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

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Project ID: PD073

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Overview

Timeline

- Project start date:
  July 1, 2005
- Project end date:
  April 30, 2012
- 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 FY10: **$50,000**
- Funding for FY11: **$388,009**

Partners

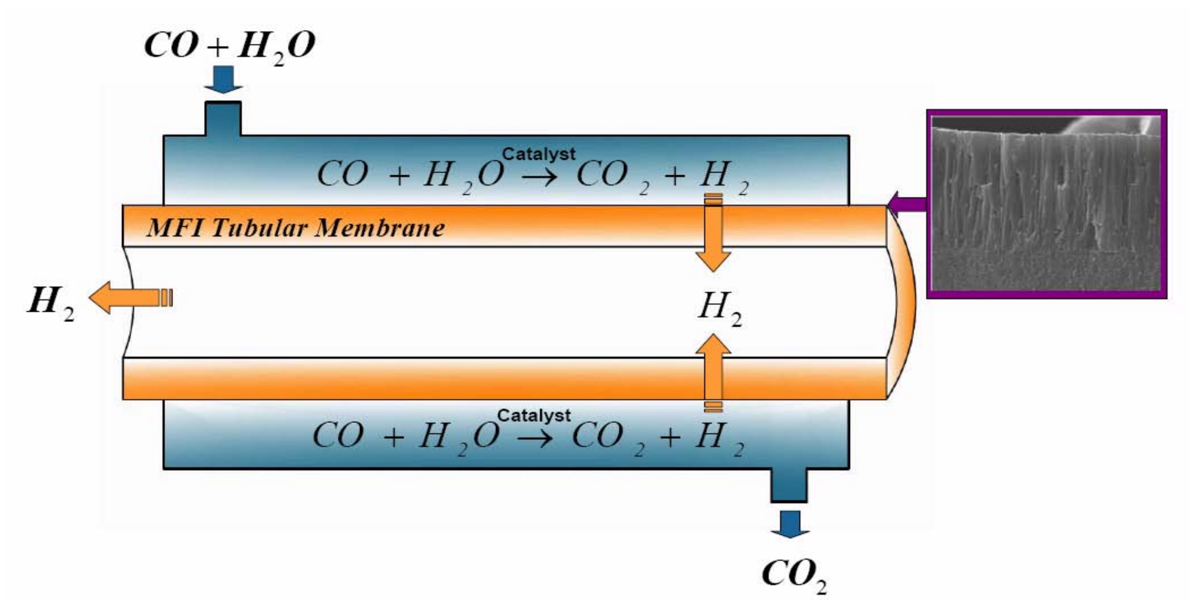
- University of Cincinnati
- Arizona State University
- Ohio State University

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*

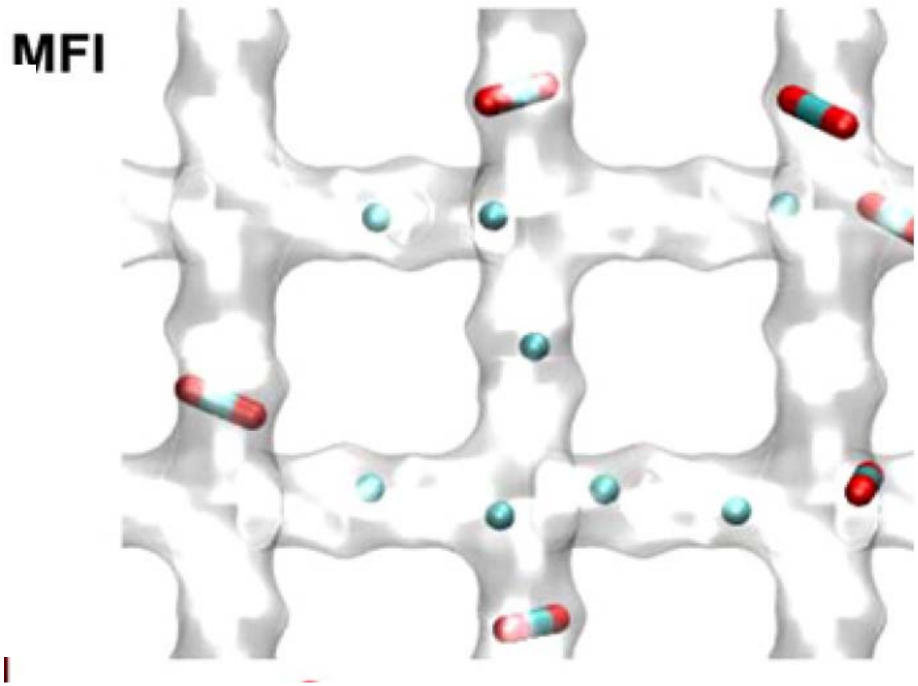
Approach – Zeolite Membrane Reactor for Water-Gas Shift Reaction



Zeolite Membrane Requirements:

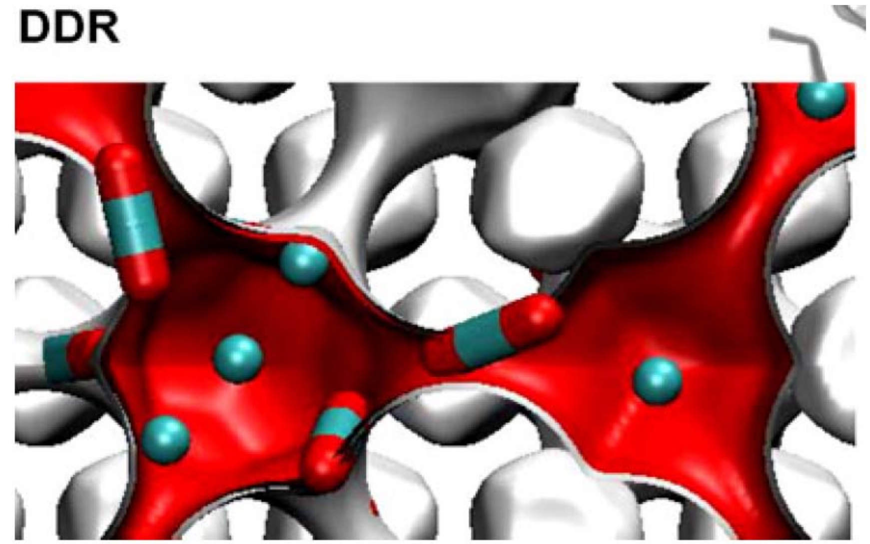
- Operate at 350-550°C
- Chemically stable in H_2S, thermally stable at ~400°C
- Hydrogen permeance ~ 5×10^{-7} mol/m^2.s.Pa
- Hydrogen selectivity ~ 50
- Two product streams: H_2 (>94% purity) and CO_2 (>97 purity)

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



Intersecting channels

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

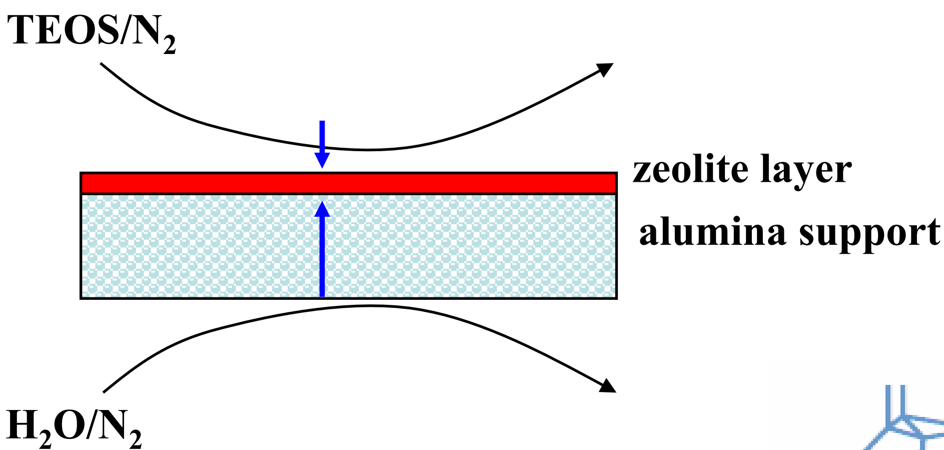


Cages separated by narrow windows

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

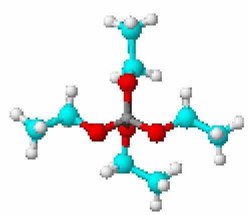
Figures from R. Krishna and J.M. van Baten, (2008)

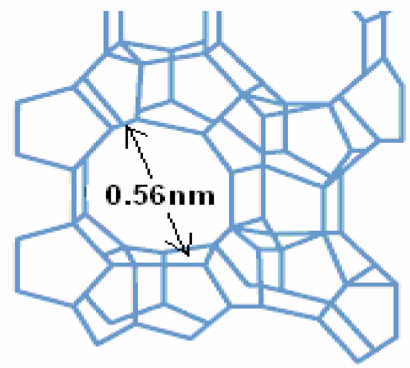
Approach – Counter-diffusion CVD of Silica for Improving Membrane Quality

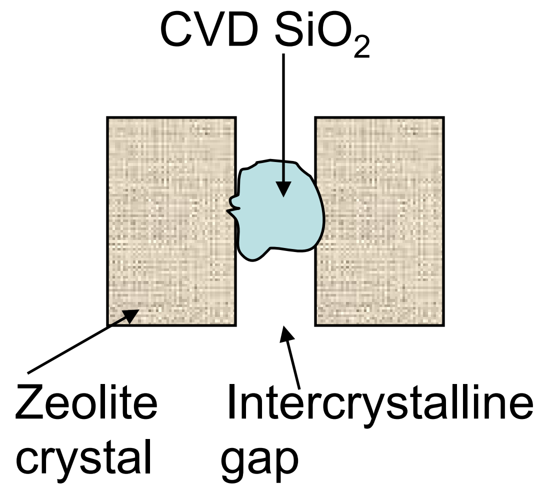


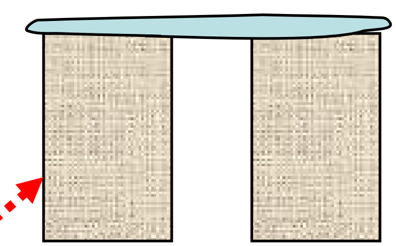
- **CVD reaction temp: 550°C,**
- **Bubbling temp: room temp.**

TEOS
0.95 nm





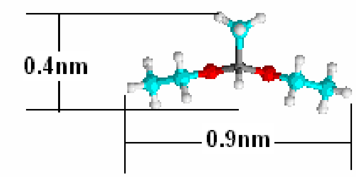


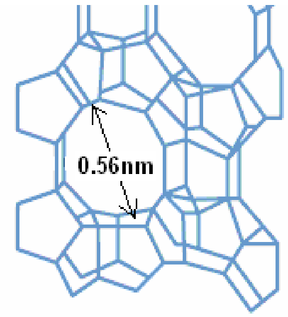


Hydrothermal stability test shows this is less likely the result of CVD

Approach – CVD Narrowing Zeolitic Pores to Further Improve Selectivity

methyldiethoxysilane
(MDES)

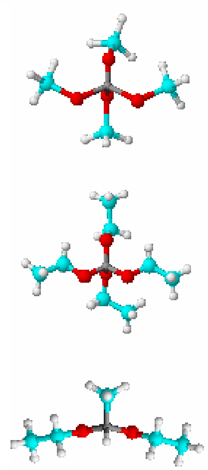


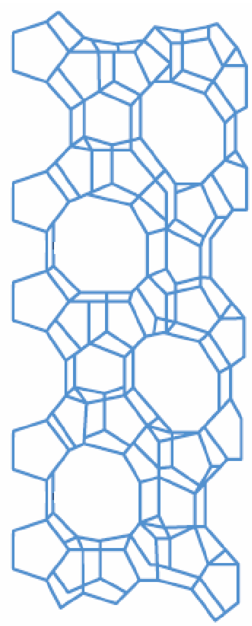


TMOS
0.89nm

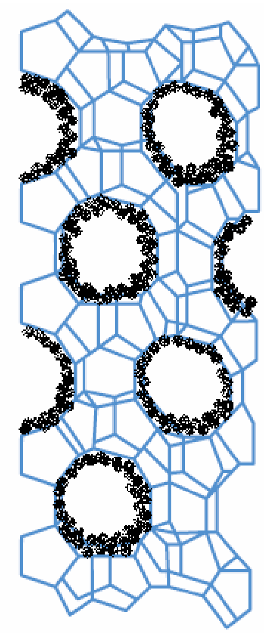
TEOS
0.95nm

MDES
0.4 × 0.9nm





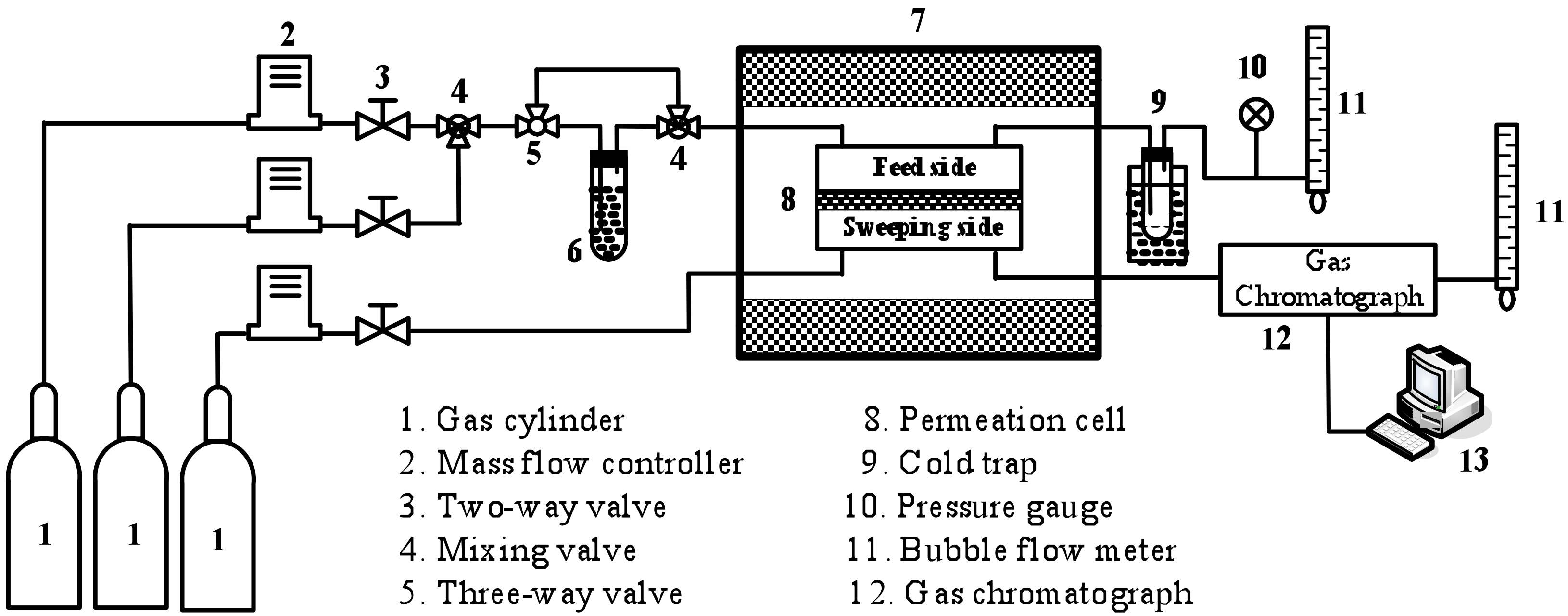
On stream
CVD



Previous Technical Accomplishments (Milestones Achieved)

- Obtain disk-shaped MFI zeolite membranes on the desired intermediate layers with H_2/CO_2 separation factor over 25 and H_2 permeance larger than $1x10^{-7}$ $mol/m^2.s.Pa$.
- Tubular membrane supports with desired intermediate barrier layers for stability improvement were developed.
- 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 – Gas Permeation/Separation and CVD Modification Study

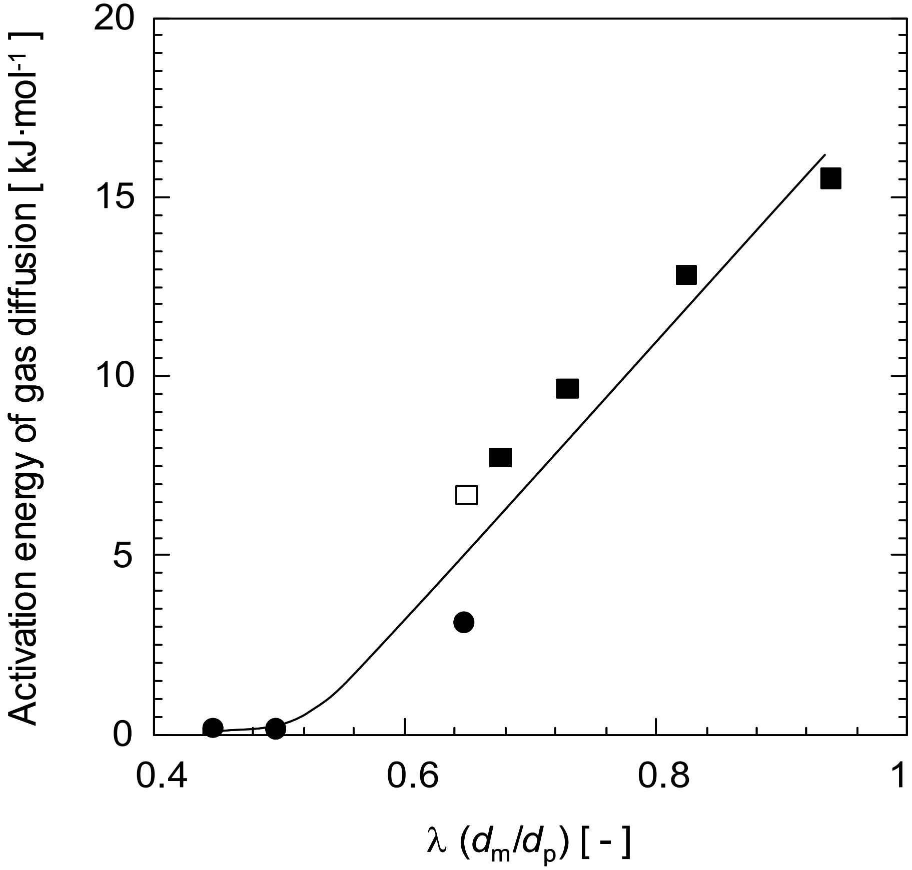


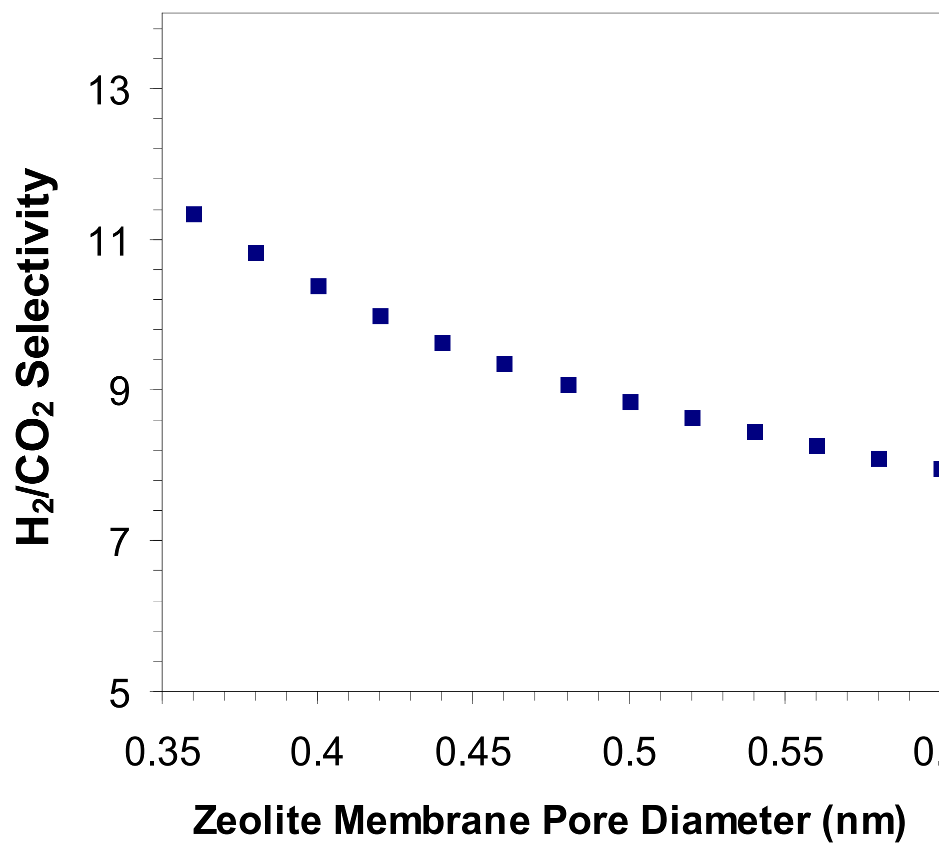
1. Gas cylinder
2. Mass flow controller
3. Two-way valve
4. Mixing valve
5. Three-way valve
6. Silane saturator
7. Box furnace
8. Permeation cell
9. Cold trap
10. Pressure gauge
11. Bubble flow meter
12. Gas chromatograph
13. Computer

	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

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

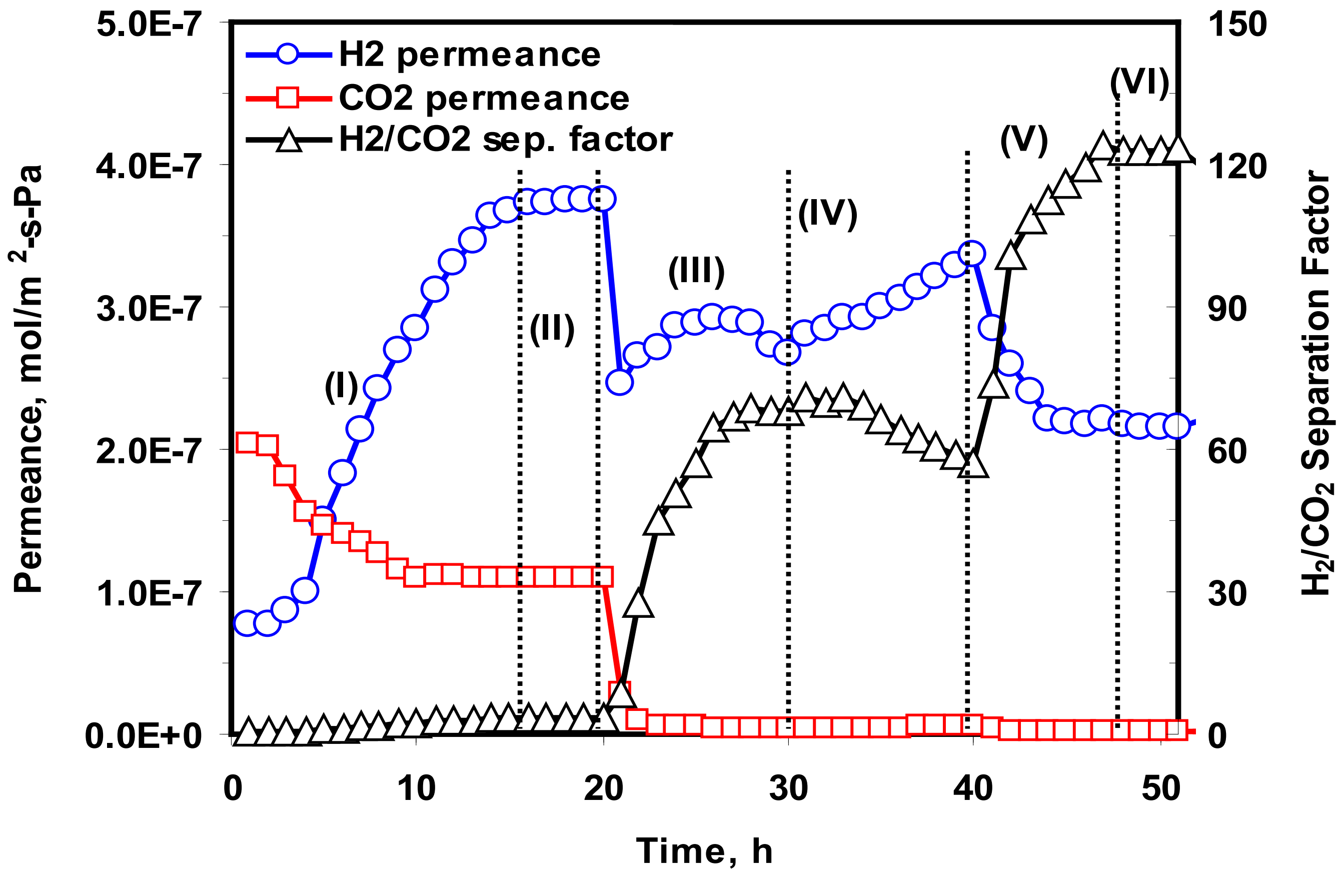




The maximum H_2/CO_2 selectivity offered by a perfect MFI or DDR zeolite membranes is about 12.

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

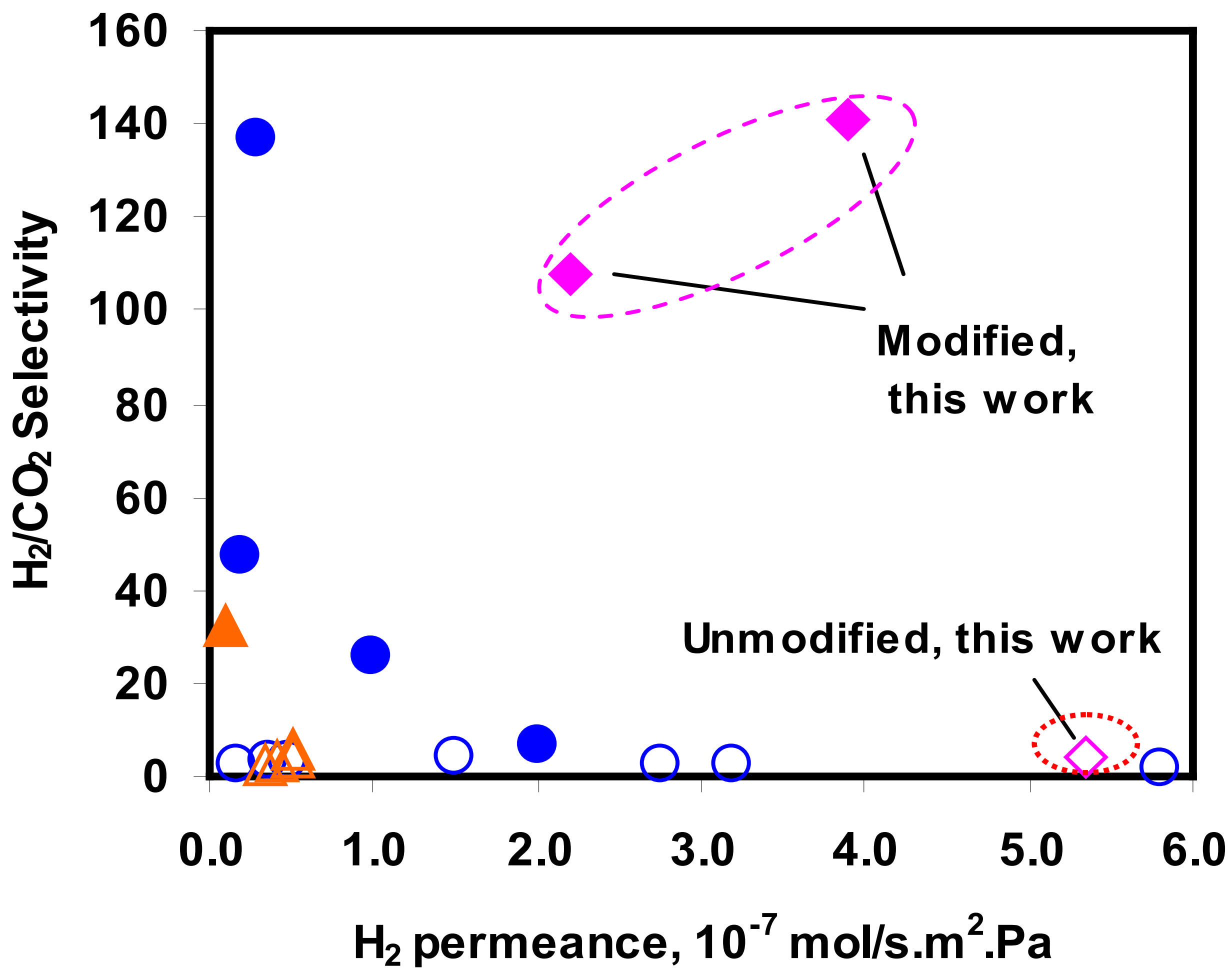
On-stream monitoring of H_2/CO_2 separation performance during the CCD modification on α-alumina-supported MFI tubular membrane



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

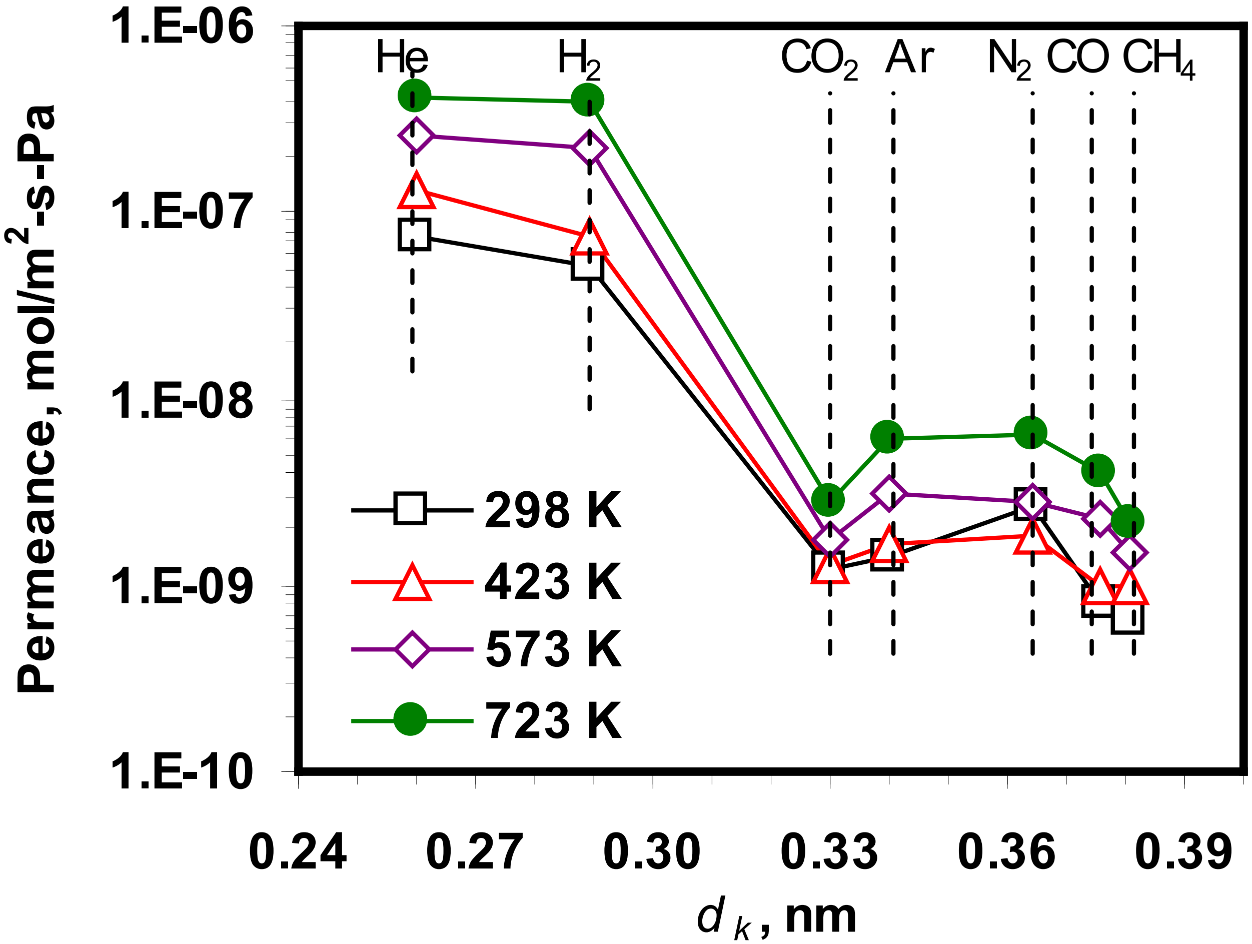
Technical Accomplishment – Zeolite Membrane with High H_2/CO_2 Perm-Selectivity

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



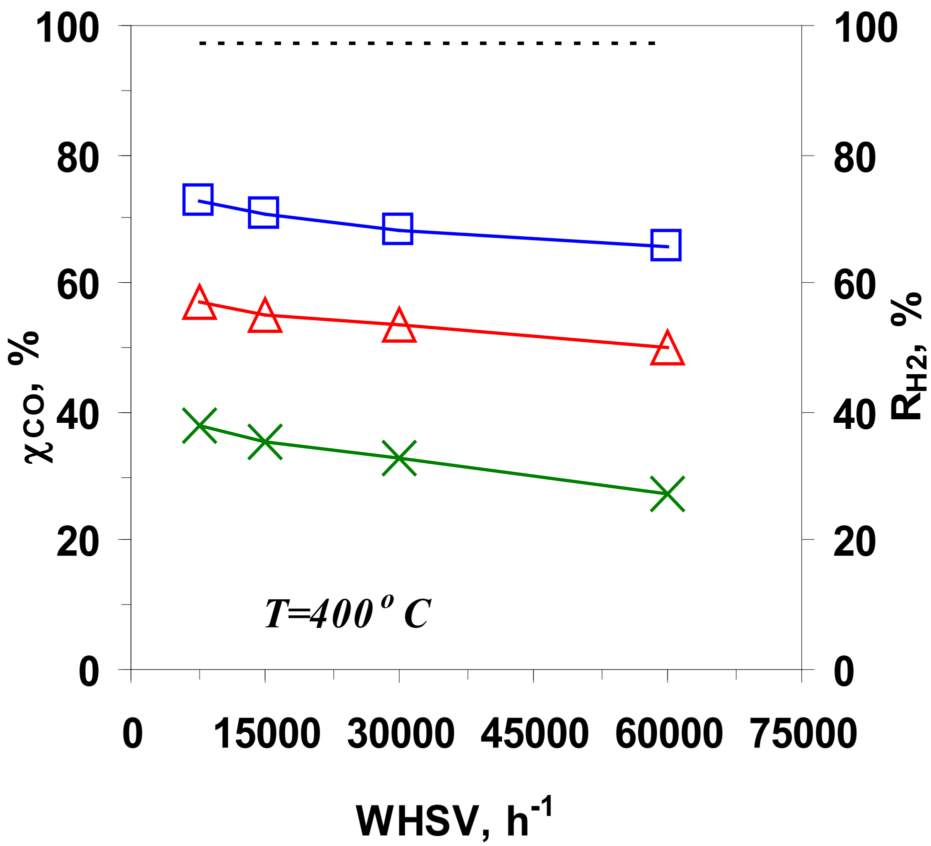
H_2/CO_2 perm-selectivity of 140 and H_2 permeance about 4×10^{-7} mol/s.m^2.Pa at 450^{o}C was obtained for the CVD modified membranes

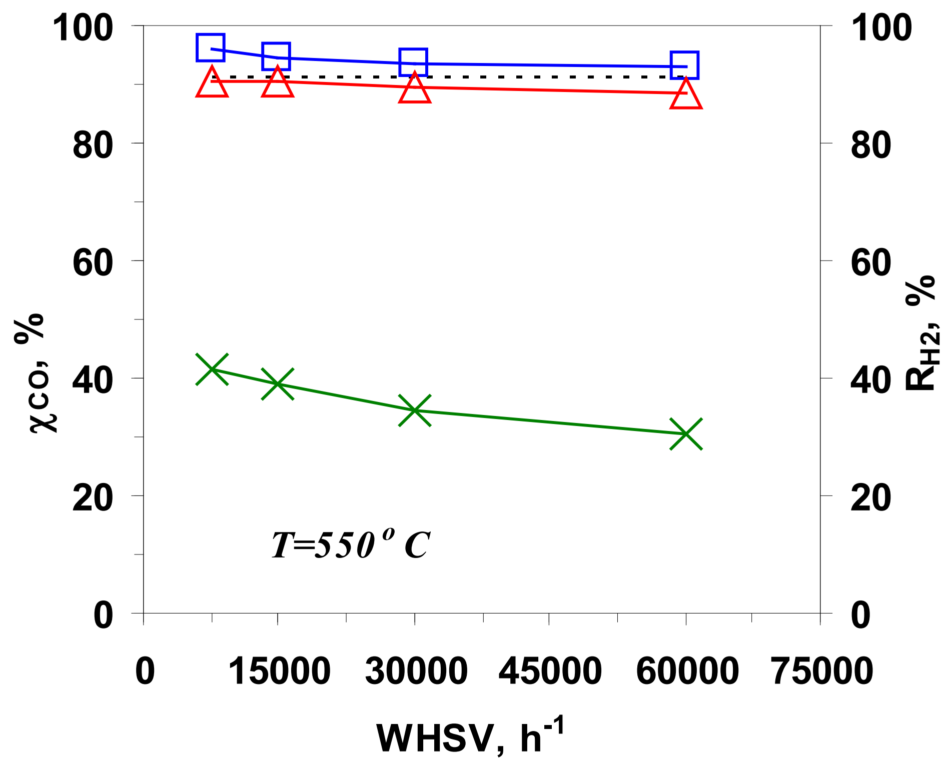
Technical Accomplishment – Single Gas Permeance of a CVD Modified Tubular Membrane at Different Temperatures



CVD modified tubular zeolite membrane exhibits molecular sieving properties

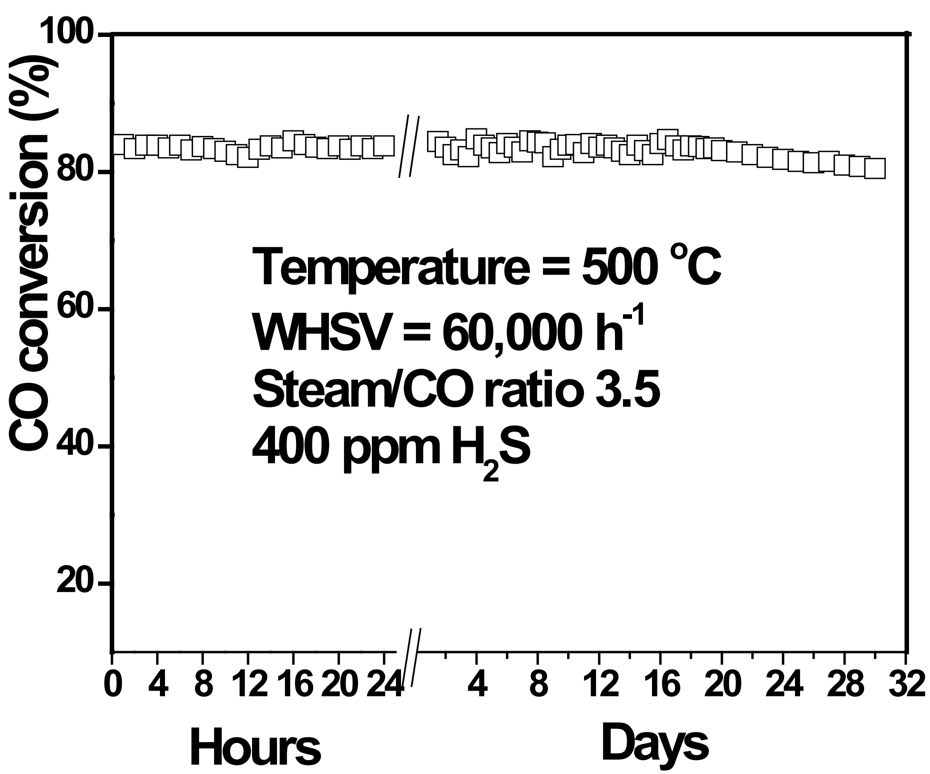
Technical Accomplishment – Water Gas Shift Reaction in a CVD Modified Tubular Membrane Reactor



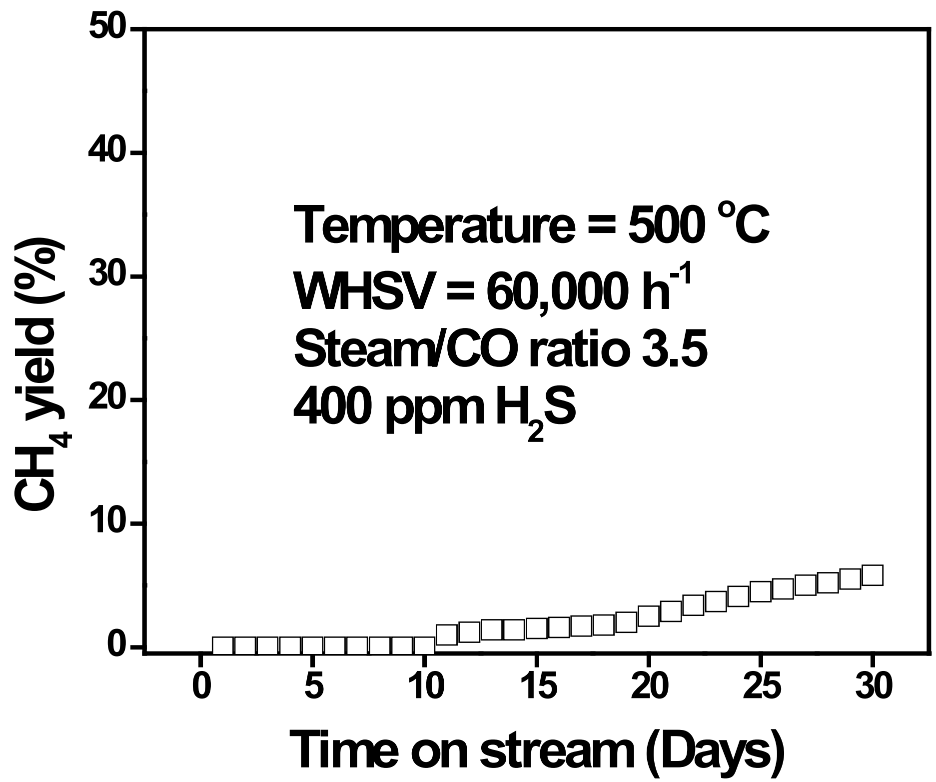


Effect of WHSV on CO-conversion and hydrogen recovery for a fixed $R_{H2O/CO}$ of 3.5: (---) Equilibrium conversion ($\chi_{CO,e}$); (□) Conversion in membrane reactor (χ_{CO}); (Δ) Conversion in traditional reactor (χ_{CO}); (×) H_2 recovery.

Technical Accomplishment – Stability Testing of Sulfur Resistant, High Temperature WGS Catalyst



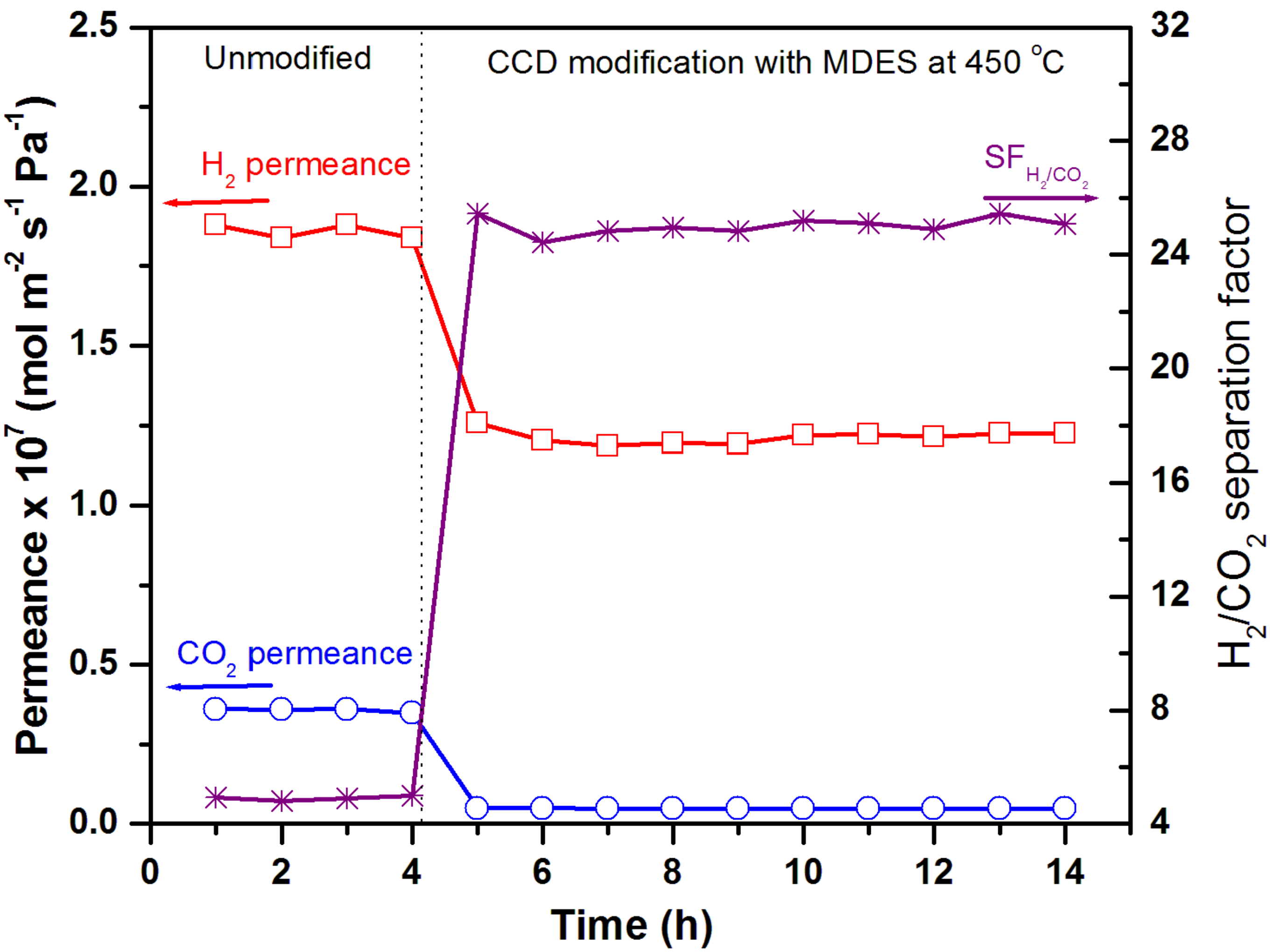
Long term time on stream stability experiments over Fe/Ce catalyst for 30 days in the presence of 400 ppm of sulfur



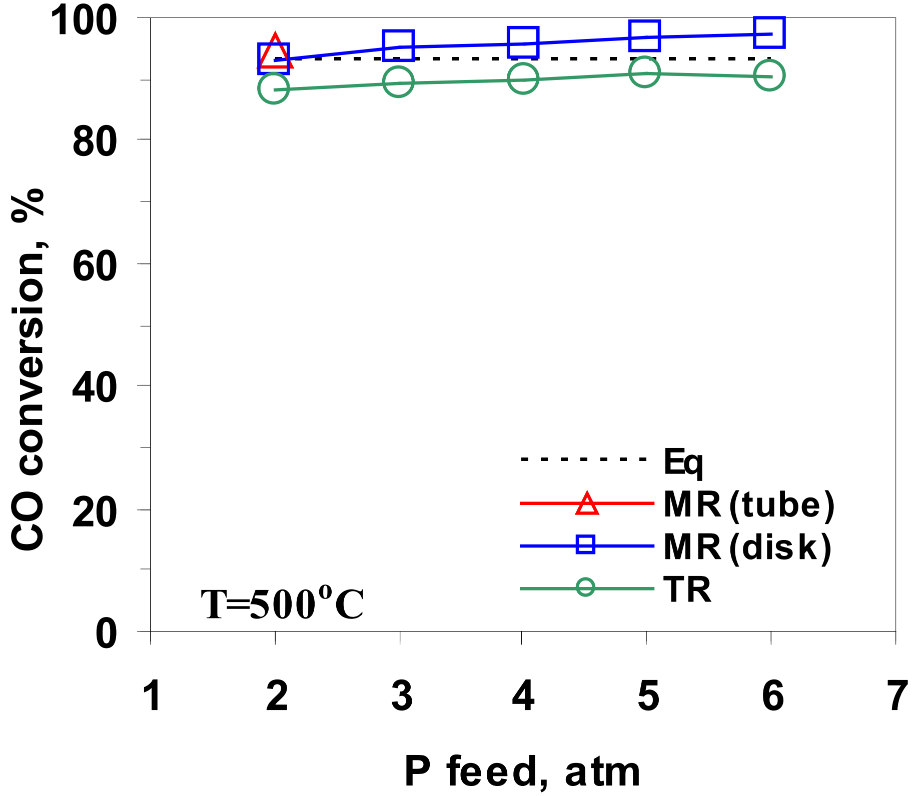
Methane yield formation during long term time on stream stability experiments over Fe/Ce catalyst for 30 days in the presence of 400 ppm of sulfur

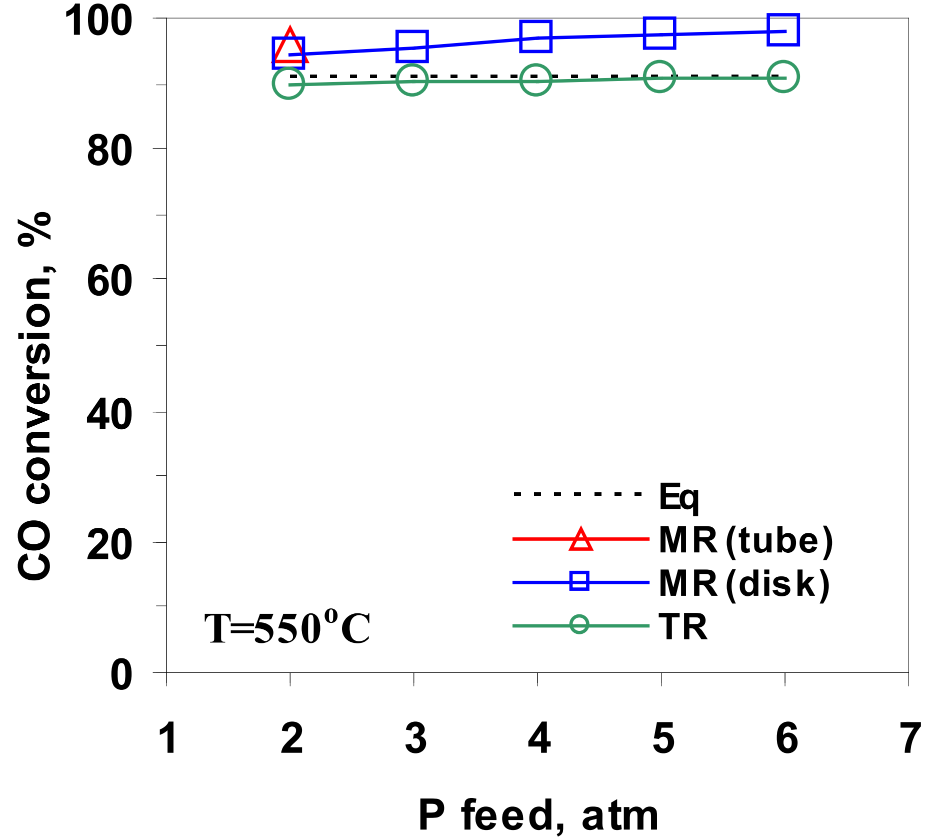
Stability testing of sulfur resistant catalyst was conducted in a traditional fixed bed reactor

Technical Accomplishment – CCD Modification of Disk MFI Zeolite Membrane with YSZ Barrier Layer



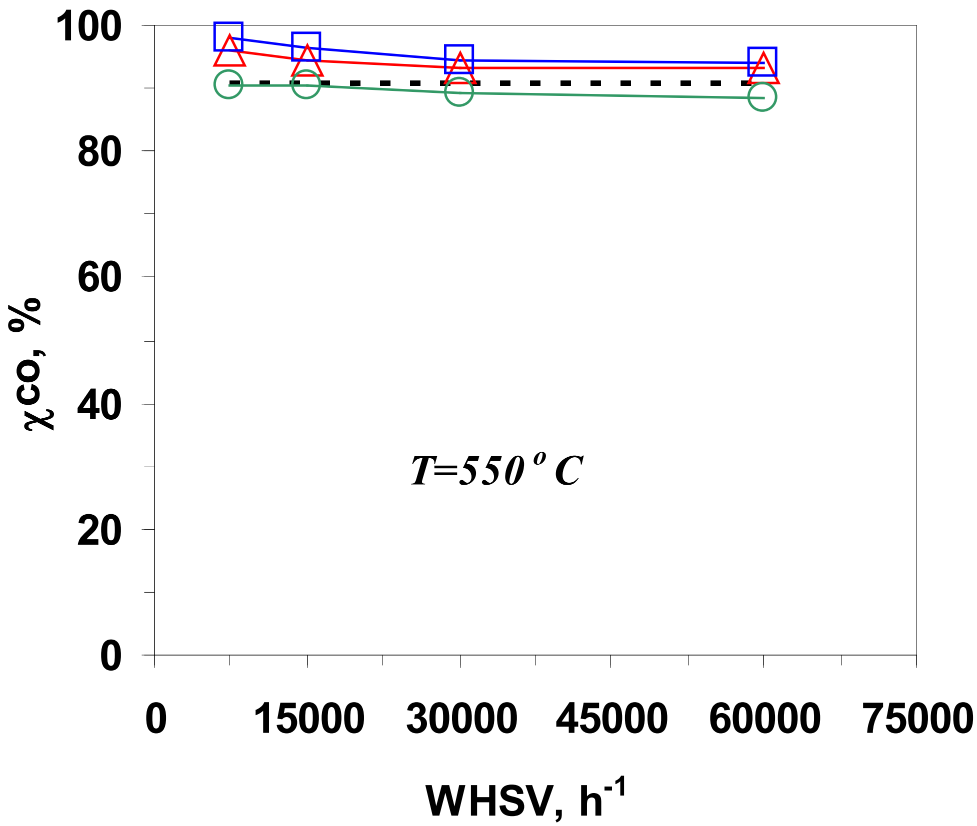
Technical Accomplishment – Water Gas Shift Reaction in a Modified Disk Membrane Reactor at Different Pressures



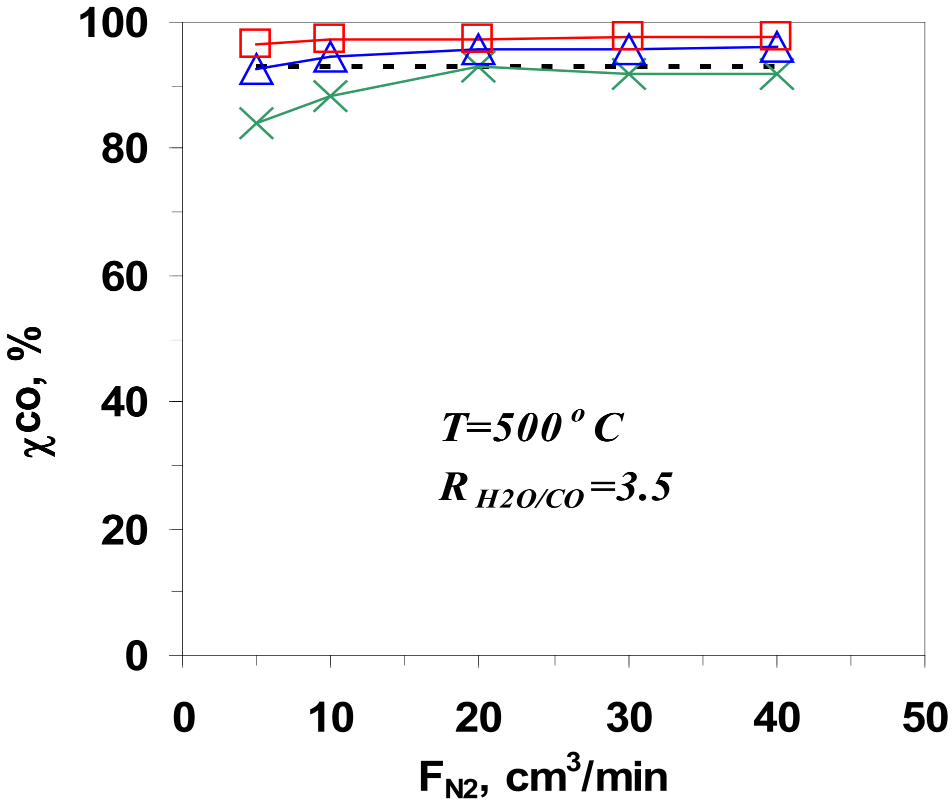


CO conversion for a fixed WHSV=7,500h^{-1} and various temperature of (a)400°C, (b)450°C, (c) 500°C and (d) 550°C: (---) equilibrium CO conversion; (Δ) CO conversion under feed pressure 1.5atm in tube MR of previous work; (□) CO conversion in disk MR; (o) CO conversion in TR.

Technical Accomplishment –Water Gas Shift Reaction in a Modified Membrane Disk Membrane at Different Conditions



Effect of WHSV on CO conversion for a fixed $R_{H2O/CO}$ of 3.5:
(---) equilibrium conversion;
(□) conversion in disc MR at P_{feed}=6atm;
(Δ) conversion in tube MR at P_{feed}=1.5atm;
(o) conversion in TR at P_{feed}=1.5atm.

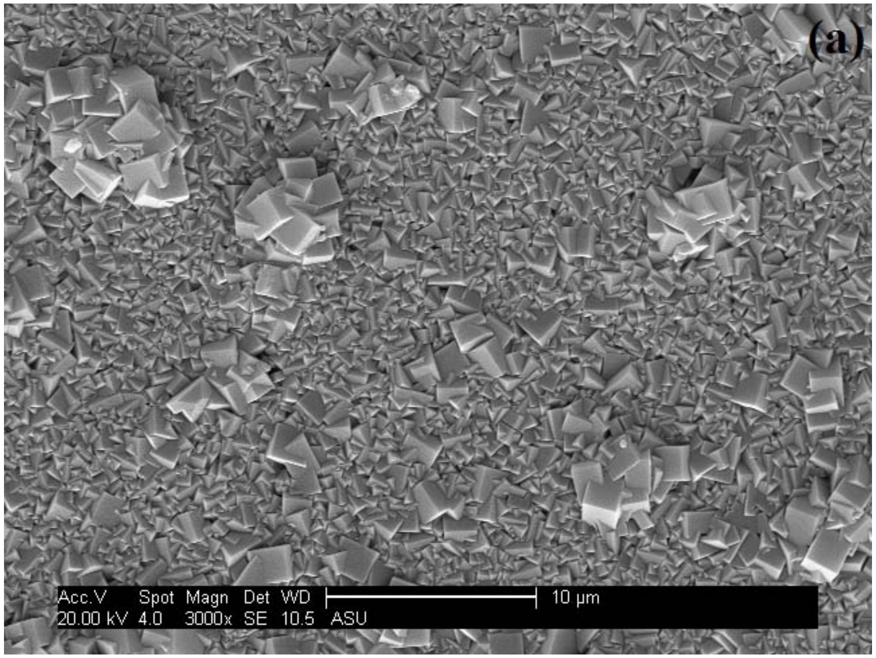


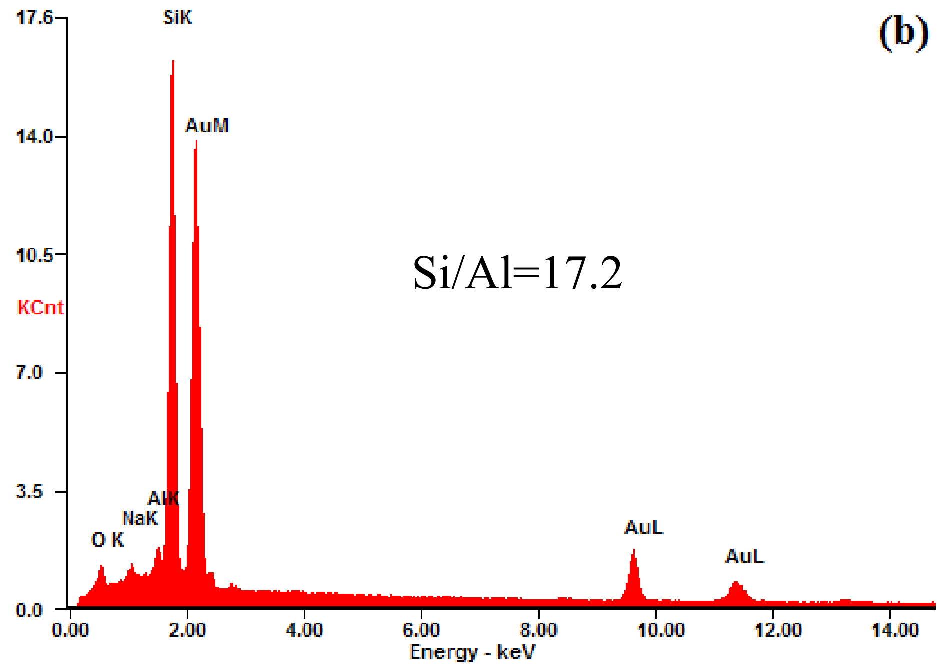
Effect of N_2 sweeping flow rate on CO-conversion for a fixed WHSV=7,500 h^{-1} and 500^oC:
(---) equilibrium conversion;
(×) conversion in disc MR at P_{feed}=2atm;
(Δ) conversion in disc MR at P_{feed}=4atm;
(□) conversion in disc MR at P_{feed}=6atm.

Long-Term Test for Alumina-Supported Modified MFI-Zeolite Membranes

Description	Operation T & P ranges	Time on stream (days)	Accumulative time on stream (days)	H_2/CO_2 perm-selectivity	H_2 permeance (*mol/s.m².Pa*)
Fresh	400 – 550°C 1 atm	NA	0	15	1.3 10^{-7}
After dry gas separation	400 – 550°C 1 atm	20	20	16	1.4 10^{-7}
After WGS	400 – 550°C 2 - 6 atm	110	130	12	0.9 10^{-7}
After WGS with H_2S	400 – 550°C 2 atm	50	180	11	0.8 10^{-7}
After WGS & Gas Sep.	400 – 550°C 2 atm	20	200	10	0.7 10^{-7}

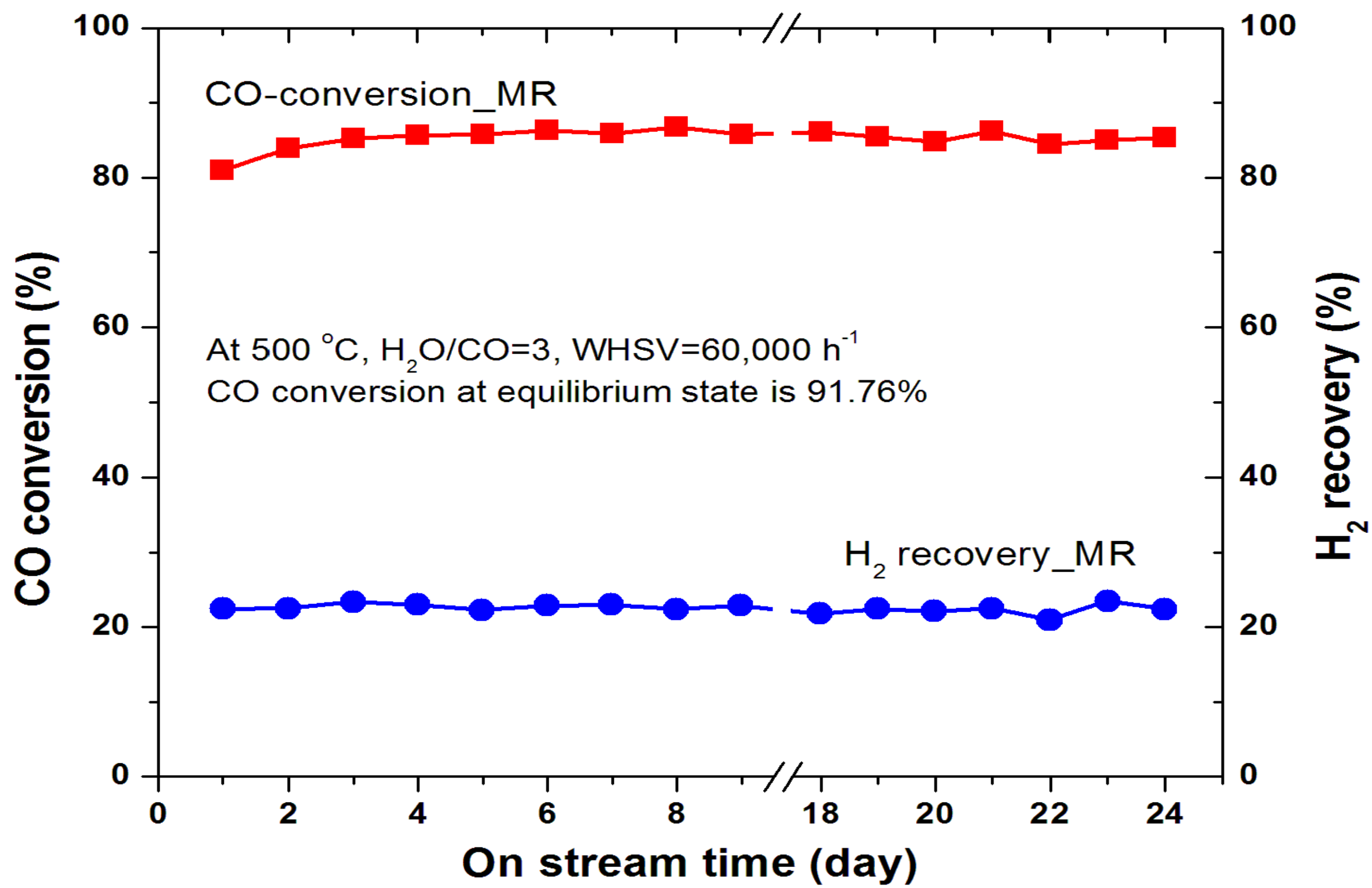
Technical Accomplishment – Synthesis of High Quality Disk MFI-Type Zeolite Membranes on YSZ Coated Alumina Porous Support



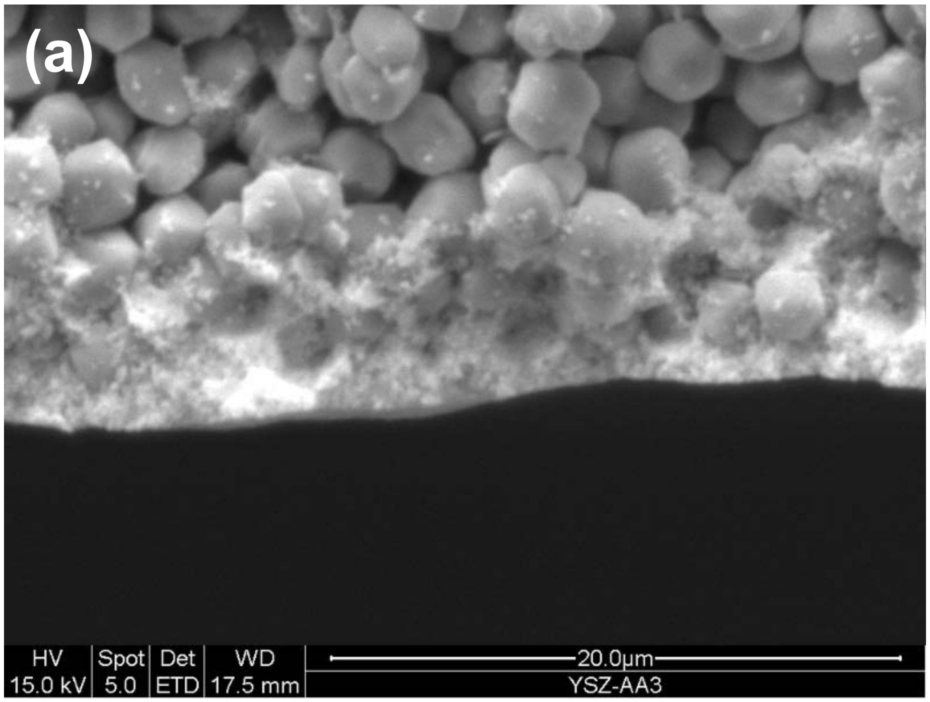


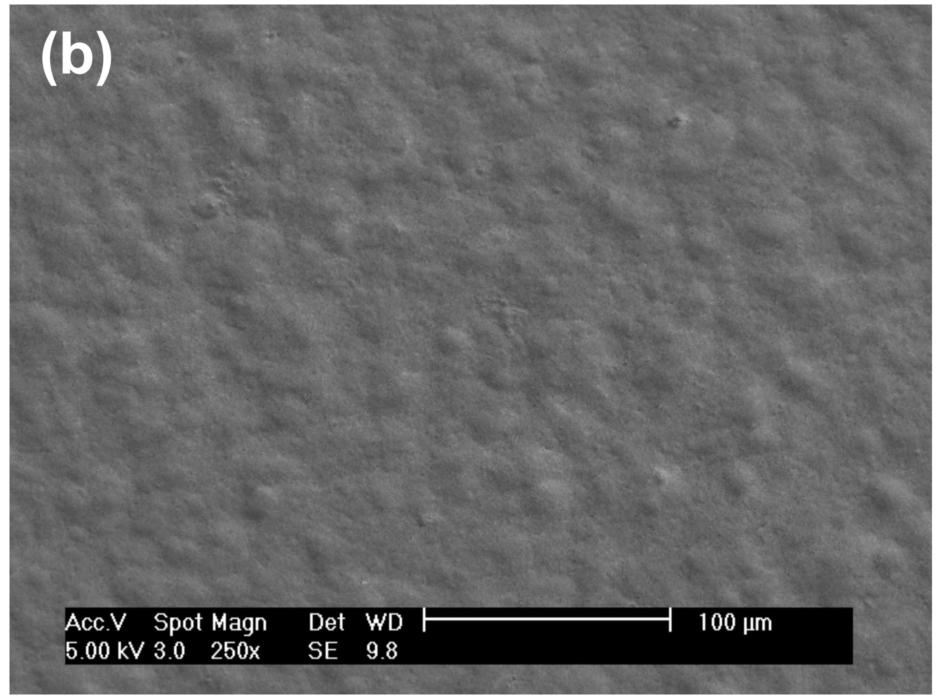
- Synthesized by a template-free secondary growth method to minimize intercrystalline gaps
- Post-CVD modification with TEOS to repair the defects
- Zeolite membranes can be prepared by microwave method
- Zeolite membranes are grown on YSZ intermediate layer to improve chemical stability

Technical Accomplishment – Stability Testing of MFI Zeolite Membrane with YSZ Barrier Layer under WGS Conditions



Technical Accomplishment – High Quality Tubular Supports with YSZ Barrier Layer for Stability Improvement





(a) SEM cross section of an YSZ-coated AA3 α-Al_2O_3 support, (b) SEM surface image of an YSZ-coated AA3 α-Al_2O_3 support.

MFI zeolite membrane will be synthesized on the tubular supports with YSZ barrier layer and subsequently modified for H_2/CO_2 separation factor improvement

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 FY11

1. Synthesis of high quality tubular silicalite membranes by secondary growth and CVD modification (UC, ASU)
   a) *H_2/CO_2 selectivity > 50, H_2 permeance > $3x10^{-7}$ mol/m^2.s.Pa*
   b) *Silicalite membranes on zirconia support with improved chemical stability*
2. Separation and stability study of silicalite membranes (ASU, UC)
   a) *Measuring single and mixture gas permeability and selectivity in larger temperature (200-500 ^oC) and pressure (1-10 atm) range.*
3. WGS reaction on silicalite membrane reactor (ASU, UC)
   a) *Improving membrane reactor system including setup (operatable up to 20 atm and 550^{o}C) and membrane module*
   b) *Optimization of the performance of WGS reaction in the silicalite membrane reactor*
   c) *Studying stability of the membrane reactor for WGS reaction under optimum conditions.*
4. 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 and stable operation with zeolite membrane reactor demonstrated.

- **Proposed Future Research**:

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