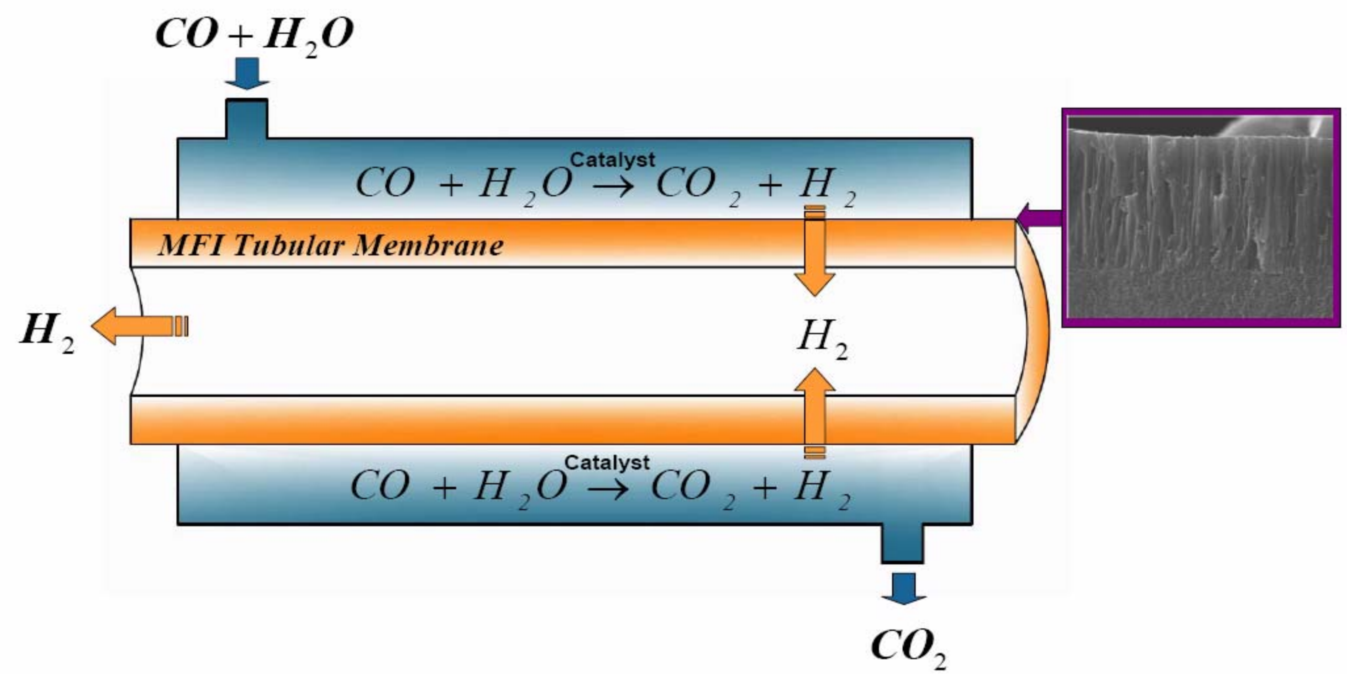
- University of Cincinnati
- Arizona State University
- Ohio State University

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

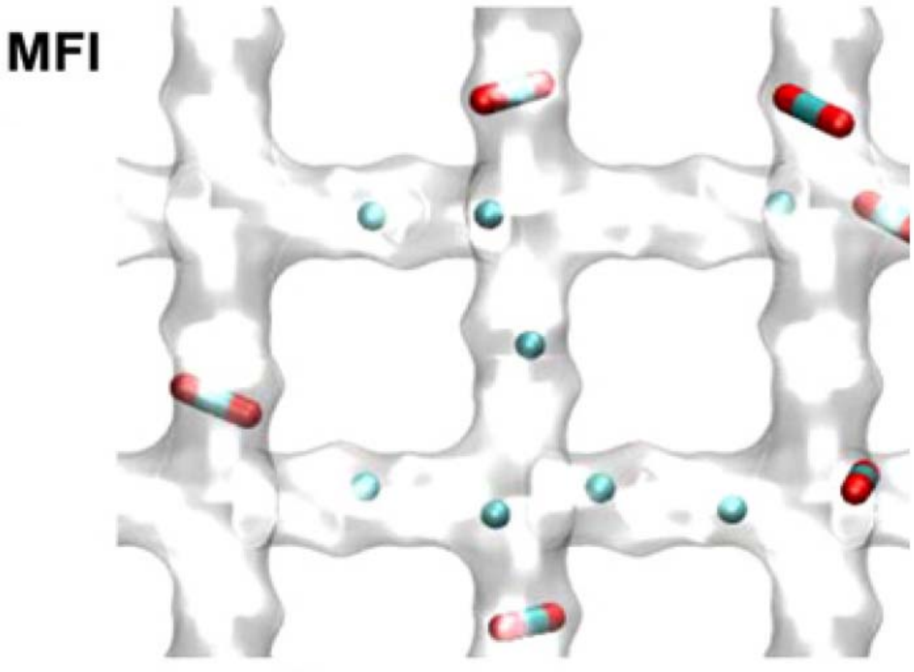


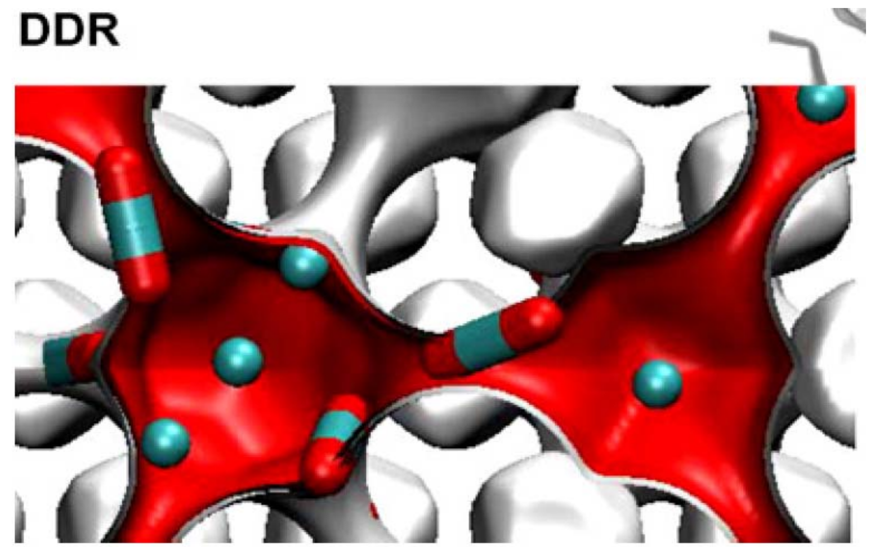
- Water-gas-shift reaction at one temperature (about 400°C)
- Two product streams: H_2 (>94% purity) and CO_2 (>97 purity)

Zeolite Membrane Requirements:

- Operated in 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

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





Intersecting channels

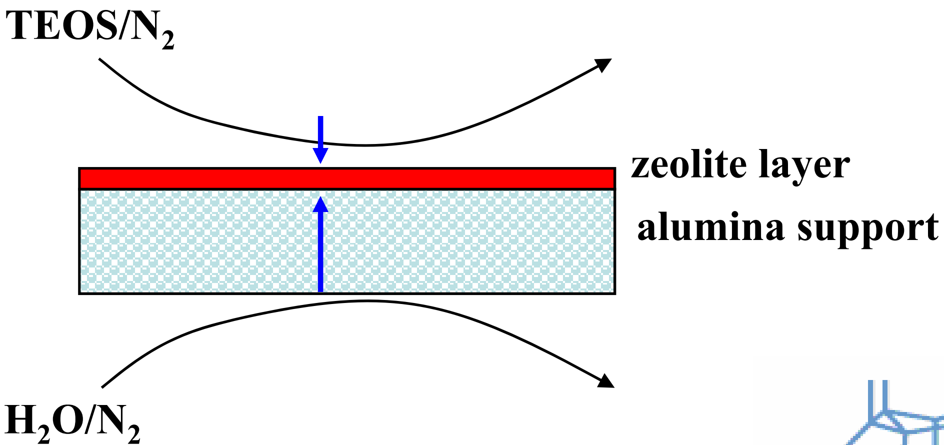
MFI (Silicalite): 10-T-Ring intersecting channels of 5.1-5.6 A in size

Cages separated by narrow windows

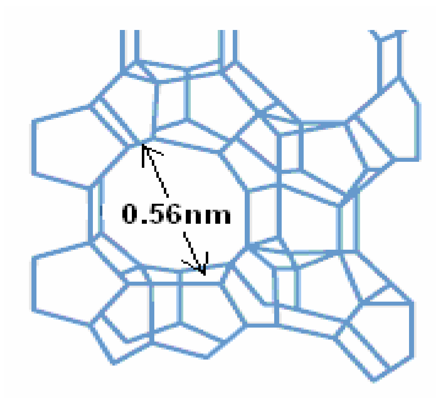
8-T-Ring, Windows of 3.6-4.4A in size in size (studied as a reference)

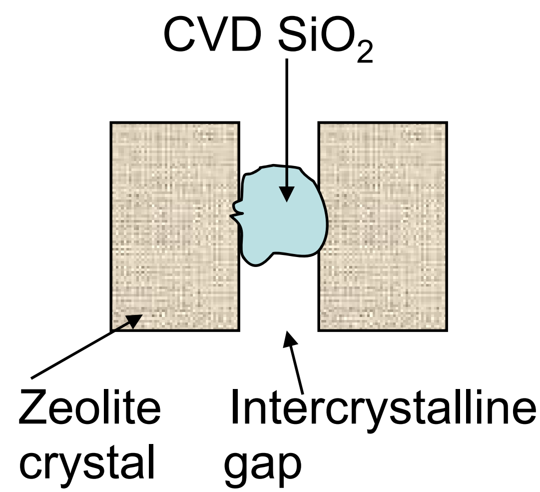
Figures from R. Krishna and J.M. van Baten, (2008)

Approach Counter-diffusion CVD of Silica for Improving Membrane Quality

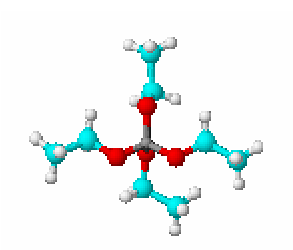


- **CVD reaction temp: 500°C,**
- **Bubbling temp: room temp.**

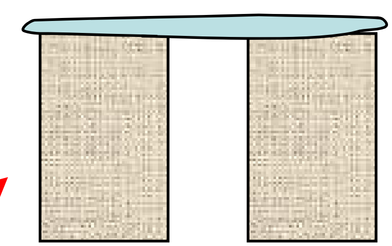




TEOS
0.95 nm

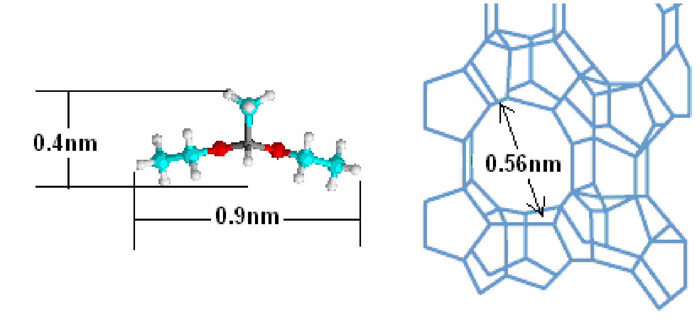


Hydrothermal stability test shows this is less likely the result of CVD



Approach – CVD Narrowing Zeolitc Pores to Further Improve Selectivity

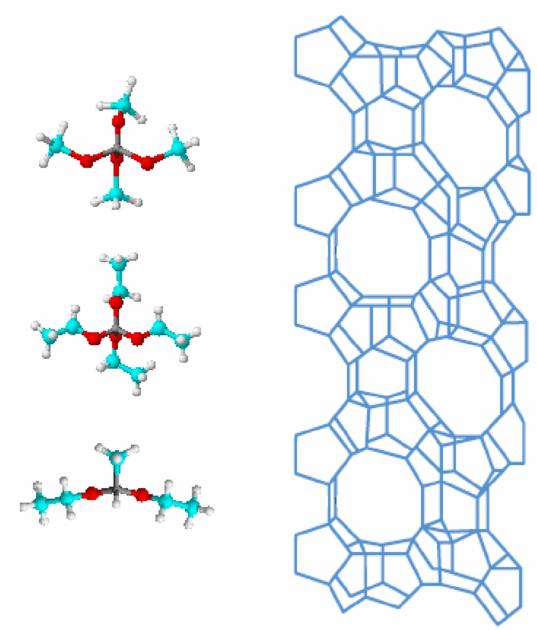
methyldiethoxysilane
(MDES)



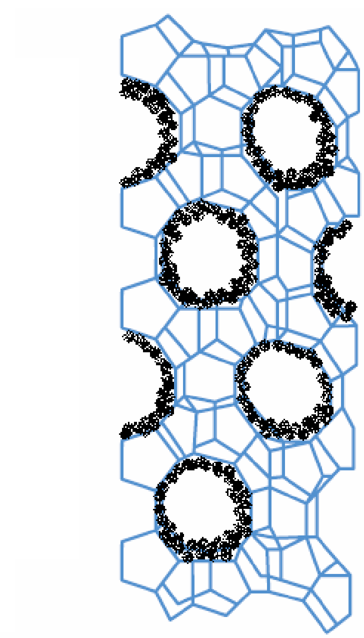
TMOS
0.89nm

TEOS
0.95nm

MDES
0.4 × 0.9nm



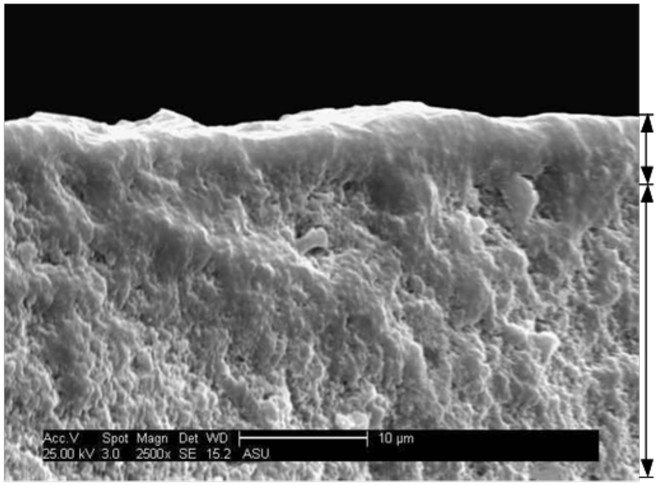
On stream
CVD



Previous Technical Accomplishments (Milestones Achieved)

- Obtain disk-shaped silicalite membranes on the desired intermediate layers with H_2/CO_2 perm-selectivity over 10 and H_2 permeance larger than $1\text{x}10^{-7}$ 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 much improved chemical stability SO_2 and H_2S containing WGS reaction stream
- 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 $1\text{x}10^{-7}$ mol/m^2.s.Pa
- Obtain disk and tubular silicalite membranes with H_2/CO_2 perm-selectivity over 50 and H_2 permeance larger than $2\text{x}10^{-7}$ mol/m^2.s.Pa

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



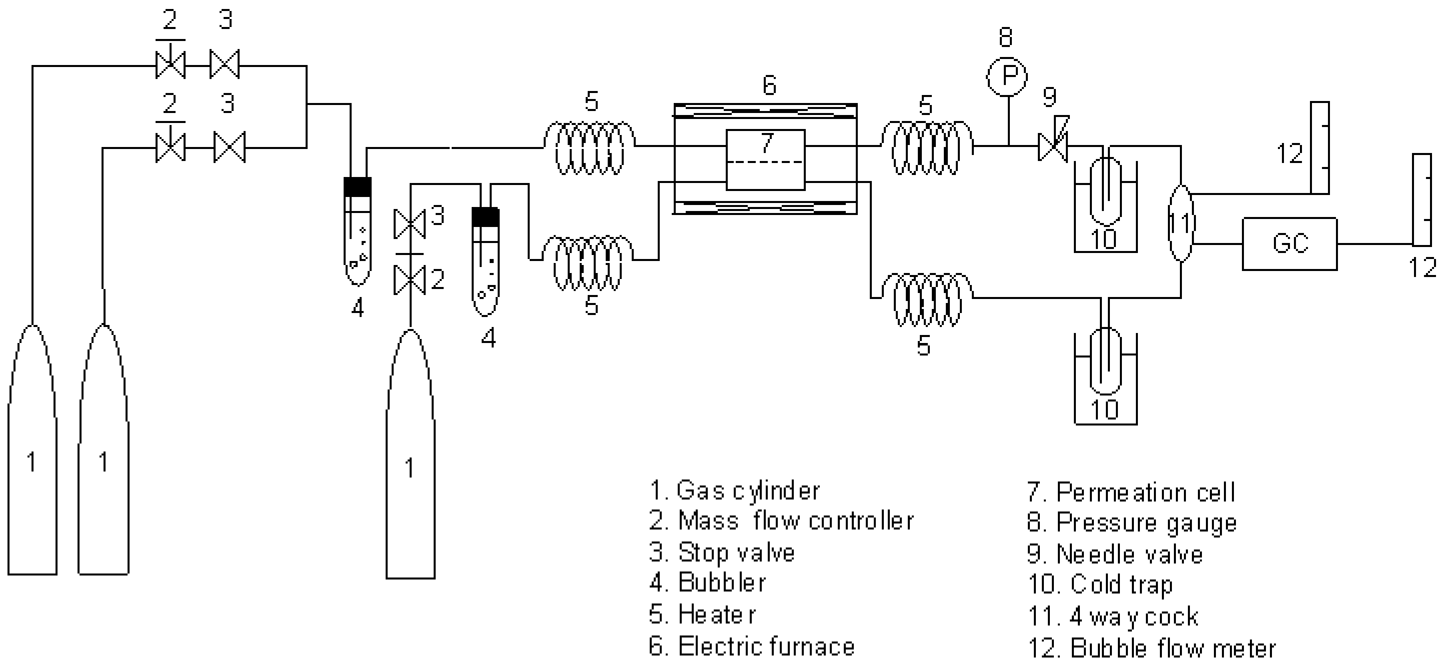
Zeolite layer (~5 μm)

α-alumina layer

P-xylene pervaporation flux ~ 1 kg/m^2.hr; p- to o-xylene (pervaporation) selectivity larger than 20

- Synthesized by 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

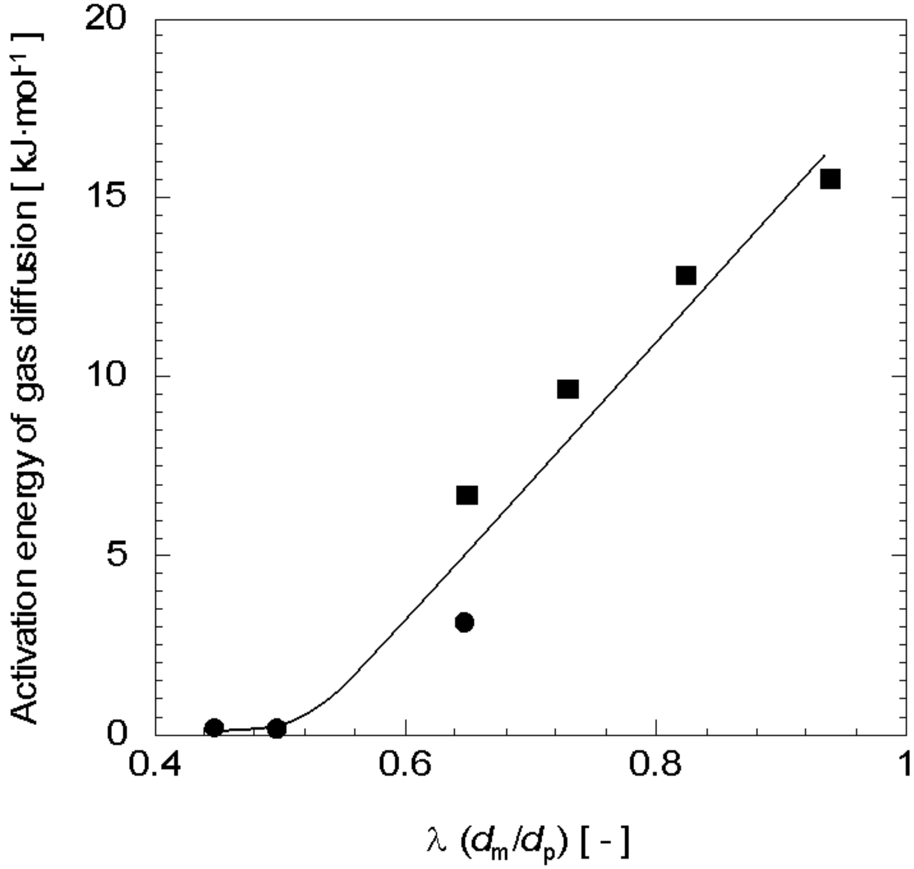
Technical Accomplishment - Gas Permeation/Separation Study

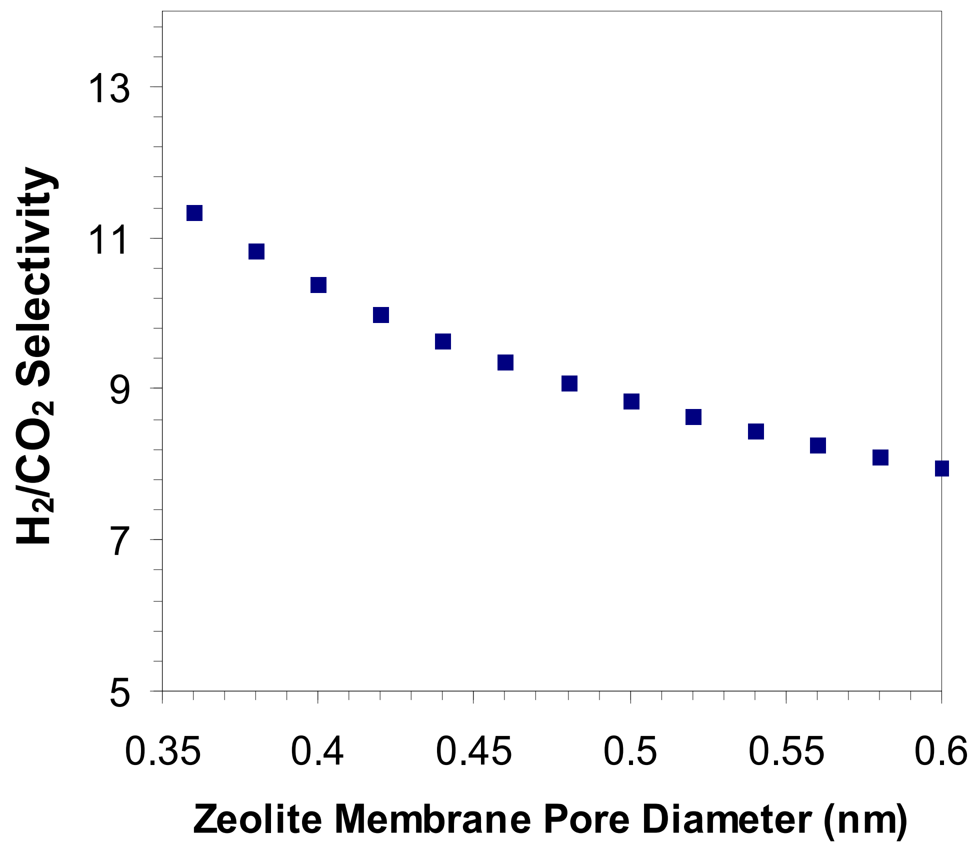


	He	H_2	CO_2	CO
Kinetic Diameter, d_m (nm)	0.26	0.289	0.33	0.376
L-J Length, σ_m (nm)	0.255	0.283	0.394	0.369
Molecular Weight, Mw (g/mol)	4	2	44	28

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

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

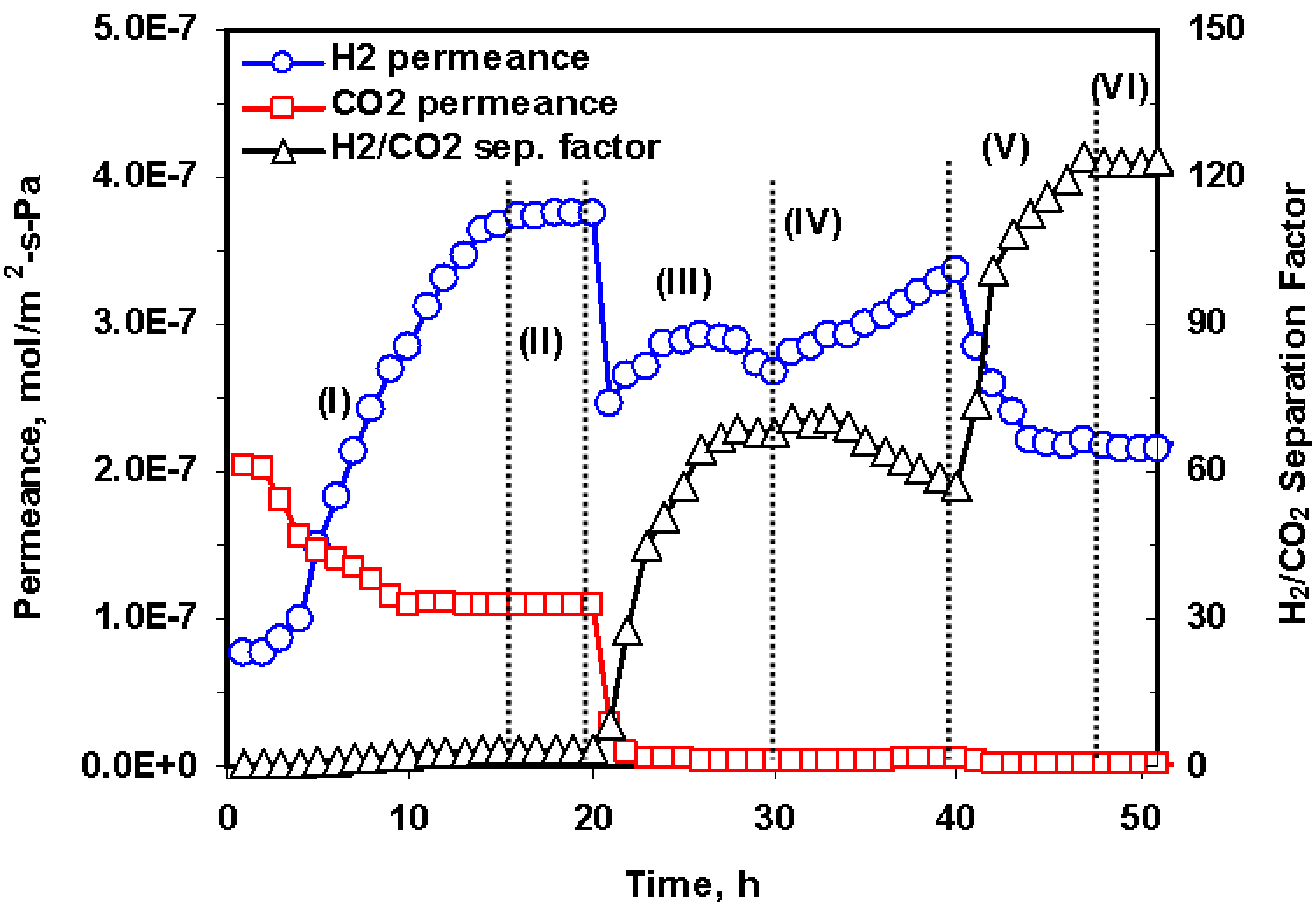




The maximum H_2/CO_2 selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.

Technical Accomplishment - CVD
Reduction of Zeolitic Pores

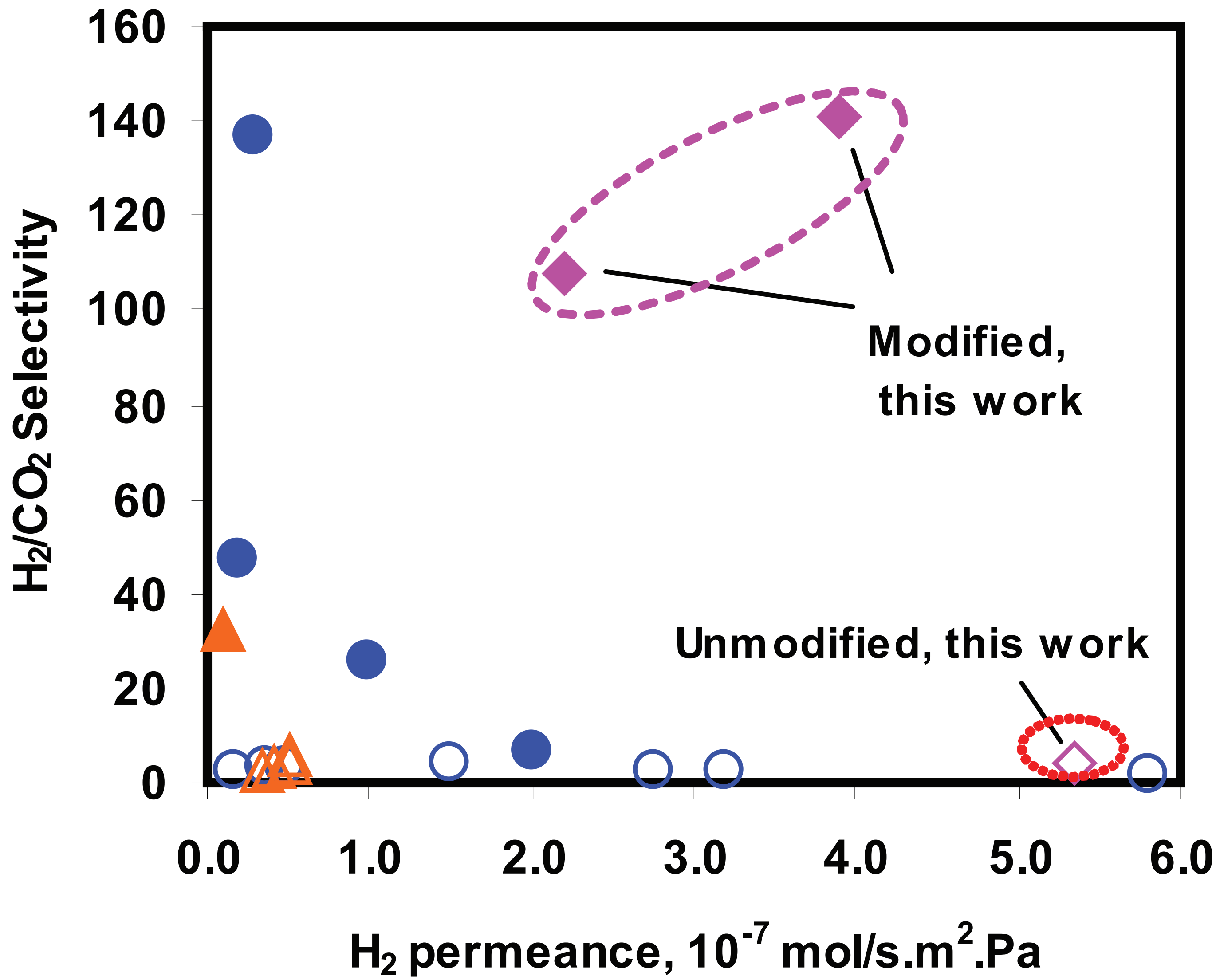
Online monitoring of H_2/CO_2 separation performance during the CCD modification on α-alumina-supported MFI membrane



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

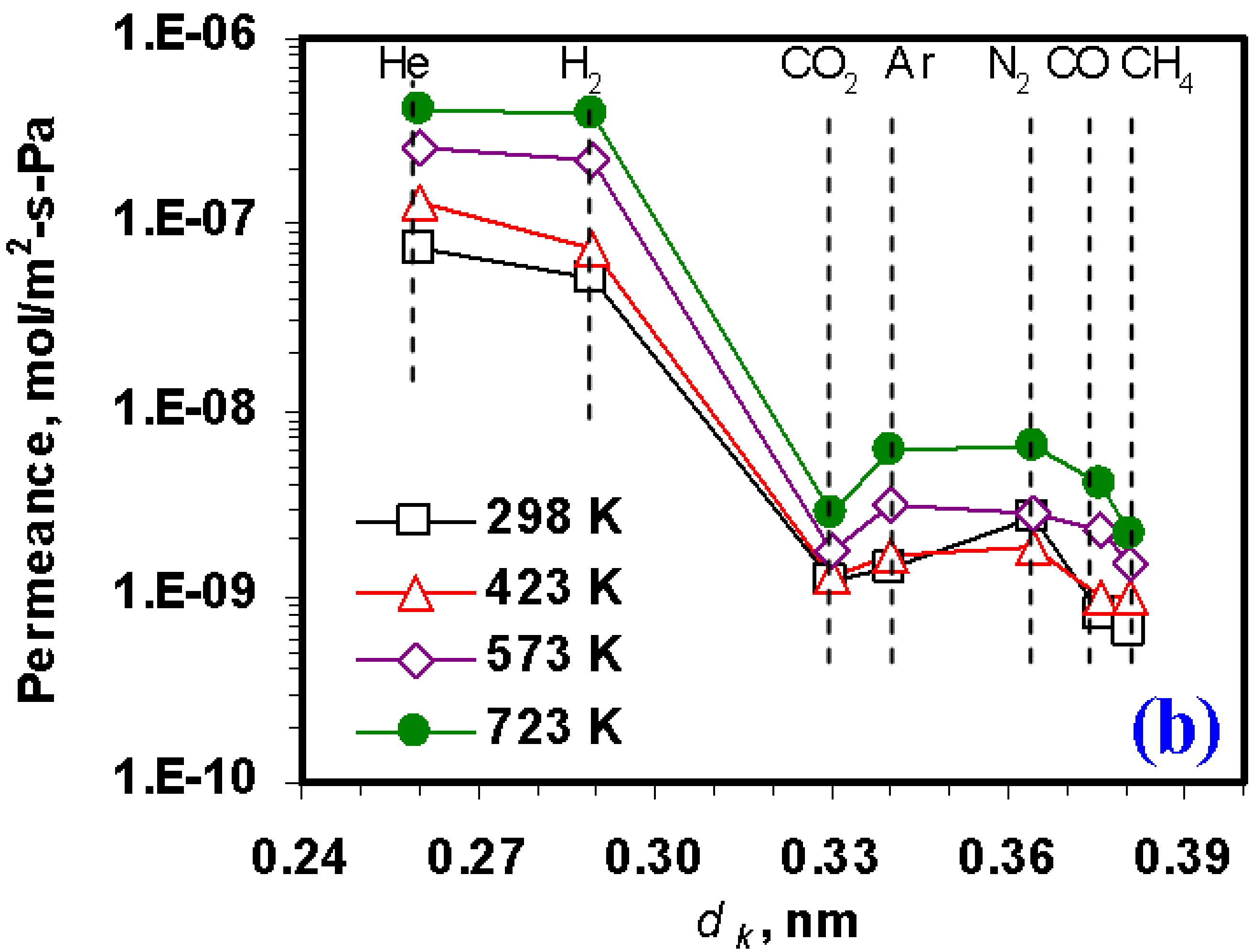
Technical Accomplishment: Zeolite Membrane with High H_2 Selectivity Selectivity

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



H_2/CO_2 selectivity of 140 and H_2 permeance about 4×10^{-7} mol/s.m^2.Pa at 450^{o}C

Technical Accomplishment: Gas Permeance at different Temperatures



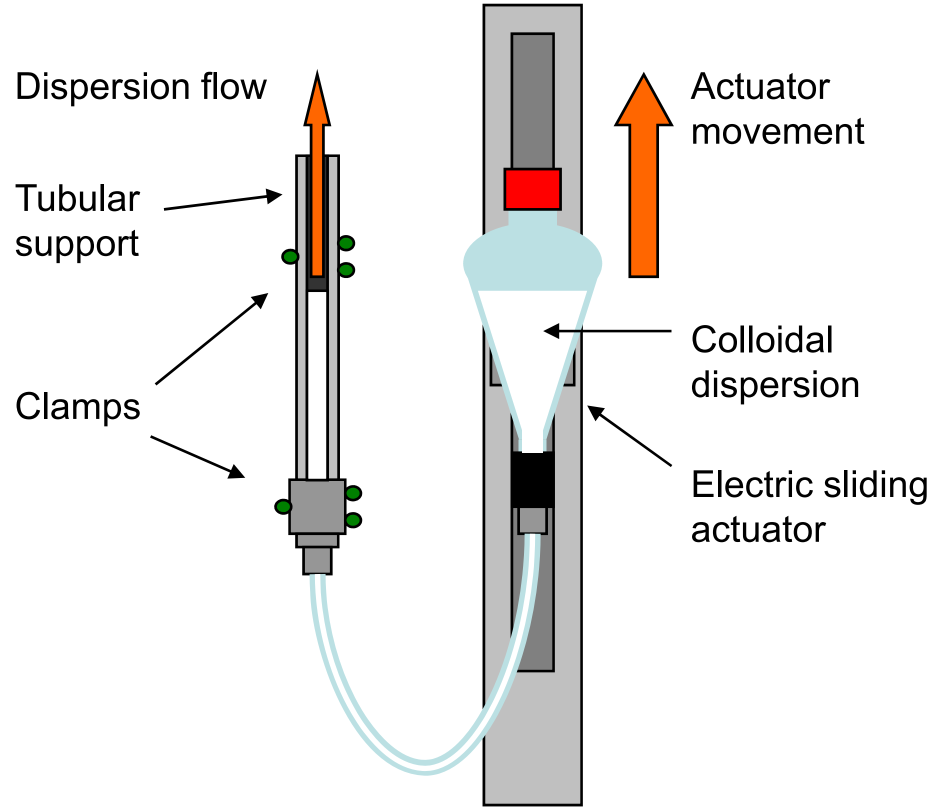
Modified zeolite membrane exhibits molecular sieving properties

Technical Accomplishment – High Quality Tubular Supports Developed

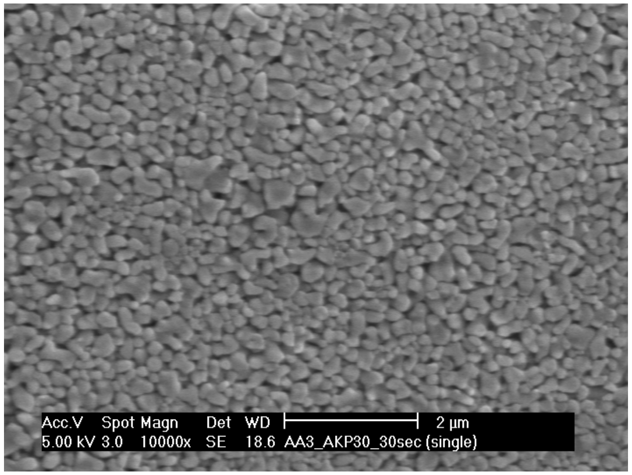
- Application of intermediate layers onto tubular supports by flow coating
  - AKP30 coating:

    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:

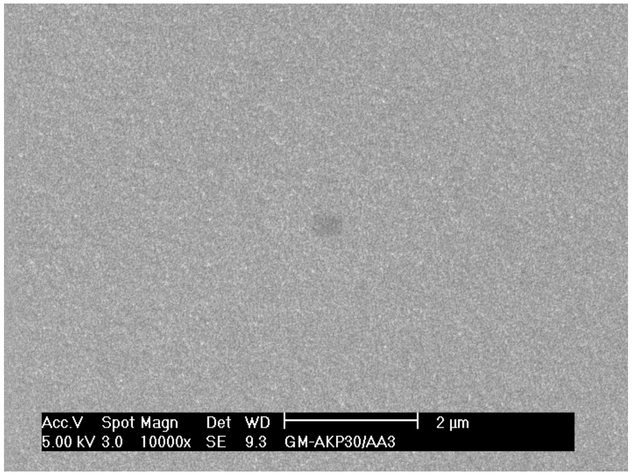
    γ-Al_2O_3 deposition onto AKP30-AA3 supports with Böhmiet sol [AlO(OH)] mixed with PVA (3:2 by vol.)



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



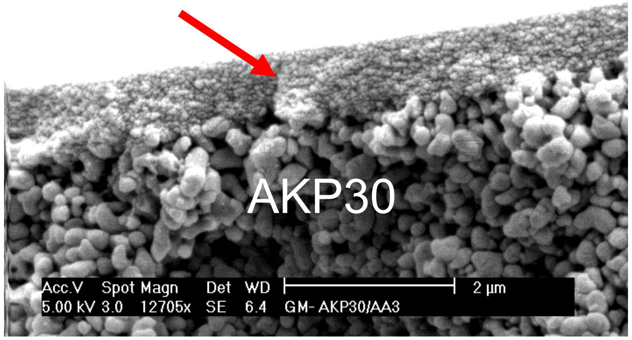
AKP30-AA3 (surface)

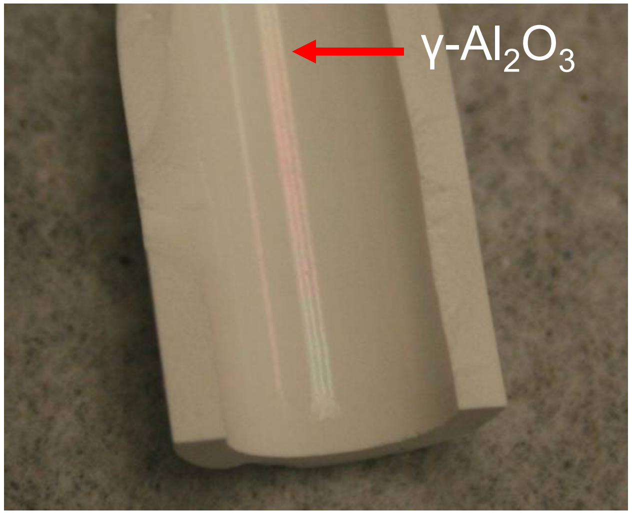


γ-Al_2O_3-AKP30-AA3 (surface)

~600 nm

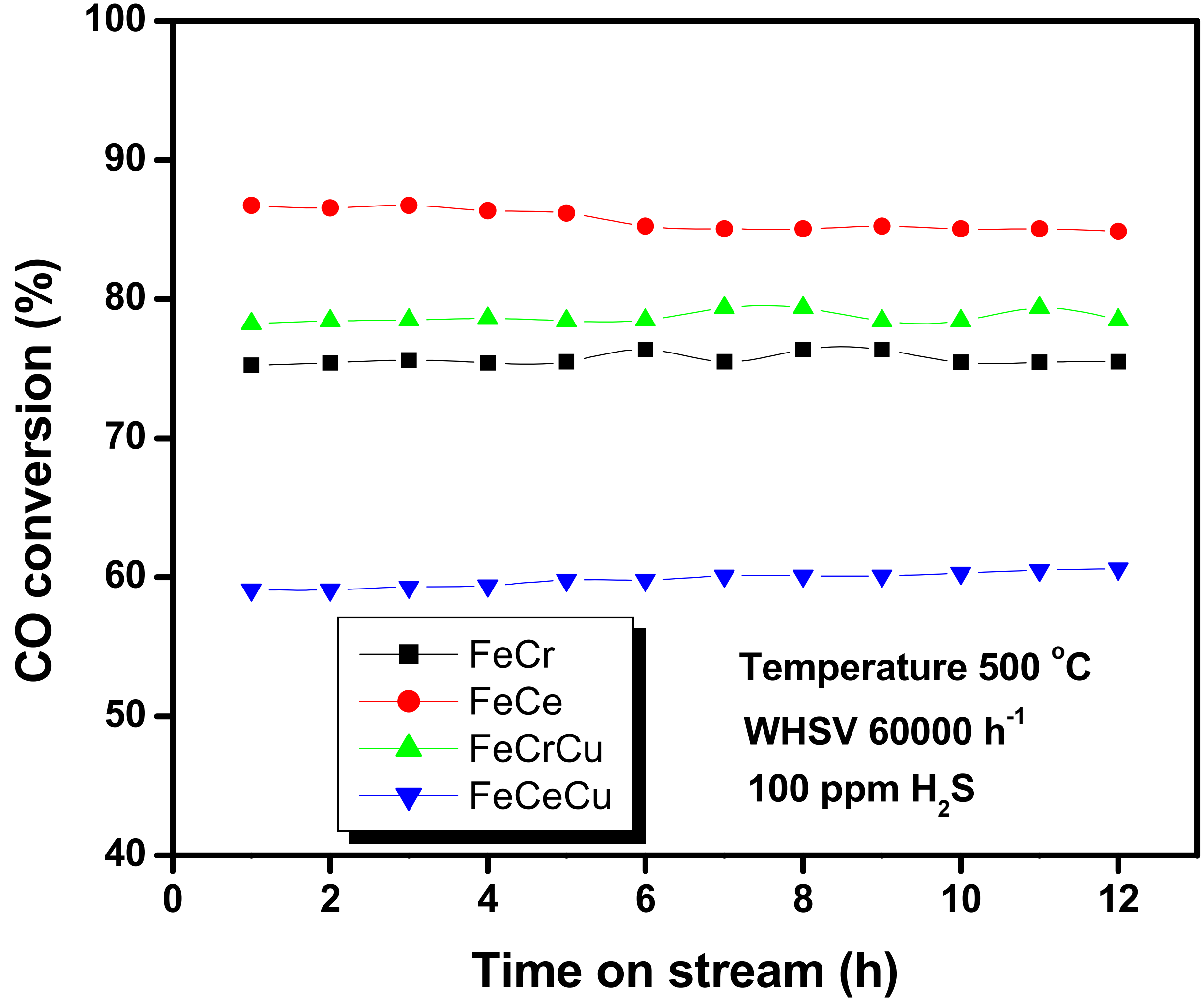
γ-Al_2O_3





Technical Accomplishment – Sulfur Resistant WGS Catalyst Developed (Cont'd)

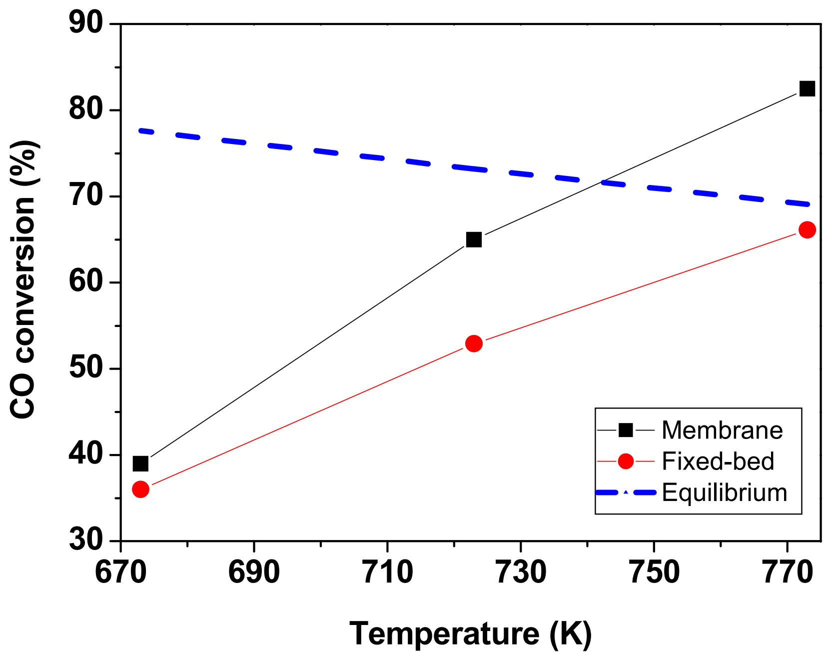
Effect of Time on stream on various modified ferrite catalysts in presence of H_2S



Sulfur Tolerant WGS Activity:

$Fe_{3-(x+y)}Cr_xCu_yO_4$ > Commercial > $Fe_{3-x}Ce_xO_4$ > $Fe_{3-x}Cr_xO_4$

Technical Accomplishment - Preliminary Test of WGS on Zeolite Membrane Reactor



CO conversion under H_2O/CO ratio of 1 and space velocity of 3500 h^{-1} in a disk-shaped silicalite membrane reactor with UC WGC catalyst – Membrane reactor gives higher CO yield

Tubluar WGS reactor also set up and tested; Zeolite membrane exhibit good hydrothermal stability under WGS reaction conditions for about 1 wk.

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 FY09 and FY10

1. Fabrication of high quality membrane supports for growing silicalite membranes (OSU)
    a) *Disk and tubular alumina supports*
    b) *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/ms.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 FY09 and FY10

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

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) *Experimental study on WGS reaction in silicalite membrane reactor*
    d) *Optimization of the performance of WGS reaction in the silicalite membrane reactor*
    e) *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 (>10^{-7} mol/m^2.s.Pa) and selectivity (>100) suitable for WGS membrane reactor application, and catalysts with improved properties for WGS reaction

- **Proposed Future Research**:

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