Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

Lie Meng and *Jerry Y.S. Lin**

Arizona State University

DOE Award:

DE-FE0026435

2018 NETL CO_2 Capture Technology Project Review Meeting

August 14, 2018, Pittsburgh, Penn

Overview

Timeline

- Project start date:
  Oct. 1, 2015
- Project end date:
  Jan. 31, 2019
- Budget Periods:
  I: 10/1/2015-7/30/2017
  II: 8/1/2017-1/31/2019

Budget

- Total project funding
  - DOE **$2,760,797**
  - Cost-share: **$689,963**
  - Total**: $3,450,760**

Research Area

2B2: Bench-Scale Pre-Combustion CO_2 Capture Development and Testing

Partners

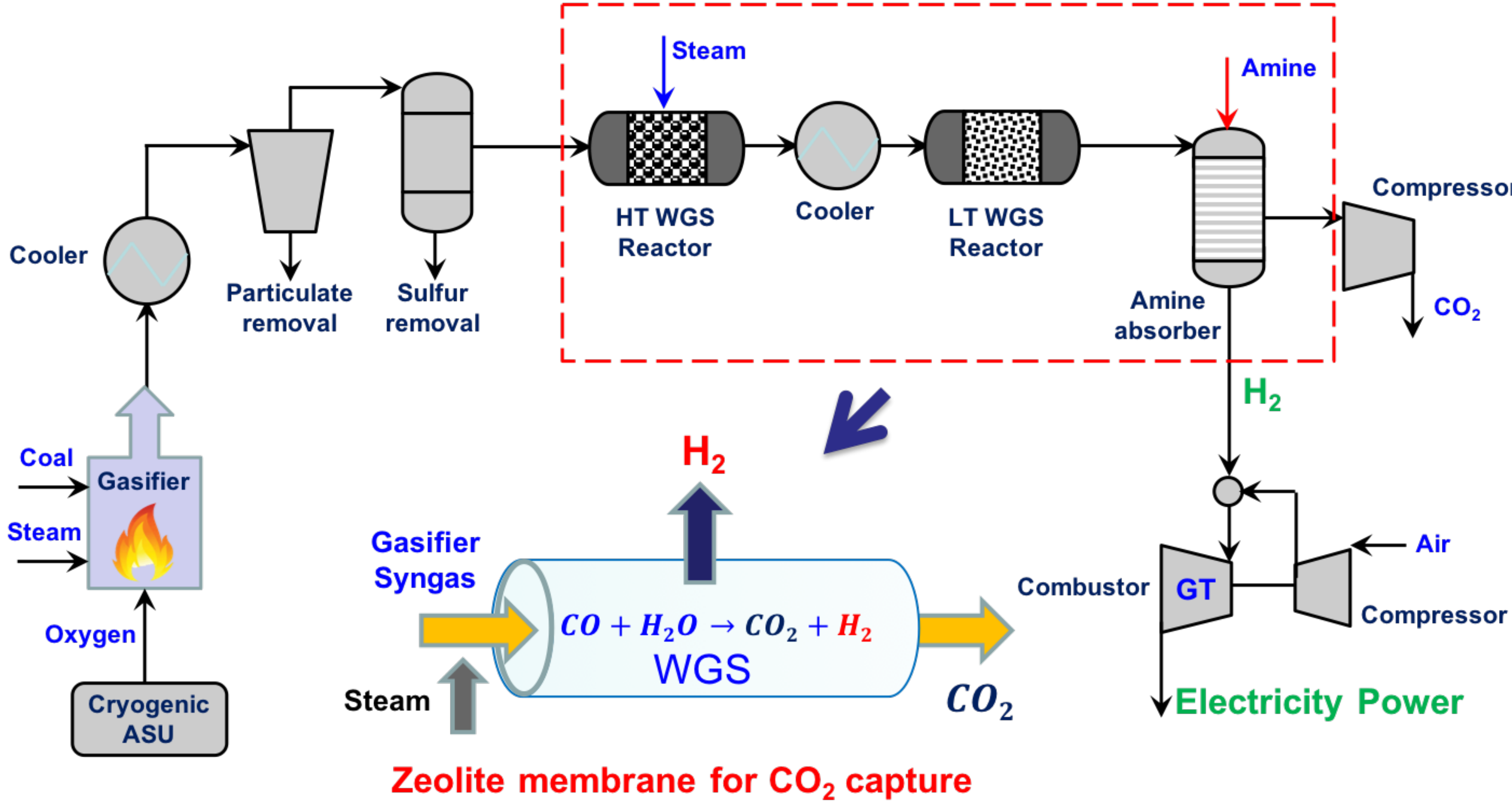
- Arizona State University (ASU)
- University of Cincinnati (UC)
- Media and Process Technology, Inc (MPT)
- Nexant, Inc.
- University of Kentucky Applied Energy Research Center

Project Objectives

To demonstrate a bench-scale zeolite membrane reactor (ZMR) for WGS reaction of coal gasification gas for hydrogen production for integration with IGCC power plant.

To evaluate the performance and cost-effectiveness of this new membrane reactor process for use in 550 MW coal-burning IGCC plant with CO_2 capture.

Zeolite Membrane Reactor for Water-Gas Shift Reaction for CO_2 Capture



Zeolite Membrane Requirements:

- **Operate at 350-550°C**
- **Chemically stable in H_2S, thermally stable at ~500°C**
- **H_2 permeance > 1×10^{-7} mol/(m^2.s.Pa) (>300 GPU) with H_2/CO_2 selectivity > 10**

DOE Project: Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture

Task description

U.S. Department of Energy | NETL

Project Manager

Andrew Jones

Arizona State University

PI: Jerry Y.S. Lin

University of Cincinnati

PI: Junhang Dong

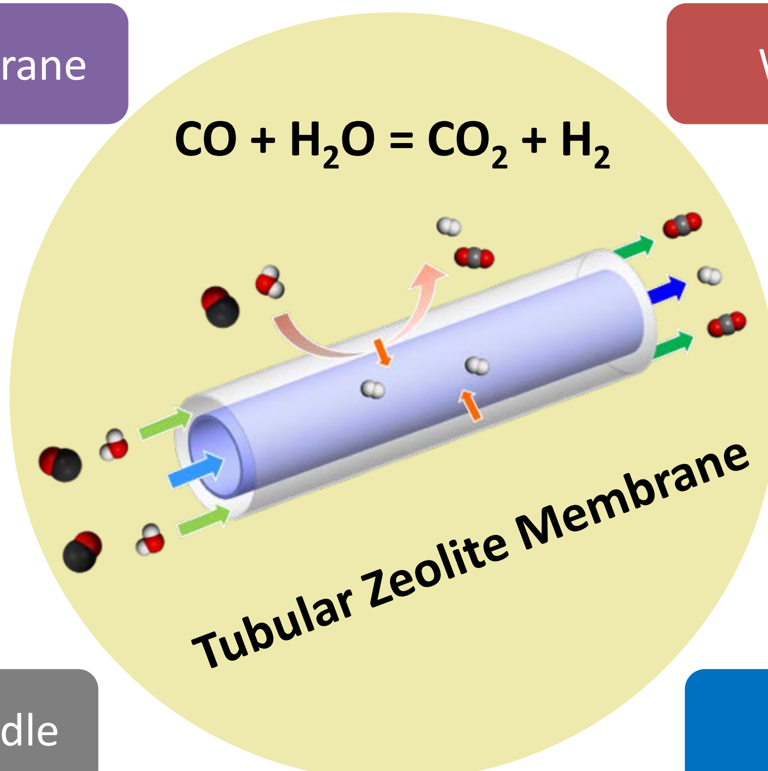
Media and Process Technology Inc.

PI: Richard Ciora

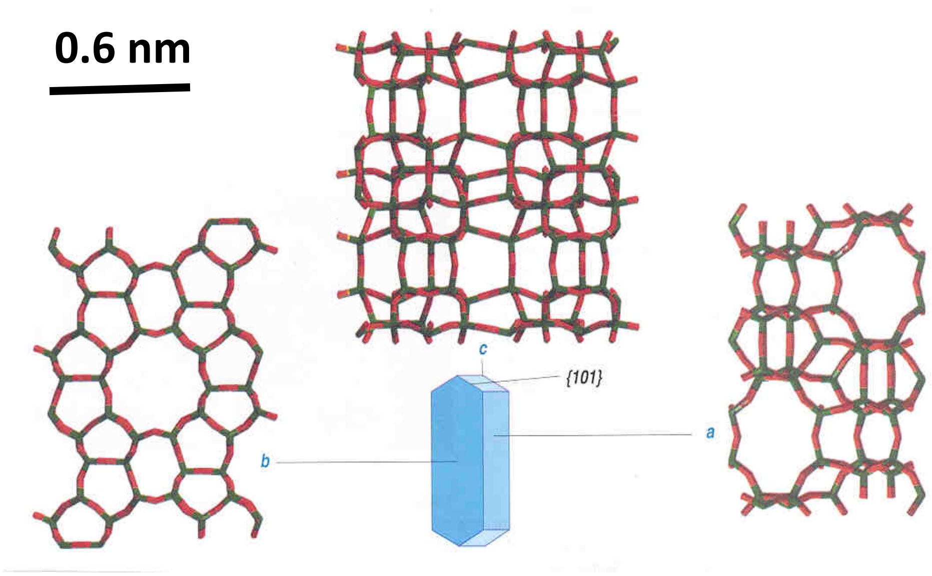
Nexant

PI: Gerald Choi

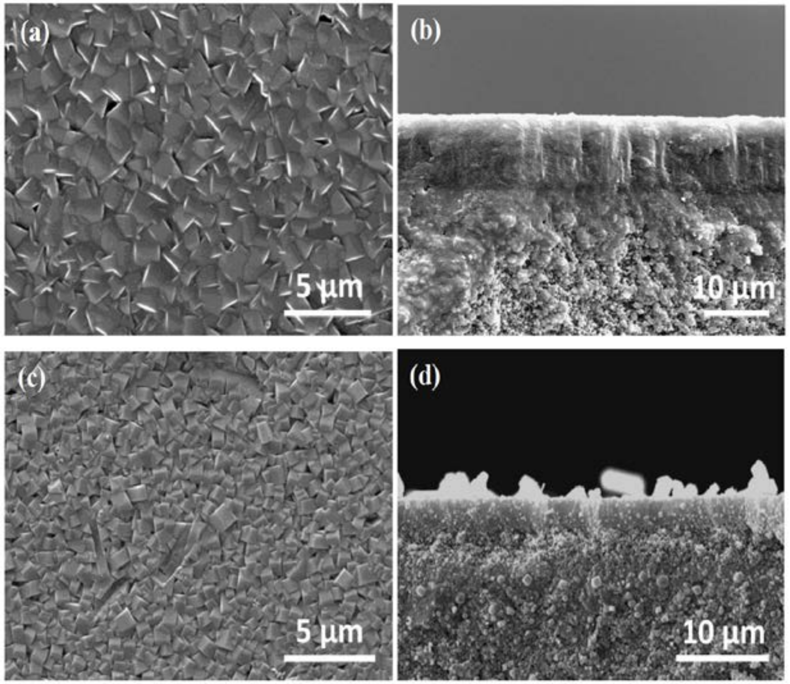
- Ceramic Support
- WGS Catalyst
- ZMR Modeling
- TEA Analysis
- Bench-scale ZMR
- Membrane Bundle
- Lab-scale ZMR
- Zeolite Membrane



MFI-type Zeolite (Silicalite-1 or ZSM-5)



- Molecular sieving at high temperatures
- Highly chemically and thermally stable (up to 700°C)

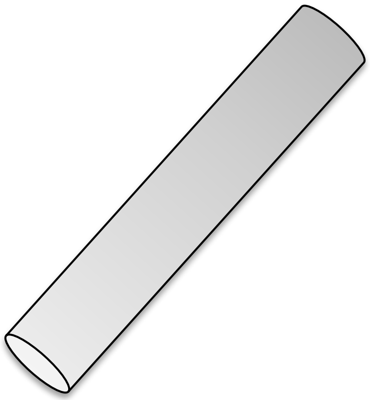


Surface and cross-section SEM images of (a, b) templated synthesized random oriented MFI membrane, and (c, d) template-free synthesized random oriented MFI membranes (from Lin lab)

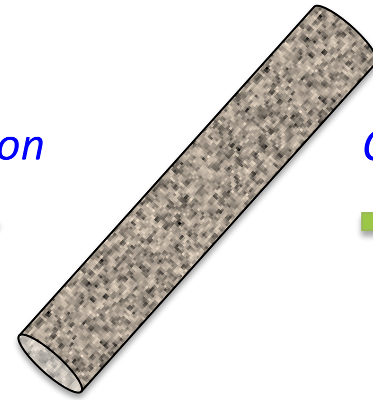
- Tailorable structure

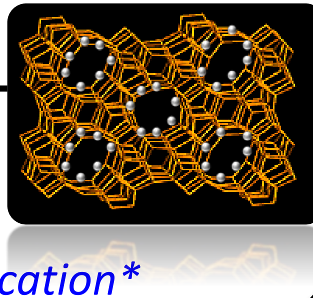
Tubular MFI-type Zeolite Membranes

Membrane preparation and property

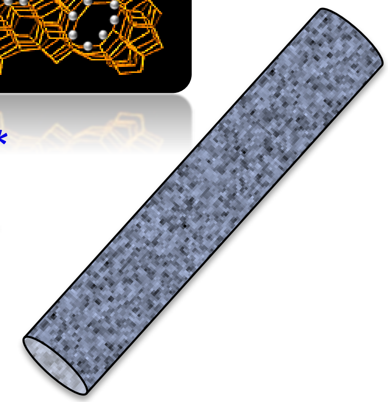


in-situ crystallization





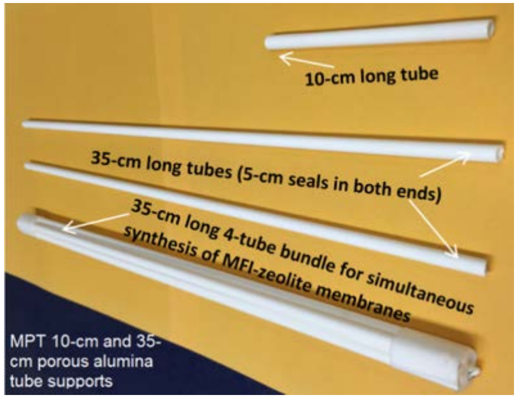
*CCD modification**

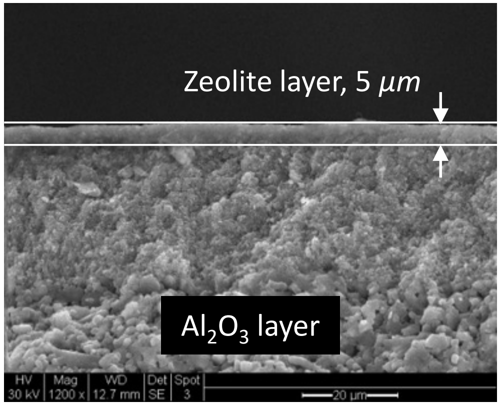


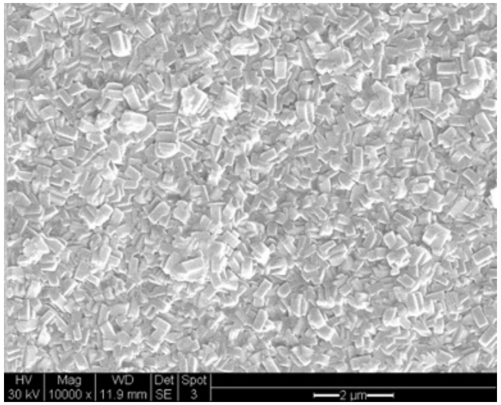
Al_2O_3 tubular support

MFI zeolite membrane

Modified zeolite membrane







OD =5.7 mm; ID =4.7 mm
Pore size < 100 nm

25°C: H_2/CO_2 = 0.1-0.4
450°C: H_2/CO_2 = 4.0-5.0

25°C: H_2/CO_2 = 1.5-3.0
450°C: H_2/CO_2 = 10-45

*Catalytic Cracking Decomposition of Methyldiethoxysilane (MDES)

Scope of work

1) **Scaling up ZMRs from lab-scale to bench-scale for combined WGS reaction and H_2 separation**

2) **Conducting a bench-scale study using these ZMRs for hydrogen production for IGCC with CO_2 capture.**

Goal is to demonstrate effective production of H_2 and CO_2 capture by the bench-scale zeolite membrane reactor from a coal gasification syngas at temperatures of 400-550°C and pressures of 20-30 atm:

- Bench-scale zeolite membrane reactor: 21 zeolite membrane tubes of 3.5 ID, 5.7 OD and 25-cm long (active)
- A system producing H_2 at rate of about 2 kg/day, equivalent to a 2 kW_{th} IGCC power plant

General Approach to Scaling up WGS-ZMR

Single-tube zeolite membrane reactor: study WGS up to 30 atm by experiments and modeling

↓

Intermediate-scale zeolite membrane reactor: 3-7 tube membrane module for WGS reaction

↓

Bench-scale zeolite membrane reactor: 21 tube membrane module for WGS reaction at UK-CBTL

→ Zeolite membrane reactor in IGCC with CO_2 capture - process design and techno-economic analysis

Progress and Accomplishments

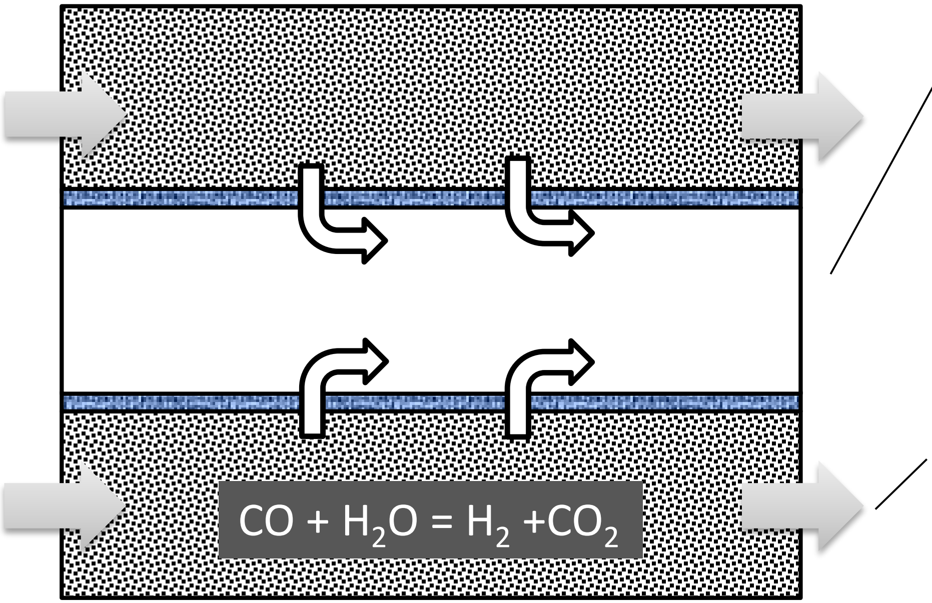
- **Modeling and Analysis of WGS in Bench-Scale Zeolite Membrane Modules (Task 10.0)**
- **Fabrication of Large Quality Tubule Supports (Task 11.0)**
- **Preparation of Large Quantity MFI Zeolite Tubule Membranes for Bench-Scale Module (Task 12.0)**
- **Design and Fabrication of Bench-Scale Zeolite Membrane Housing (Task 13.0)**
- **Building Bench-Scale Zeolite Membrane Reactors (Task 14.0)**
- **Testing WGS Reaction in Bench-Scale Membrane Reactor (Task 15.0)**
- **Process Design, Techno-Economic and EH&S Analyses (Task 16.0)**

Task 10: Modeling and Analysis of WGS in Bench-Scale Zeolite Membrane Modules

Research target for ZMR performance

Feed stream

syngas mixture



CO conversion:

$$X_{CO} = \frac{F_{CO,feed} - F_{CO,reten} - F_{CO,perm}}{F_{CO,feed}} > 99\%$$

Permeate stream

H_2 recovery:

$$R_{H_2} = \frac{F_{H_2,perm}}{F_{H_2,reten} + F_{H_2,perm}} > 92\%$$

H_2 purity:

$$G_{H_2} = \frac{F_{H_2,perm}}{F_{total,perm}}$$

Retentate stream

CO_2 capture:

$$R_{CO_2} = \frac{F_{CO_2,reten}}{F_{CO_2,reten} + F_{CO_2,perm}} > 90\%$$

CO_2 purity:

$$G_{CO_2} = \frac{F_{CO_2,reten}}{F_{total,reten}} > 95\%$$

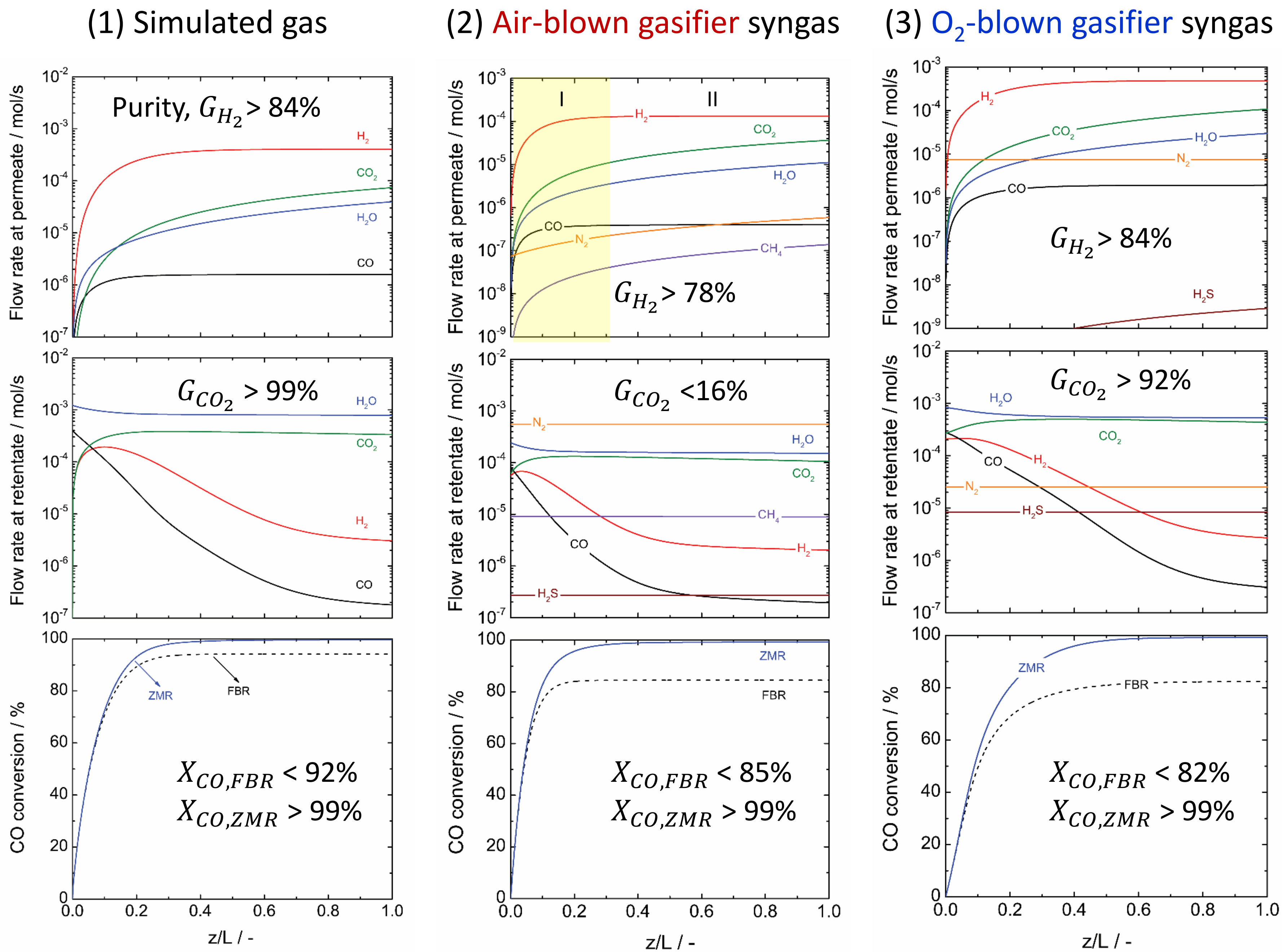
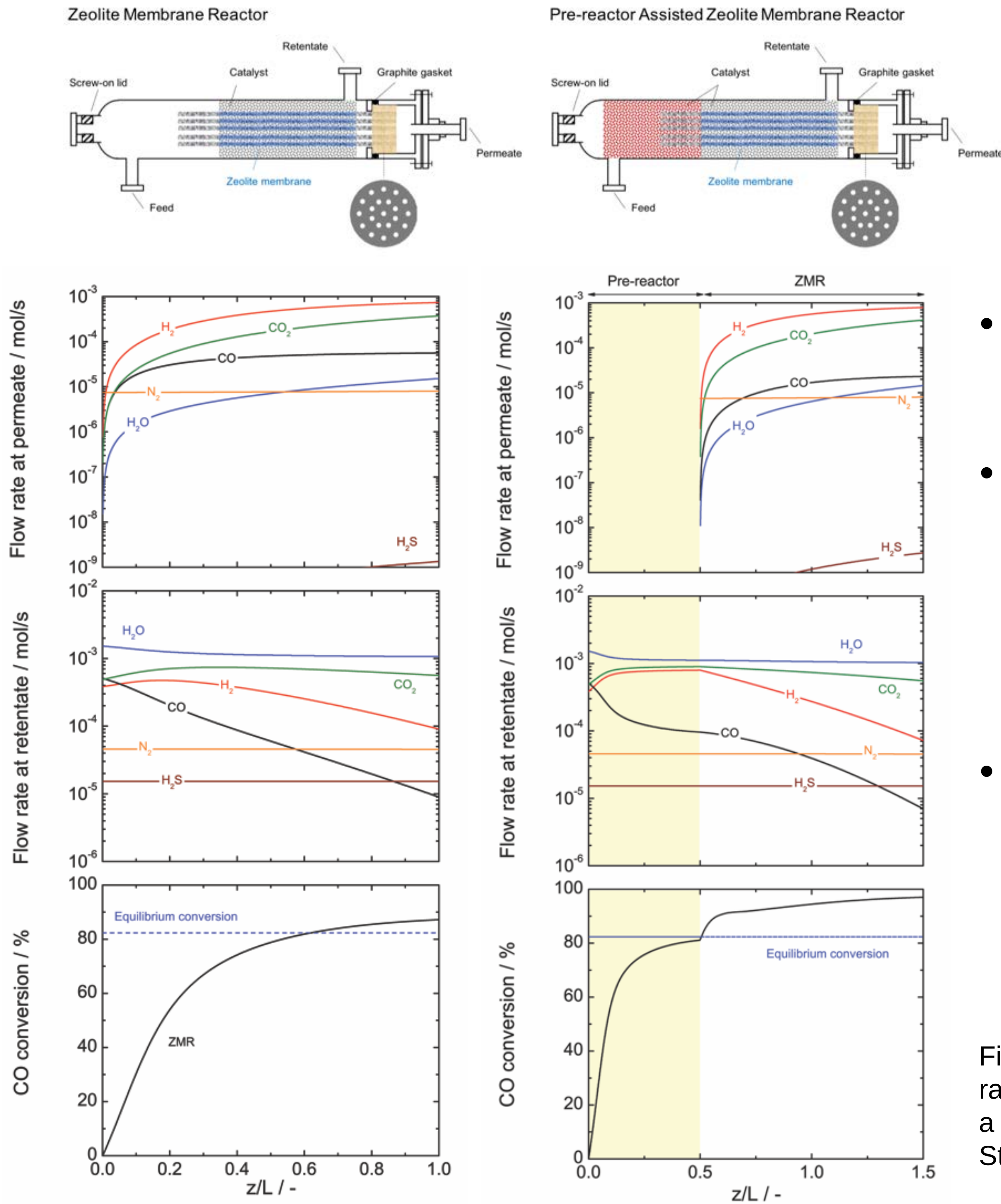


Figure 1. Profile of CO conversion and gas flow rates in zeolite membrane reactor and fixed-bed reactor.



- CO conversion:

  87.2% → 97.0%.

- Pre-reactor effect:

  equilibrium conversion

  a higher H_2 partial pressure for but a lower CO partial pressure.

- Catalyst packing

  UC: 30%

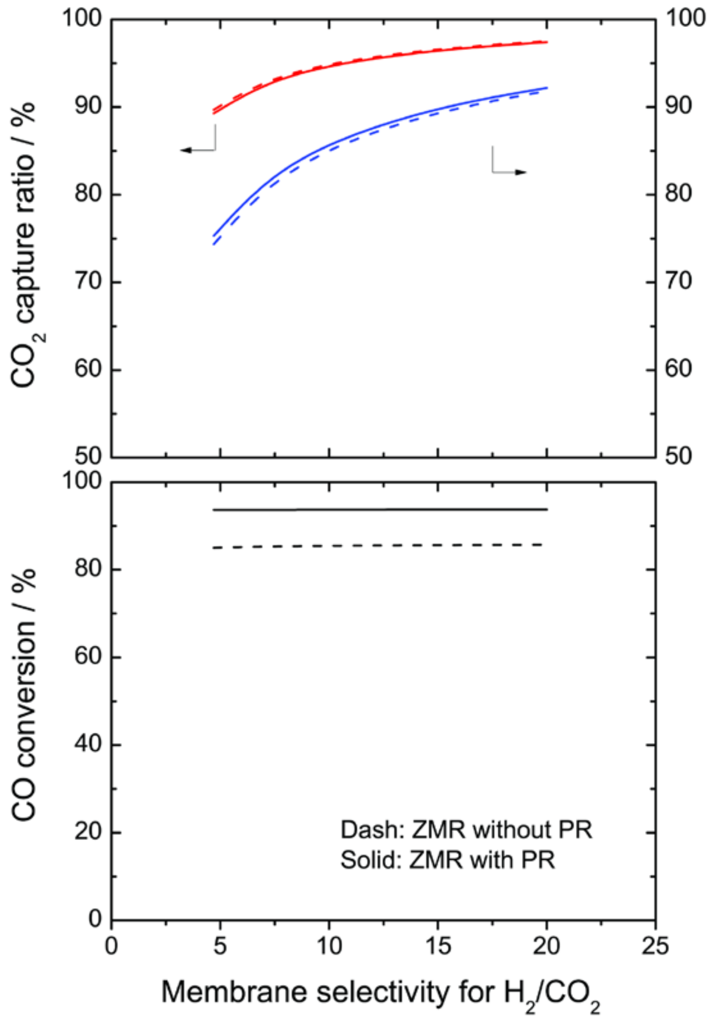
  Simulation: 50%

Figure 2. Profile of CO conversion and gas flow rates in a zeolite membrane reactor with/without a pre-reactor at 450°C. Pressure: 30 bar; Steam/CO mole ratio: 3.0.

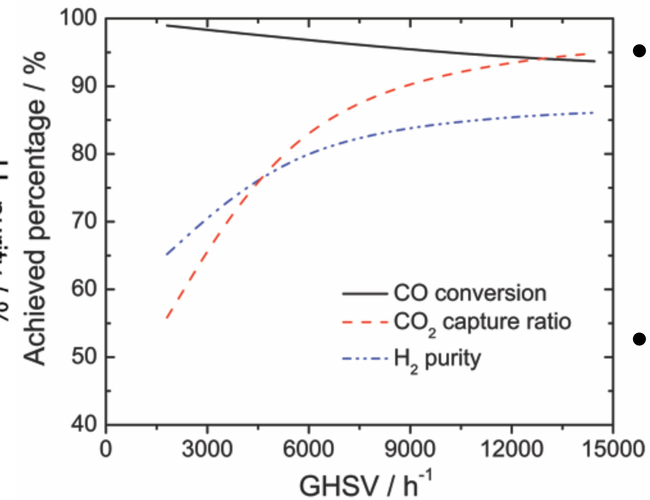
Task 10: Modeling and Analysis of WGS in Bench-Scale Zeolite Membrane Modules

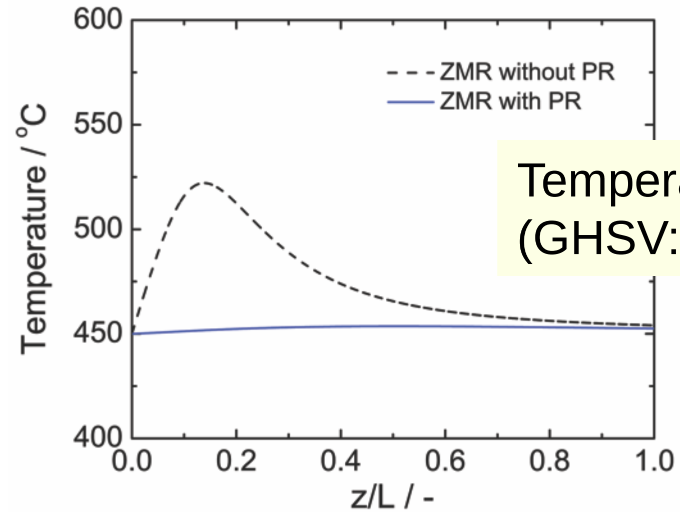
Performance improvement with pre-reactor (PR)

Effect of H_2/CO_2 selectivity
(GHSV: 14446.5 h^{-1})



Effect of GHSV
(H_2/CO_2 Selectivity: 10)





Temperature profile
(GHSV: 5417.5 h^{-1})

- PR enhances the CO conversion but less enhancement in the CO_2 capture and H_2 purity.
- Increasing GHSVs improves the CO_2 capture ratio significantly .

Inlet temperature: 450°C; Pressure: 30 bar; Steam/CO mole ratio: 3.0.

Task 11: Fabrication of a Large Quantity of Tubular Supports

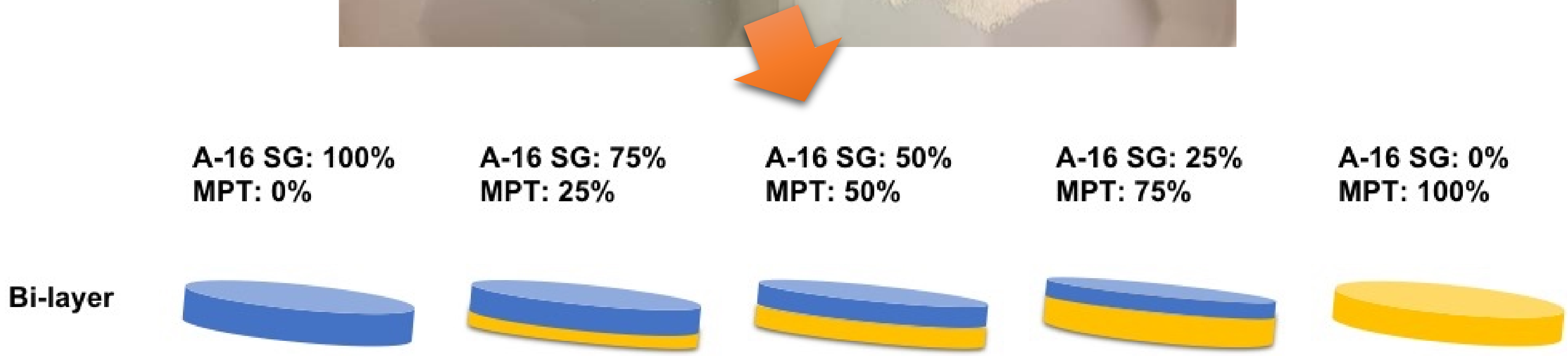
Tubular Substrate Supply

Over 250 tubular substrates of various types and formulations have been prepared

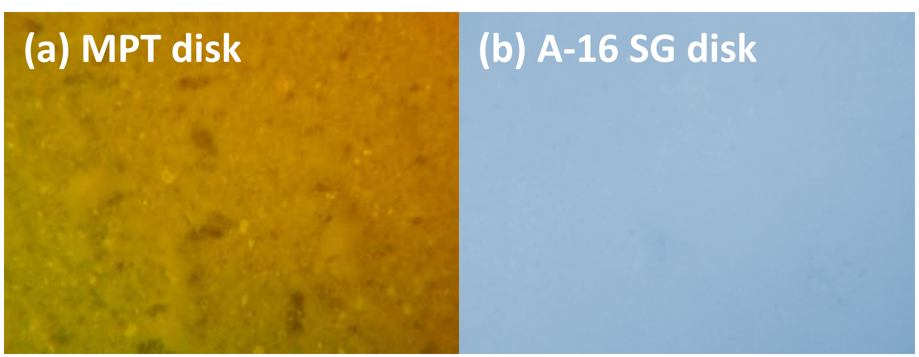
UC-#	Batch-#	Date shipped	Items	Qty.	Description
B5	MPT-4	8/29/2017	1	10	96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends
B6	MPT-5	9/6/2017	1	4	99.9% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends (These are test pieces for 99.9% A
			2	4	96% Alumina body, 5.7x1.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends (These are thick-wall substrate.)
			3	3	96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on the sealed end, 25cm glass on the open end (For A
			4	9	99.9% Alumina body, 5.7x3.5mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal (These are test pieces for 99.9% Aluminum body.)
			5	6	96% Alumina body, 5.7x1.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal (These are thick-wall substrate.)
B7	MPT-6	9/21/2017	1	11	96% Alumina body, 5.7x1.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal (thick-wall substrate)
			2	12	96% Alumina body, 5.7x1.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends (thick-wall substrate)
			3	10	96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm, 5cm glass glaze on both open ends (thick-wall substrate)
B8	MPT-7	10/17/2017	1	38	96% Alumina body, 5.7x2.9mm(ODxID), 10cm, outside coated 0.05 µm, NO glass end seal
			2	10	96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm 5cm glass glaze on both open ends
			3	9	96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm 5cm glass glaze on the open and tipped end
B9	MPT-8	12/7/2017	1	21	96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm (25cm long), 5cm glass glaze on tipped end, 5cm glass glaze on open e
			2	5	96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm (5cm long), 5cm glass glaze on tipped end, 25cm glass glaze on open e
			3	5	96% Alumina body, 5.7x3.5mm(ODxID), 35cm, outside coated 0.05 µm (10cm long), 5cm glass glaze on tipped end, 20cm glass glaze on open
B10	MPT-9	1/9/2018	1	18	96% Alumina body, 5.7x2.9mm(ODxID), 35cm, outside coated 0.05 µm (25cm long), 5cm glass glaze on tipped end, 5cm glass glaze on open en
B11	MPT-10	3/8/2018	1	4	99-3070, 5.7x3.5mm (ODxID), 3x10in, 1x7in, no top layer/glass glaze
			2	1	99-115, 5.7x3.5mm (ODxID), 1x5in, no top layer/glass glaze
			3	1	99-114, 5.7x3.5mm (ODxID), 1x5in, no top layer/glass glaze
			4	23	96%, 5.7x2.9mm (ODxID), 35cm, 5cm glass glaze on the tipped & open ends
B12	MPT-11	3/22/2018	1	2	99-3070, 5.7x3.5mm (ODxID), 35cm long, no glass end seal
B13	MPT-12	5/17/2018	1	3	99-3070, 5.7x3.5mm (ODxID), 2x6.5in, 1x7.5in, no top layer/glass glaze, fired at 1650°C
B14	MPT-13	6/14/2018	1	5	96%-body, 5.7x2.9mm (ODxID), 35cm long, outside coated 0.05 µm, 5cm glass glaze on the open & tipped ends
		UC	2	1	96%-body, 5.7x2.9mm(ODxID), 35cm long, outside coated 0.05 µm (10cm), 5cm glass glaze on the tipped end, 20cm glass on the open end
			3	2	96%-body, 5.7x3.5mm(ODxID), 35cm long, outside coated 0.05 µm (10cm), 5cm glass glaze on the tipped end, 20cm glass on the open end
			4	1	96%-body, 5.7x2.9mm(ODxID), 35cm long, outside coated 0.05 µm (5cm), 5cm glass glaze on the tipped end, 25cm glass on the open end
			5	2	96%-body, 5.7x3.5mm(ODxID), 35cm long, outside coated 0.05 µm (5cm), 5cm glass glaze on the tipped end, 25cm glass on the open end
			6	15	96%-body, 5.7x3.5mm(ODxID), 35cm long, outside coated 0.05 µm (25cm), 5cm glass glaze on two open ends
			7	200 grams	MPT-114-99% powders, for discs
		6/14/2018 ASU	1	200 grams	MPT-114-99% powders, for discs (Shipped to Lie Meng, ASU)
B15	MPT-14	7/2/2018	1	23	96%-body, 5.7x3.5mm (ODxID), 35cm long, outside coated 0.05 µm, 5cm glass glaze on the open & tipped ends
			Total =	**258**	

Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

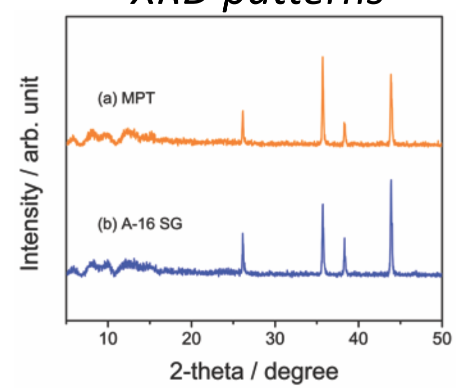
Alumina leaching in the synthesis of MFI zeolite membranes



microscope digital images



XRD patterns



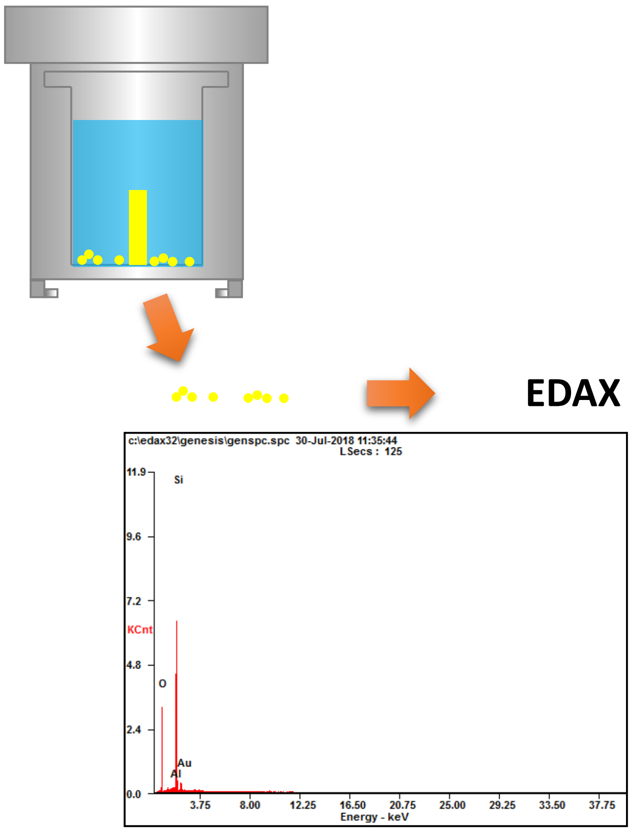
Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

Alumina leaching in the synthesis of MFI zeolite membranes

in-situ crystallization at 180°C,

3 hours using 0.055 SiO_2: 0.0058

NaOH: 0.017 TPAOH: 0.92 H_2O



Arvanitis et al. *J. Membr. Sci.* 549 (2018) 575–580.

High Al content was found in the MFI zeolite formed in the synthesis of zeolite membranes supported by disks pressed with MPT powder.

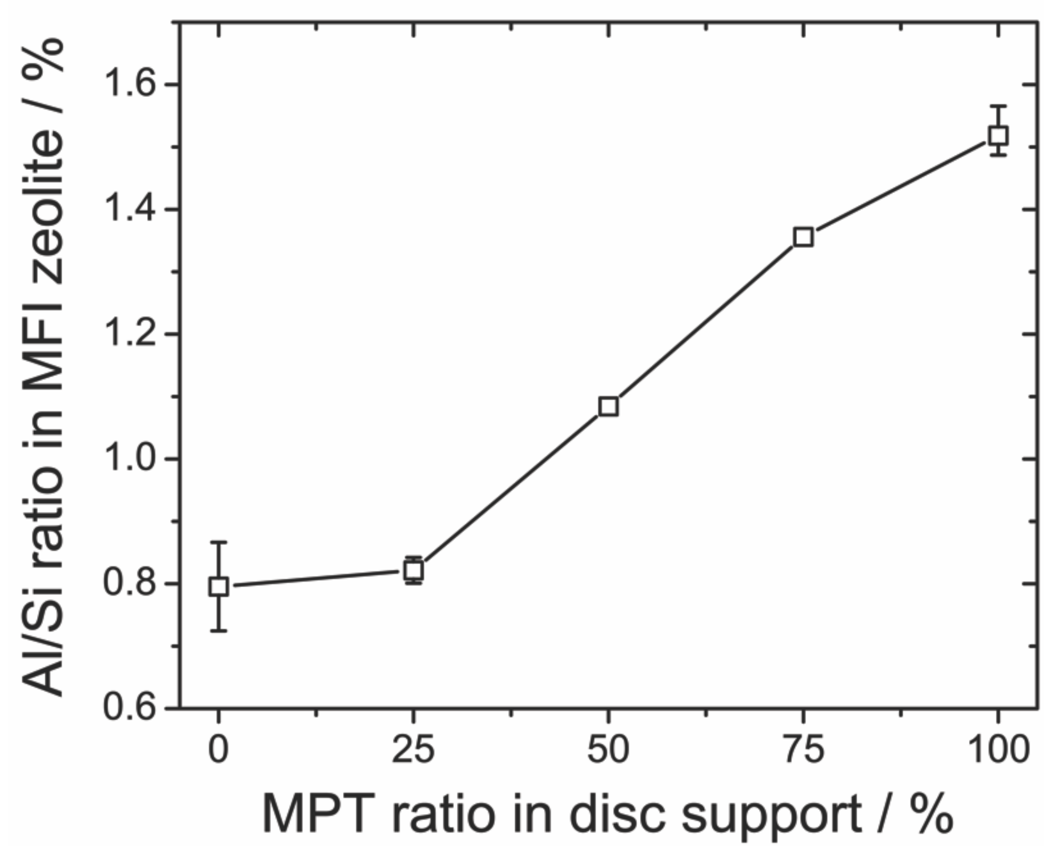
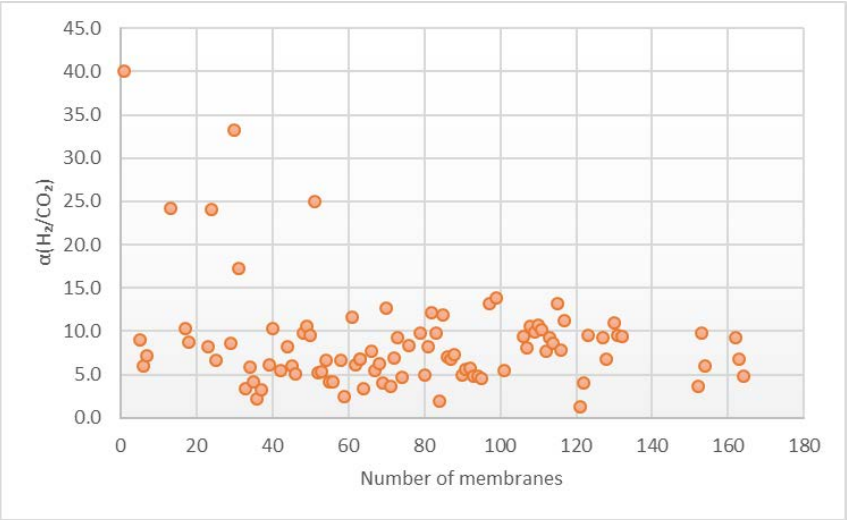
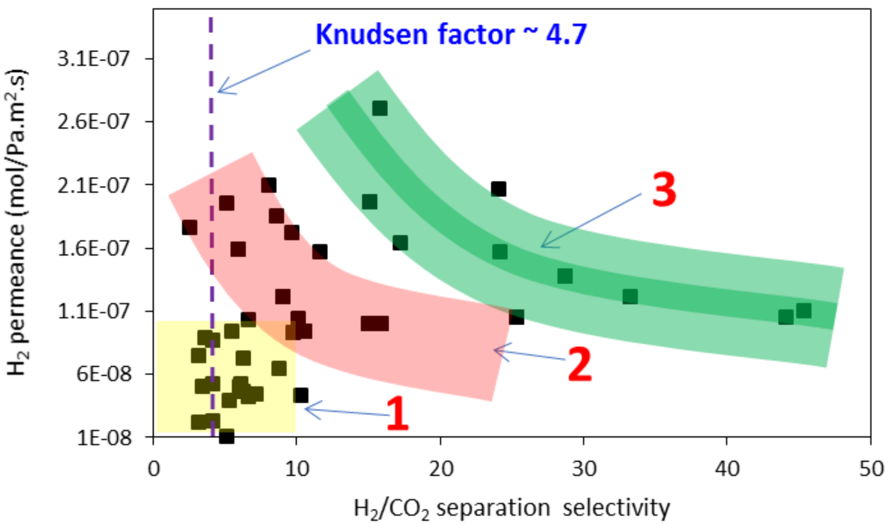


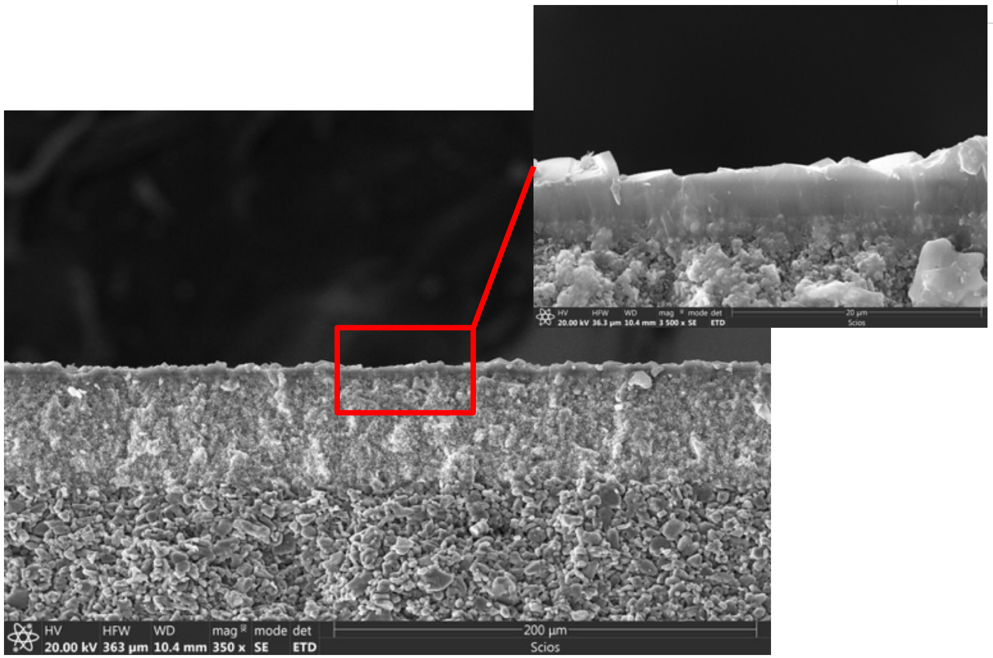
Figure 4. Al/Si ratio in powders collected at the bottom of autoclaves for in-situ synthesis of MFI zeolite membranes supported by varied disks.

Task 12: Preparation of Large Quantity Zeolite Membranes for Bench-Scale Module

Quality of modified tubular MFI zeolite membranes







Crystal size 600 nm

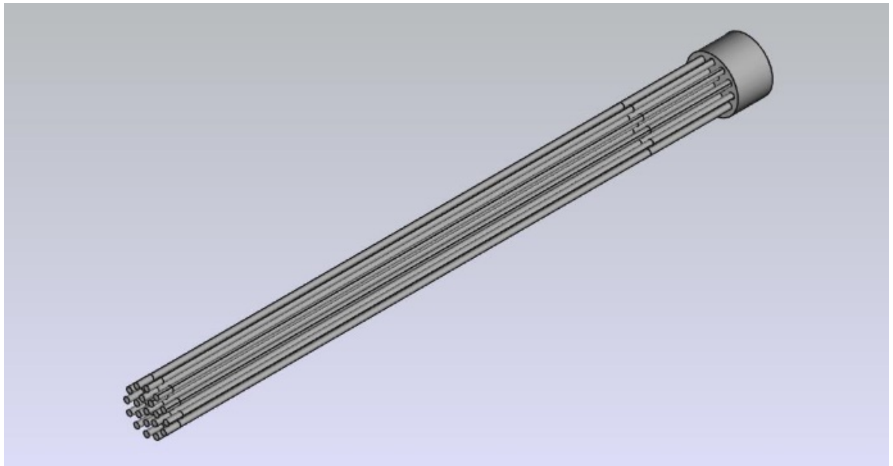
Layer thickness 5-8 μm

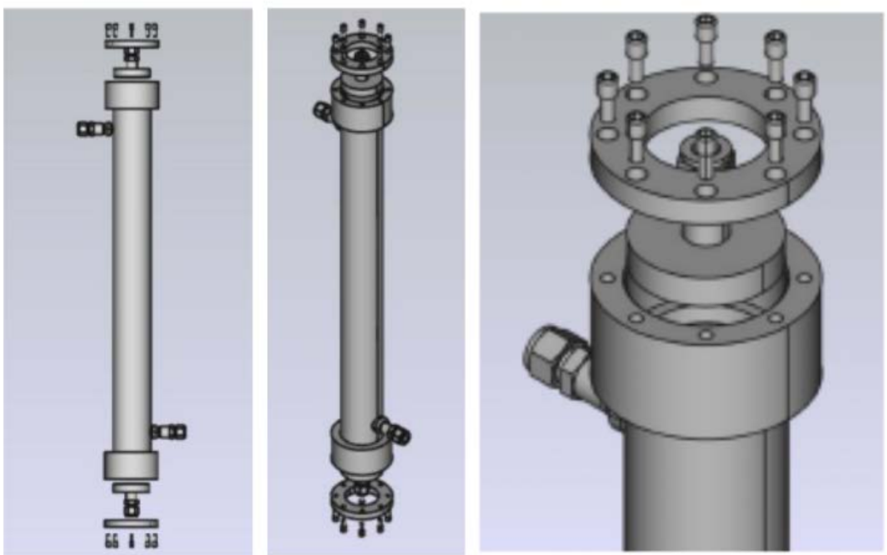
Excellent surface coverage

75% membrane reproducibility

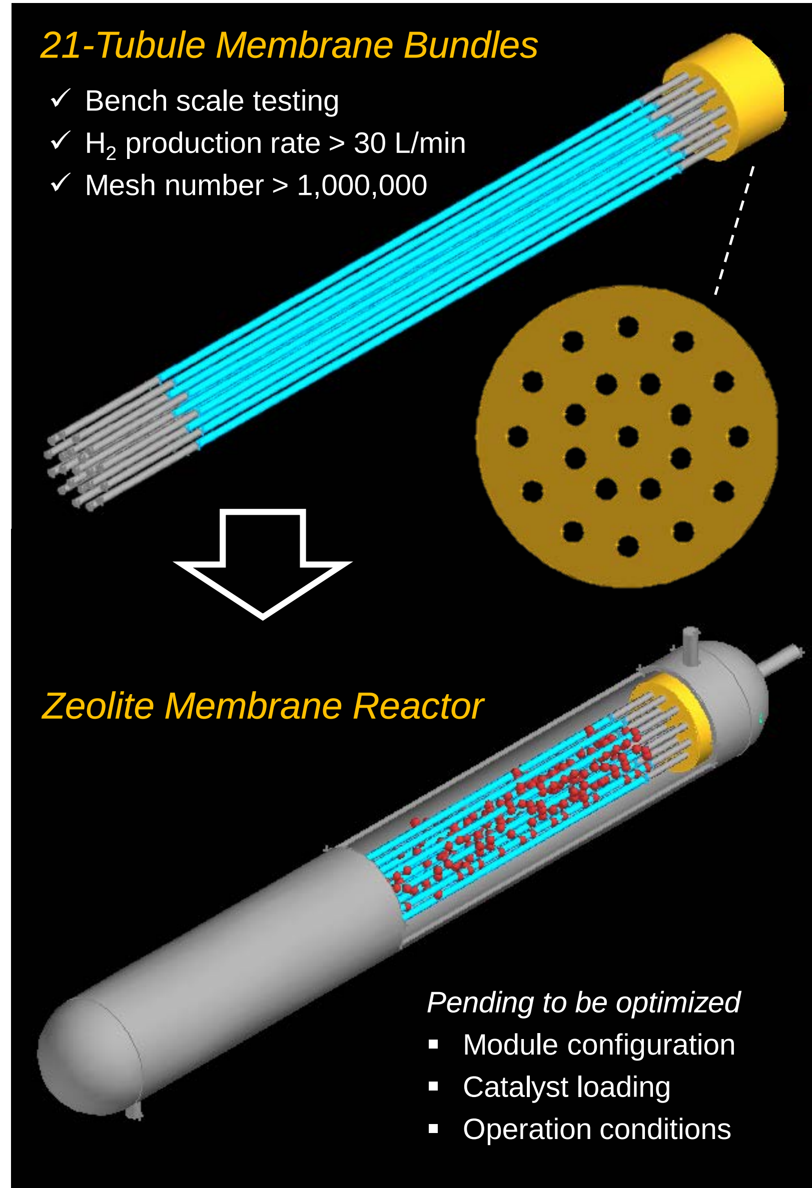
Task 13: Design and Fabrication of Bench-Scale Zeolite Membrane Module Housing

On-going work: design of bench-scale membrane module





Module material: SS316

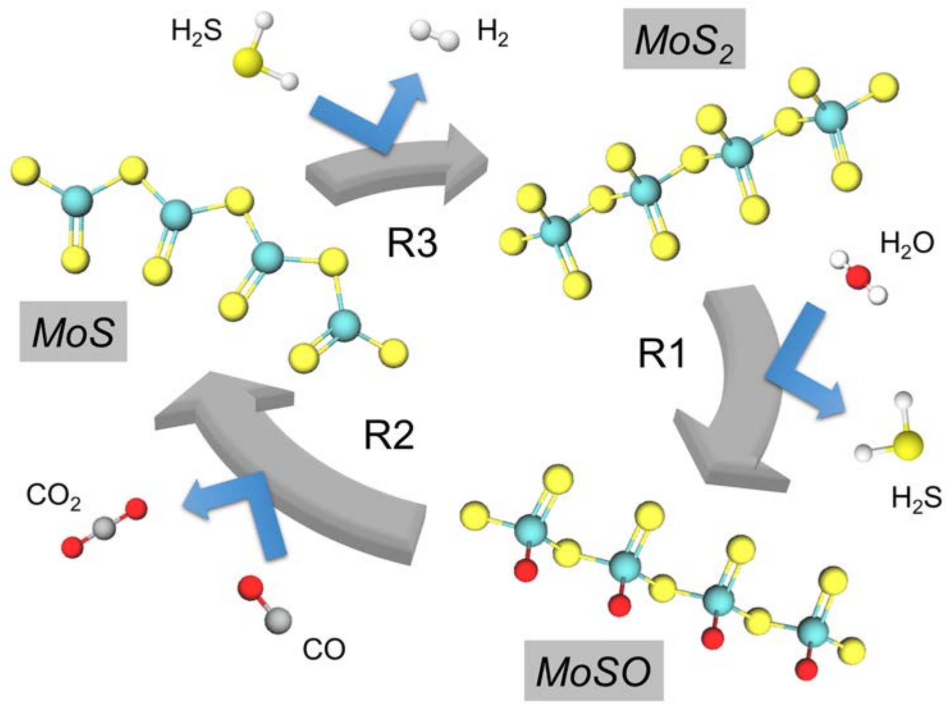


Task 14: Building Bench-Scale Zeolite Membrane Reactors

Fabrication and evaluation of WGS catalyst for bench-scale WGS reaction

Kinetic model for the Co-Mo catalyst in the high-temperature WGS

Reaction pathway of WGS over Co-Mo catalysts



Sulfidation (pre-treatment):

$$MoO_3 + 2H_2S + H_2 \rightarrow MoS_2 + 3H_2O$$

WGS:

R1: $MoS_2 + H_2O \rightarrow MoSO + H_2S$

R2: $MoSO + CO \rightarrow MoS + CO_2$

R3: $MoS + H_2S \rightarrow MoS_2 + H_2$

The power-law model $$r_{CO} = k_0 \exp\left(\frac{-E_a}{RT}\right) P_{CO}^a P_{H_2O}^b P_{CO_2}^c P_{H_2}^d (1-\beta)$$

$$\beta = \frac{1}{K}\frac{P_{CO_2}P_{H_2}}{P_{CO}P_{H_2O}}$$

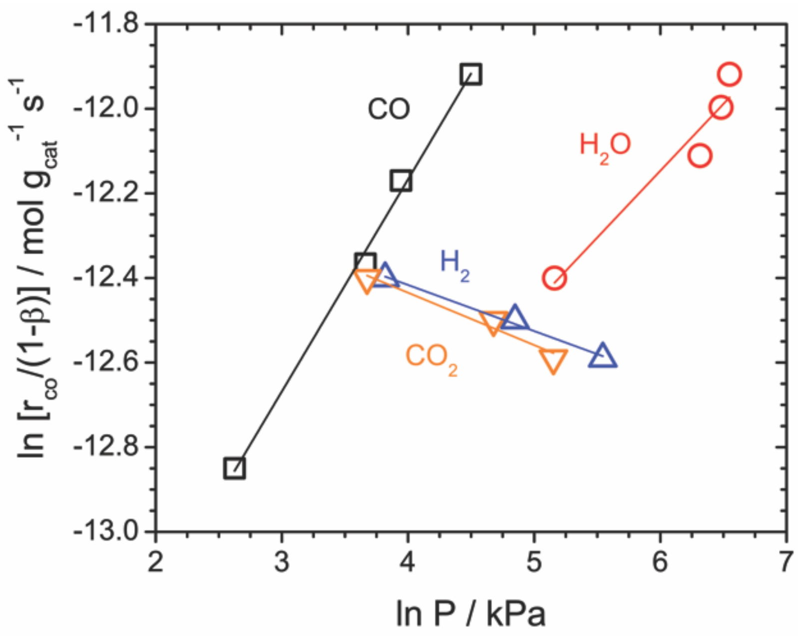
SSK-10 catalyst (Co-Mo-Mg$(AlO_2)_2$)

Task 14: Building Bench-Scale Zeolite Membrane Reactors

Fabrication and evaluation of WGS catalyst for bench-scale WGS reaction

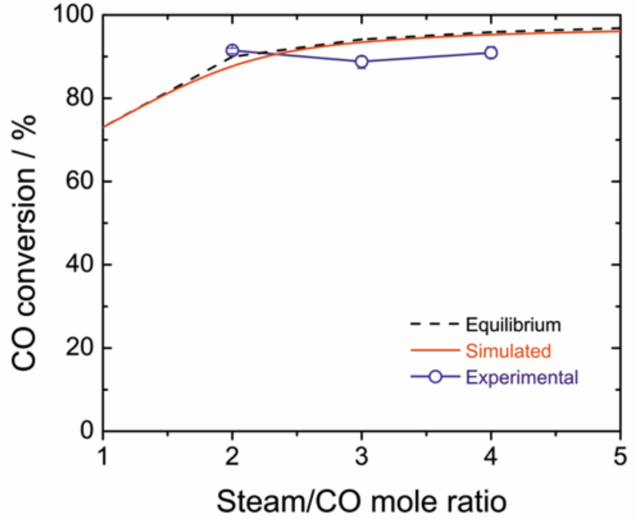
Determination of power-law model reaction orders

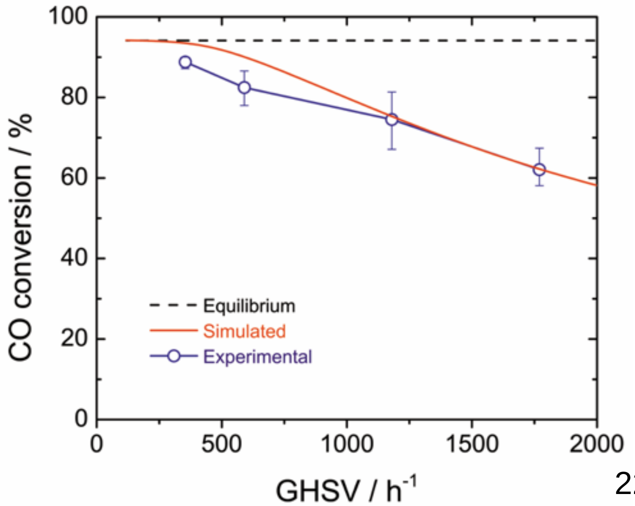
Log-log plots for the effect of CO, H_2O, CO_2, and H_2 partial pressure on reaction rates over Co-Mo catalyst.



$$r_{CO} = 1.58 \times 10^{-4} exp\left(\frac{-37.99}{RT}\right) P_{CO}^{0.50} P_{H_2O}^{0.32} P_{CO_2}^{-0.12} P_{H_2}^{-0.11} \left(1 - \frac{1}{K} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}\right)$$

CO conversion in a WGS-FBR
(450°C. Pressure: 10 bar)





Task 14: Building Bench-Scale Zeolite Membrane Reactors

Assembling and Testing Bench Scale Zeolite Membrane Reactor

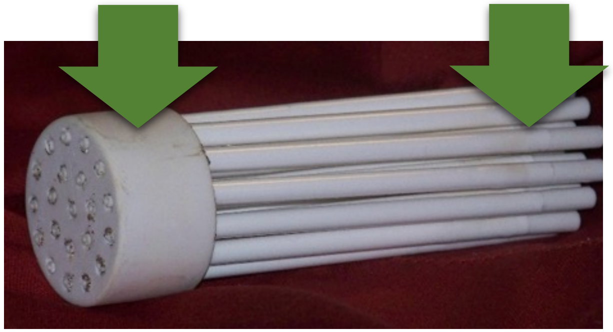
Thermal Stability Testing of Mock 21-tube Membrane Bundle

<u>Testing Conditions:</u> T = 450°C; P = 300 to 350 psig

21-Tube Candle Filter Bundle

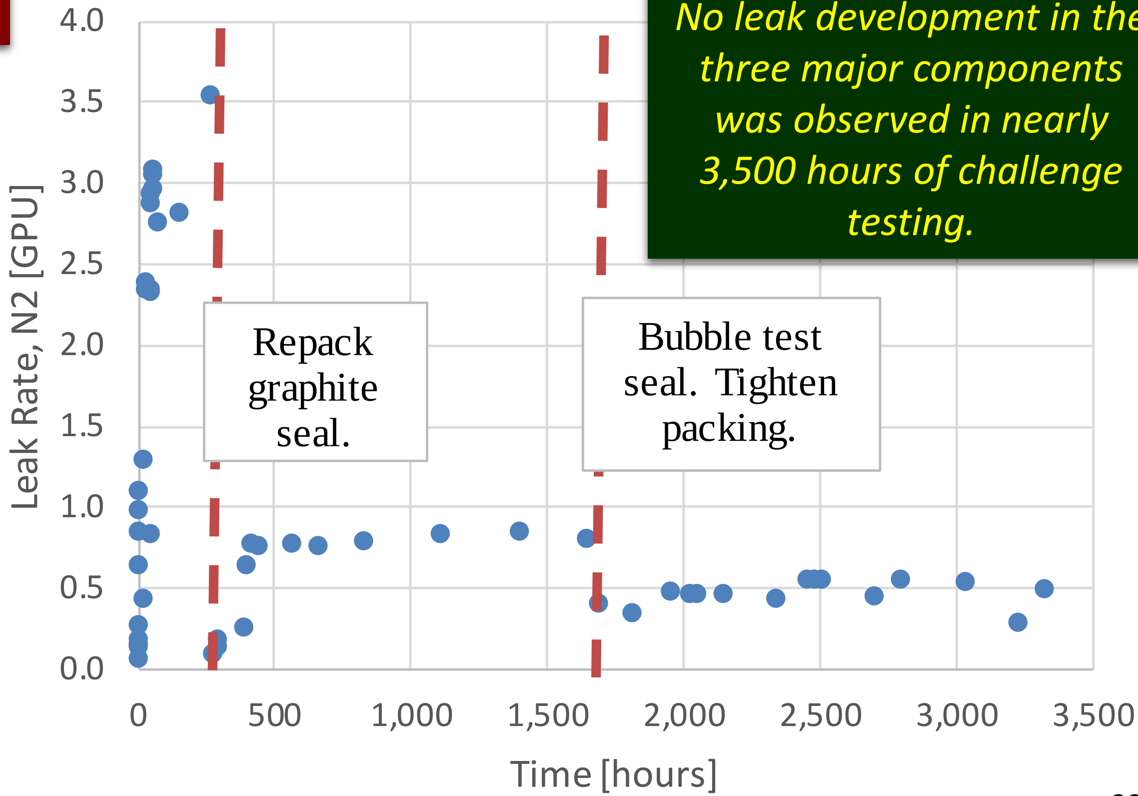
Ceramic Tube Sheet and Ceramic/Glass Potting

Impermeable Ceramic Tip



High Temperature Test Housing

Bundle Leak Rate during Challenge Testing



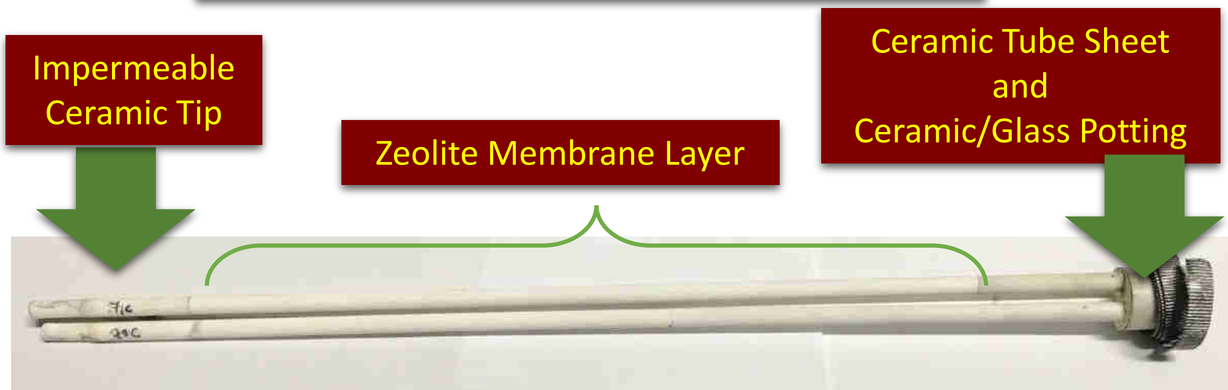
No leak development in the three major components was observed in nearly 3,500 hours of challenge testing.

Task 14: Building Bench-Scale Zeolite Membrane Reactors

Assembling and Testing Bench Scale Zeolite Membrane Reactor

Fabrication and Performance Testing of a 3-tube Zeolite Membrane Bundle

3-Tube Candle Filter Bundle (ID: K3-3)



Single-gas permeation at 200°C

	Gas permeance ($m^3/m^2/hr/bar$)	
	He	N_2
Tube 70B	1.449	0.811
Tube 70C	1.336	0.711
Tube 71C	1.422	0.742
Tube average	1.400	0.755
3-tube bundle	1.310	0.707

Task 14: Building Bench-Scale Zeolite Membrane Reactors

Modification and Installation of Bench-Scale Reactor Test Skid

Back View: Major Bench Scale Reactor Test Skid Subsystems

Pressure Control Panel

Mass Flow Meter Enclosure

Reject and Permeate Liquid Knockout Pots

Steam Injection Subsystem

Water Sampling Subsystem

Front View: Oven Chamber with Membrane Test Module and a 3” x 85-tube Membrane Bundle for Perspective

Oven Controls

3” x 85-tube Membrane Bundle

Power Distribution Skid

Conclusions

- Mathematical models of WGS-ZMR and Reaction kinetics of WGS catalysts established.
- 25-cm long CCD-modified zeolite membranes scaled up on alumina substrates.
- Multiple-tube ZMRs assembled and evaluated, and test skid for bench-scale test modified.

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Thank You!