Catalytic Membrane Reactors Based on Carbon Molecular Sieve Hollow Fiber Membranes for Sustainable and Modular H_2 Production (DE-FE0032209)

Haiqing Lin[1], Mark Swihart[1], Carl Lund[1],
and Rajinder Singh[2]

[1]University at Buffalo, State University of New York;
[2]Los Alamos National Laboratory;

DOE Project Review Meeting
Pittsburgh, PA

4/23/2024

Outline

- Project overview
- Our approach: catalytic membrane reactors (CMRs)
  - Simulation and optimization
  - Nano-catalyst development
  - Carbon molecular sieve (CMS) membranes
  - Preliminary data on CMRs vs packed-bed reactors (PBRs)
- Summary

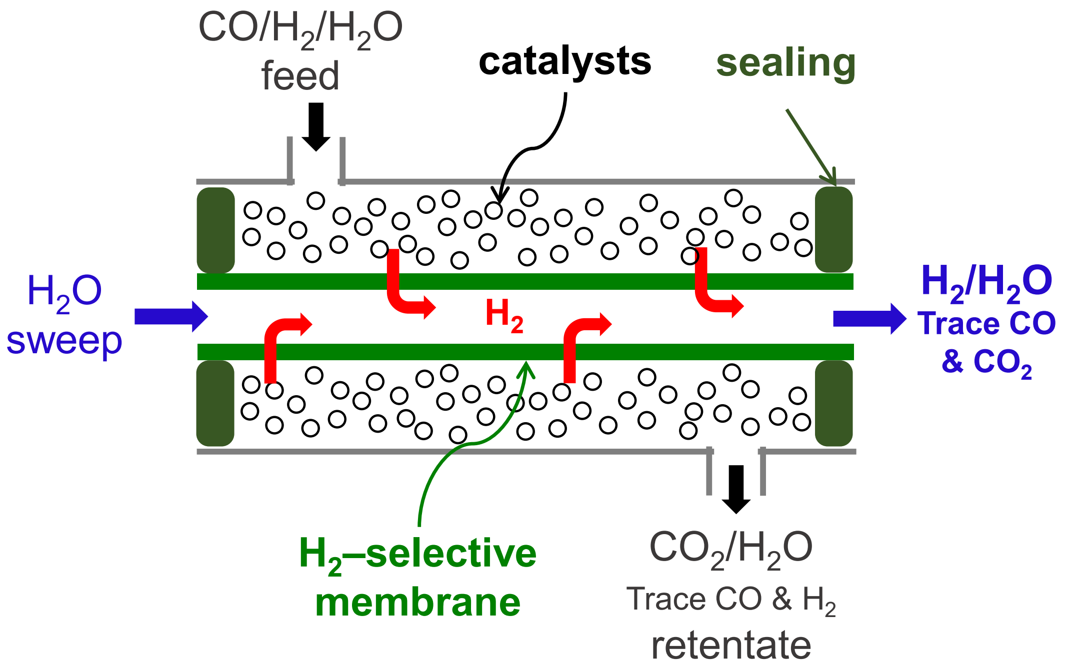
Project Information

Award number: DE-FE0032209

Project period: 10/1/22 to 9/30/24

Program manager: John P. Homer

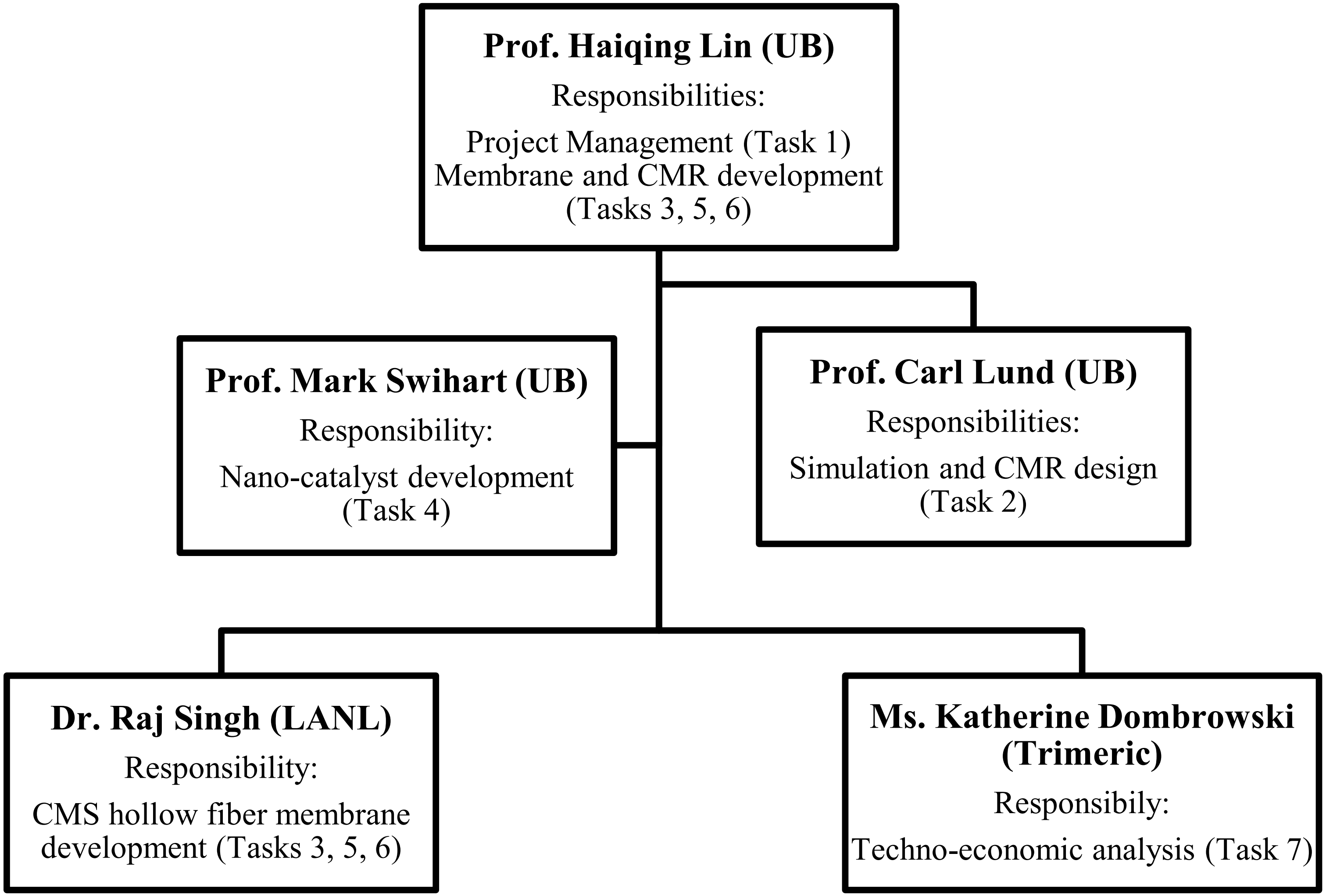
Project Objective: Demonstrate a process-intensified process for economically viable, modular H_2 production from waste biomass using catalytic membrane reactors (CMR) based on carbon molecular sieve (CMS) hollow fiber membranes.



Specific Objectives

- Design ***membrane reactors*** for high-temperature WGS reaction by integrating H_2-selective membranes, catalysts, and optimized process designs;
- Prepare and optimize ***CMS hollow fiber membrane modules*** to achieve H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 100 at pressures up to 20 bar and temperatures up to 400 °C;
- Design and prepare ***nano-catalysts*** with high WGS activity and stability under CMR conditions;
- Prepare and characterize the ***CMRs*** for high-temperature WGS reactions using simulated and real syngas containing H_2S, CO, and water vapor; and
- Conduct the ***process design*** and analysis based on the newly developed membranes for H_2/CO_2 separations.

Organization Chart and Roles



Simulation on Water-gas Shift Reaction

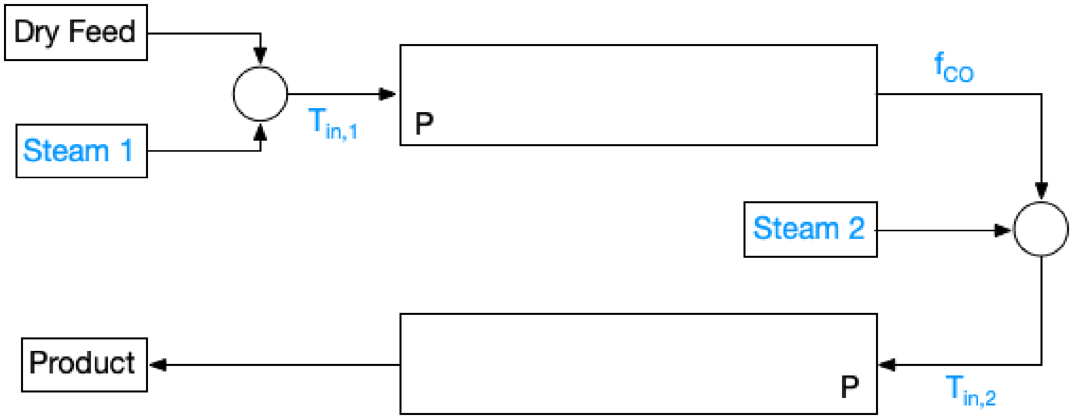
$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Feed	Dry gas composition (mol%)			
	H_2	CO	CO_2	CH_4
Natural Gas	74	17	6	3
Biomass 1	50	25	20	5
Biomass 2	35	40	10	15

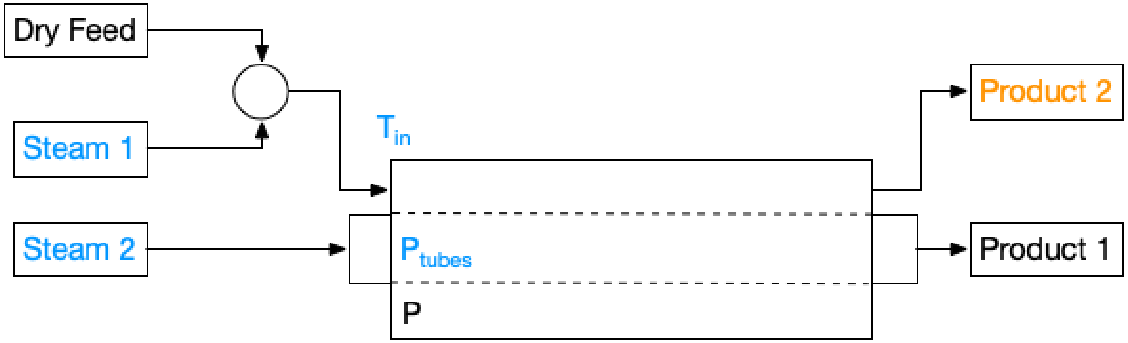
Dry gas hourly space velocity (DGHSV)

$$DGHSV = \frac{\dot{V}_{CO,in} + \dot{V}_{H_2,in} + \dot{V}_{CO_2,in} + \dot{V}_{CH_4,in}}{V}$$

Reactor Configurations

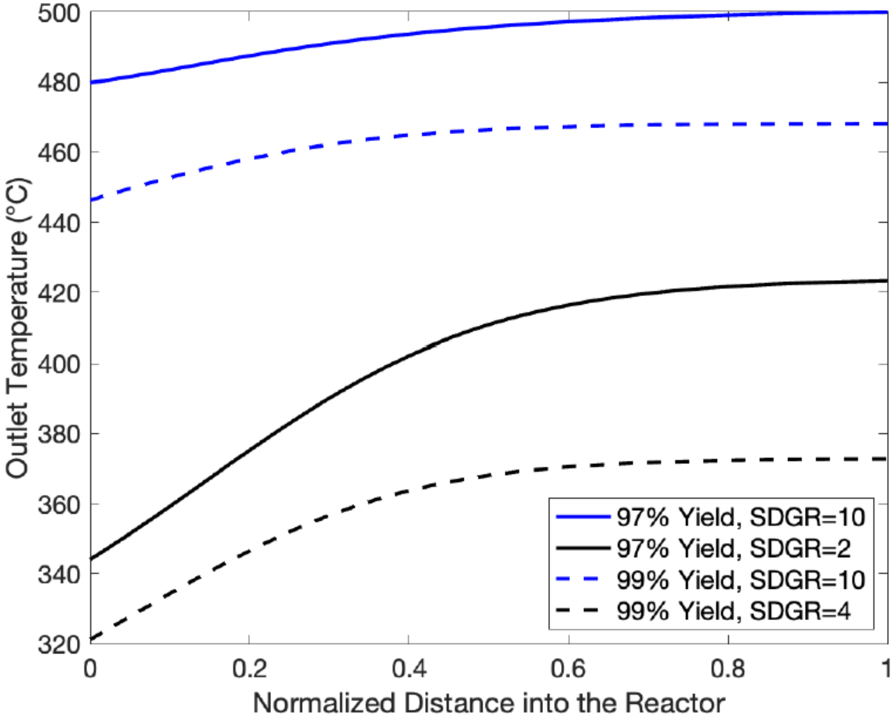


Traditional packed bed reactor (PBR):
high-temperature followed by low-temperature

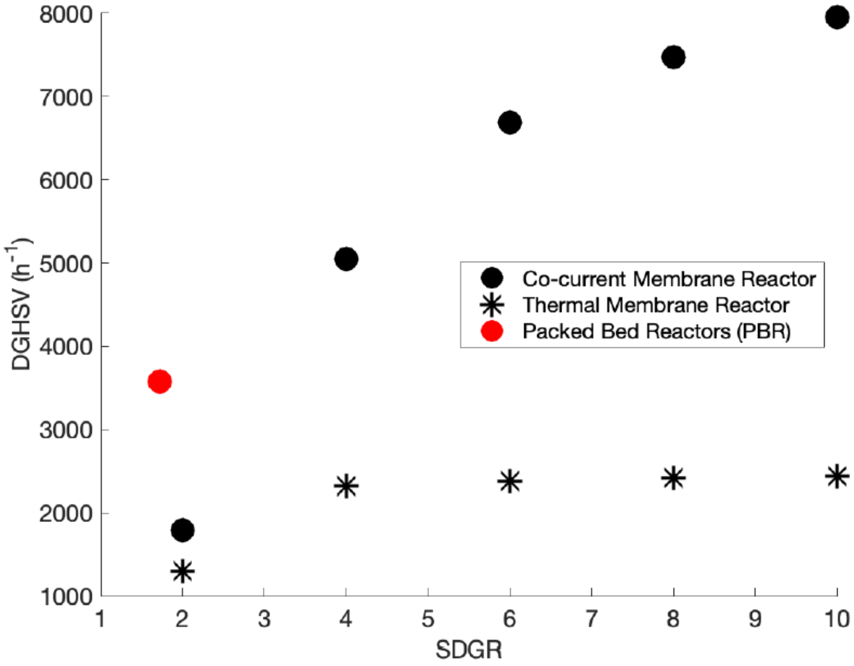


Catalysis membrane reactor (CMR)

Optimize Temperature and Membranes



Co-current membrane reactor temperature profiles during processing of the Biomass 1.



Optimum DGHSV for an impermeable thermal membrane reactor processing the Biomass 1 feed at 97% H_2 yield.

A greater DGHSV indicates a smaller volume

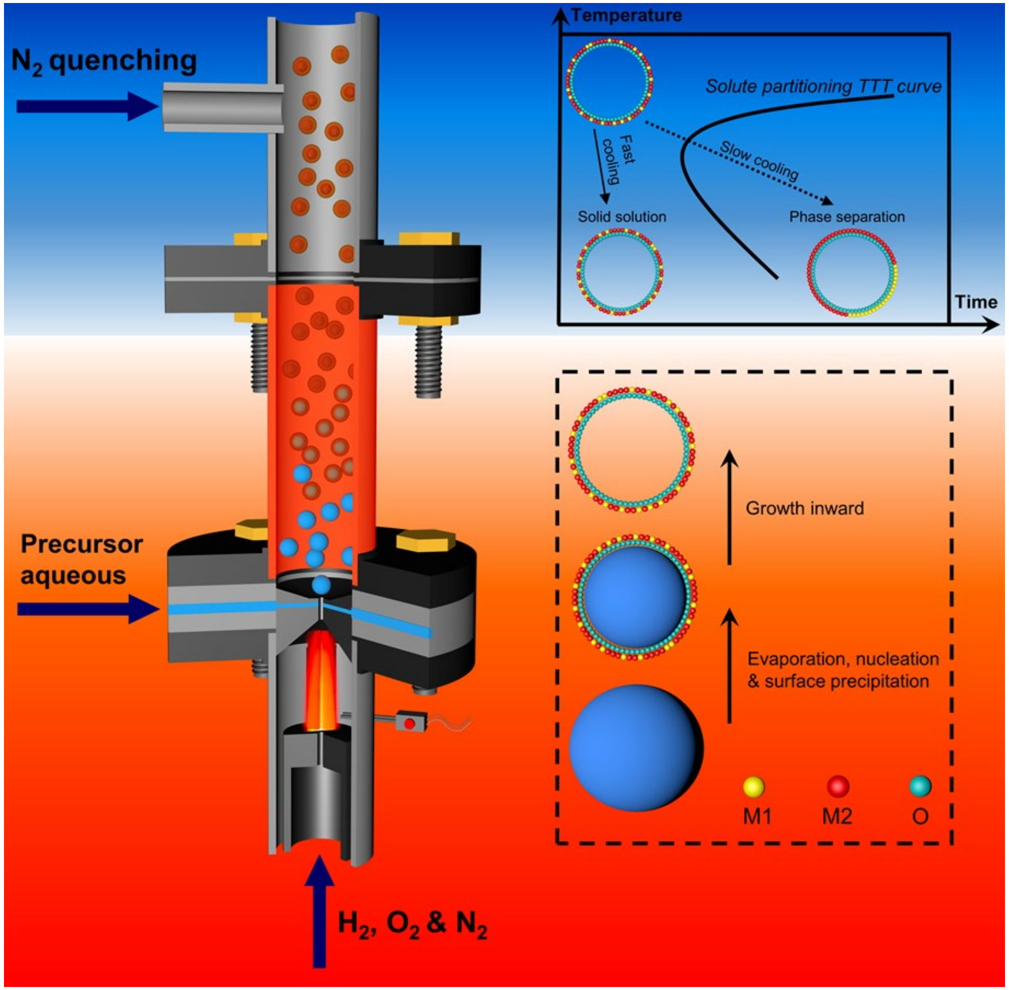
CMR vs PBRs by DGHSV

Feed	H_2 yield (%)	DGHSV (mL/(g h))	
		PBRs	CMRs
Natural Gas	95	7,640	32,200
Natural Gas	97	5,310	21,300
Natural Gas	99	3,120	9,660
Biomass 1	95	4,680	11,200
Biomass 1	97	3,580	7,950
Biomass 1	99	2,300	2,560
Biomass 2	95	3,260	6,520
Biomass 2	97	2,620	4,850
Biomass 2	99	1,800	600

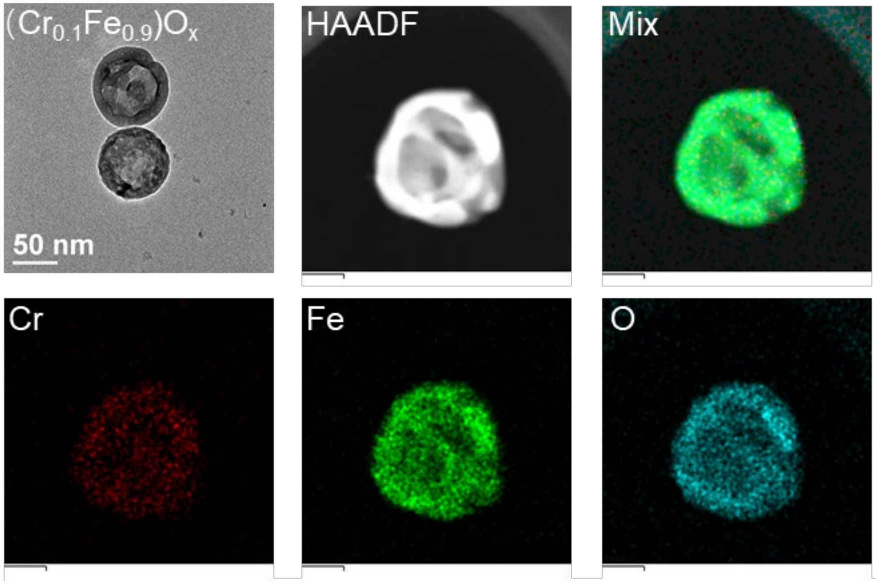
A greater DGHSV indicates a smaller volume

Nano-catalysts for WGS Reaction

Solid solution catalysts design route in the flame aerosol process

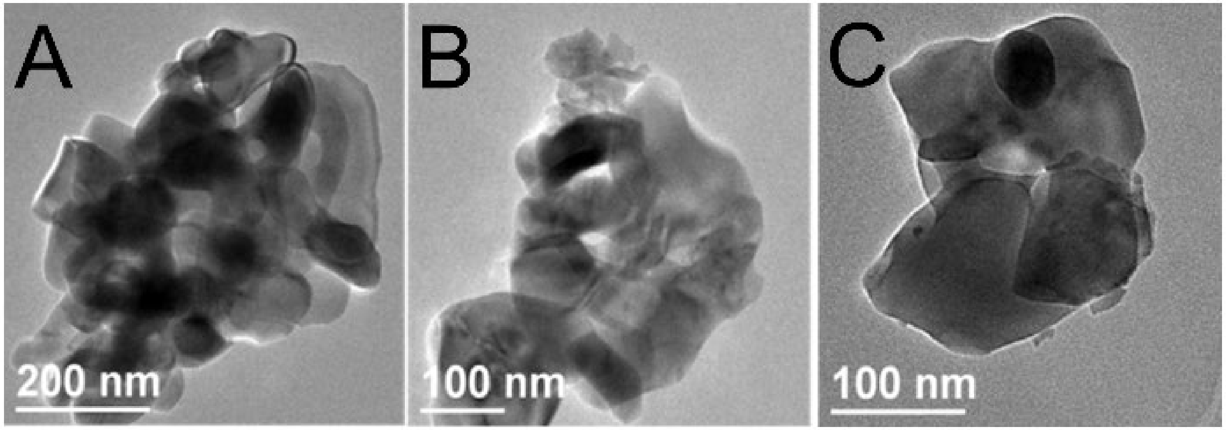


$(CrFe)O_x$ solid solution catalyst

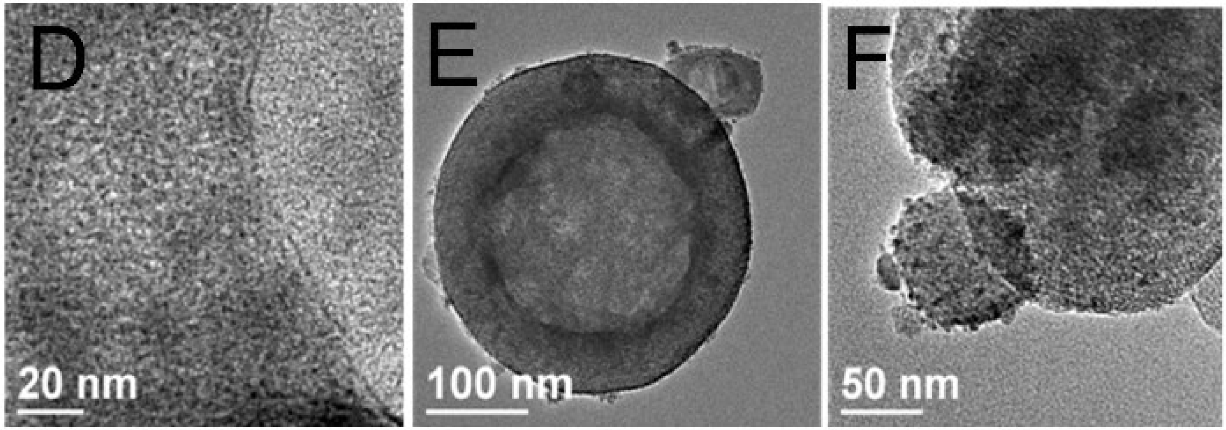


Fe_2O_3-based Catalyst for WGS Reaction

I. Carbon promoted Fe_2O_3 catalyst: prepared in the liquid phase by a sacrificial template method



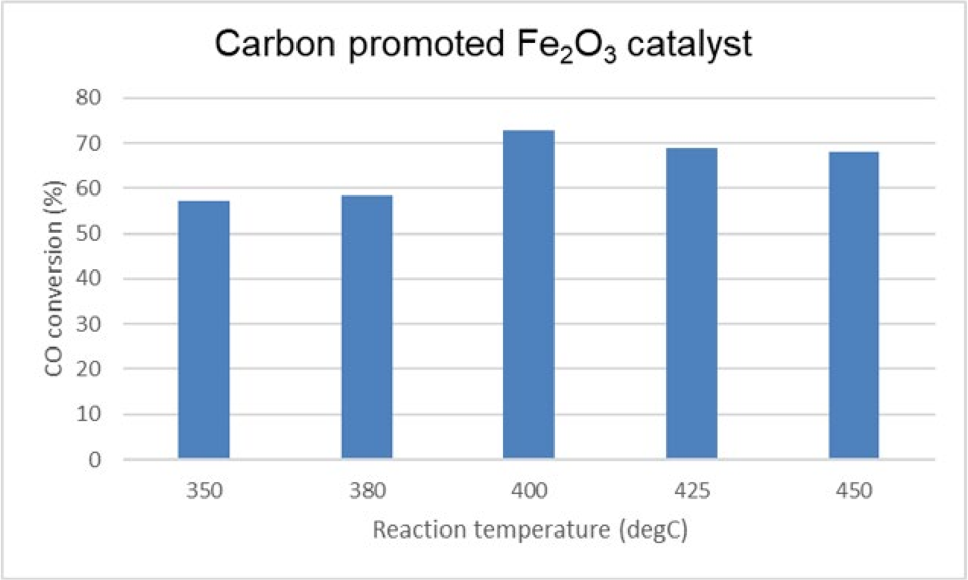
II. Silica-supported Fe_2O_3 catalyst: prepared in a flame aerosol reaction in vapor phase

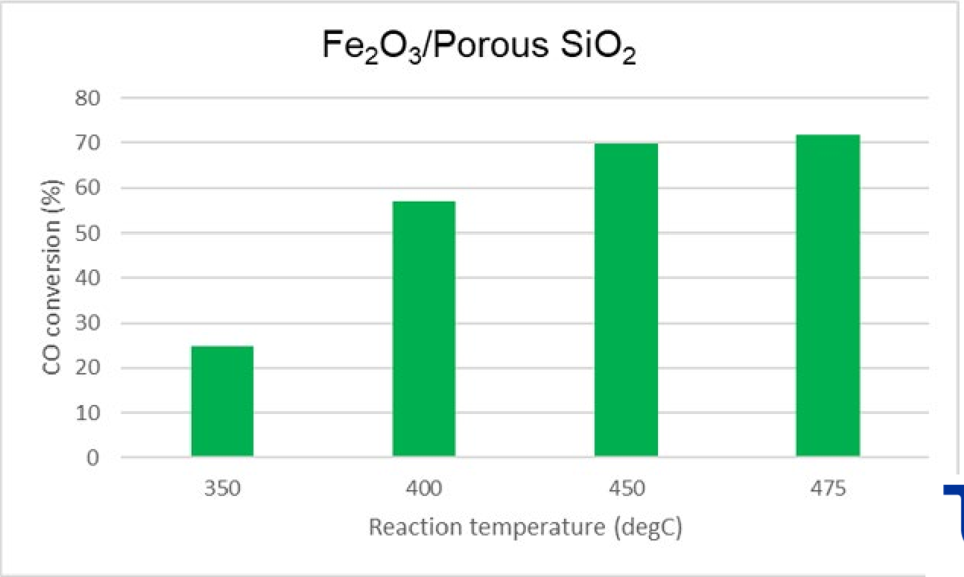


Performance of Two Catalysts

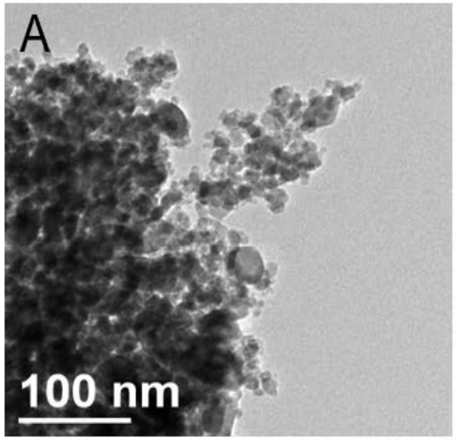
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

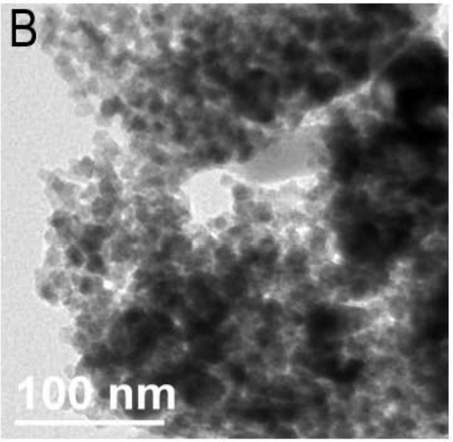
GHSV = 42,000 mL/(g h)

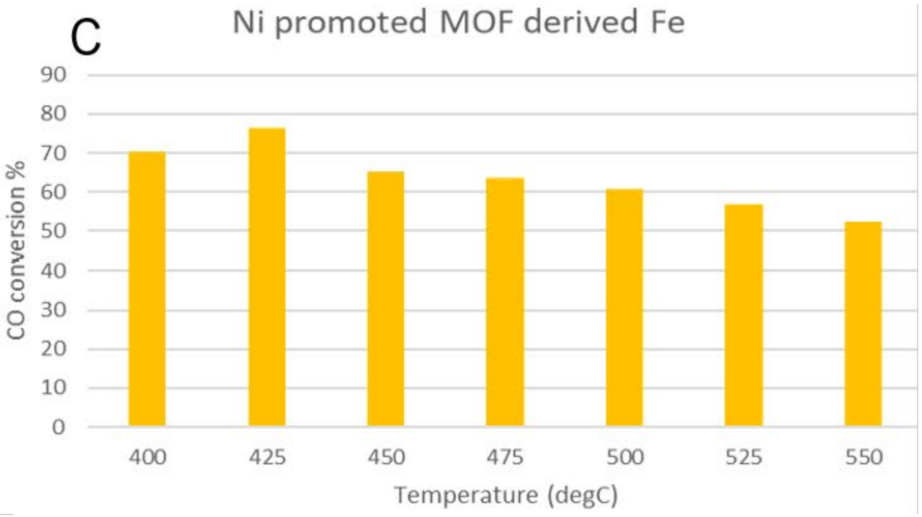


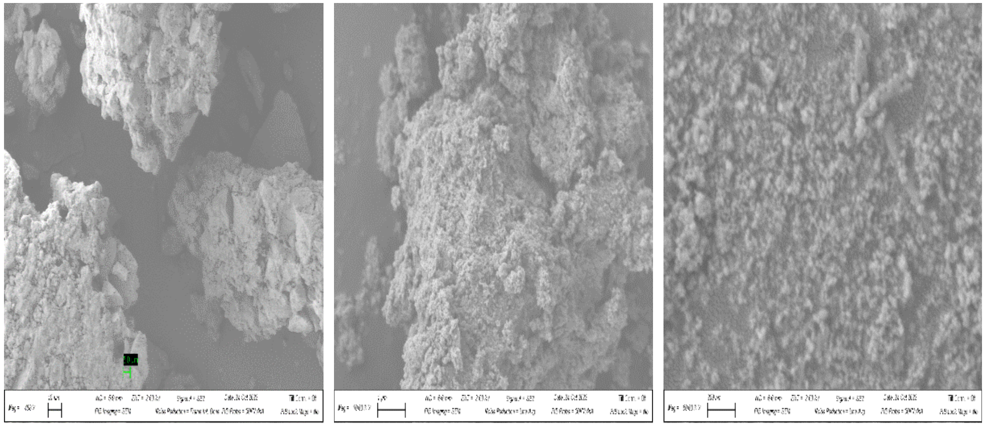


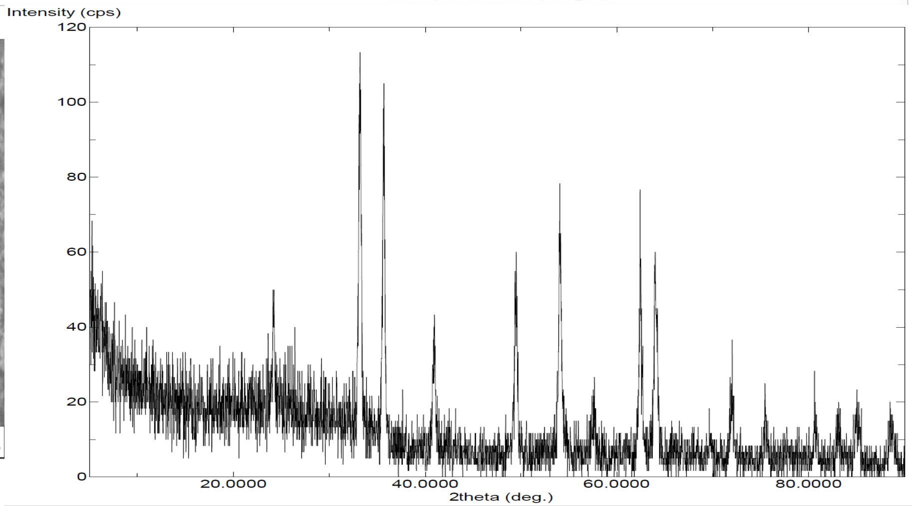
Ni-promoted MOF-derived Fe_2O_3 Catalyst





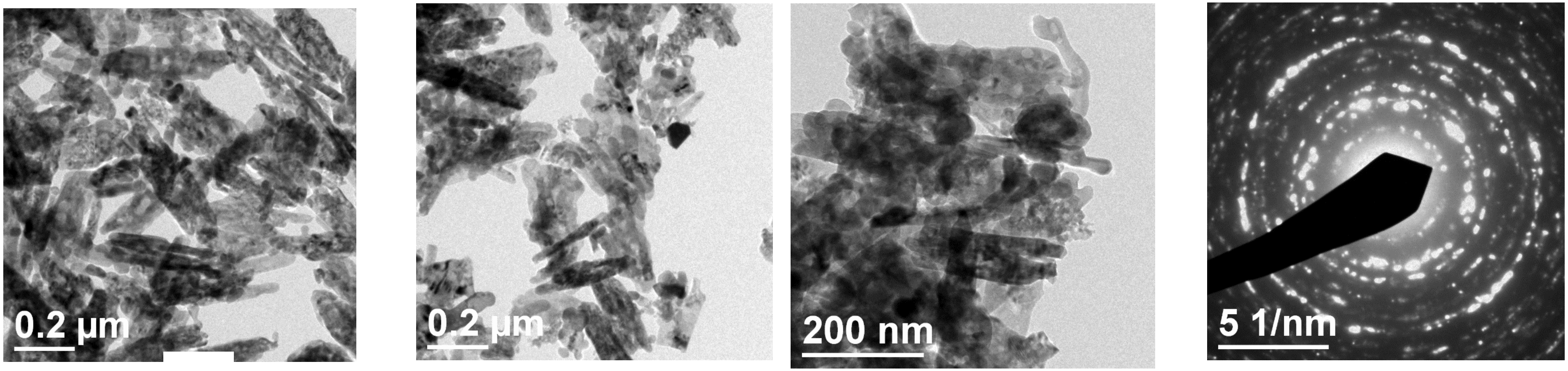


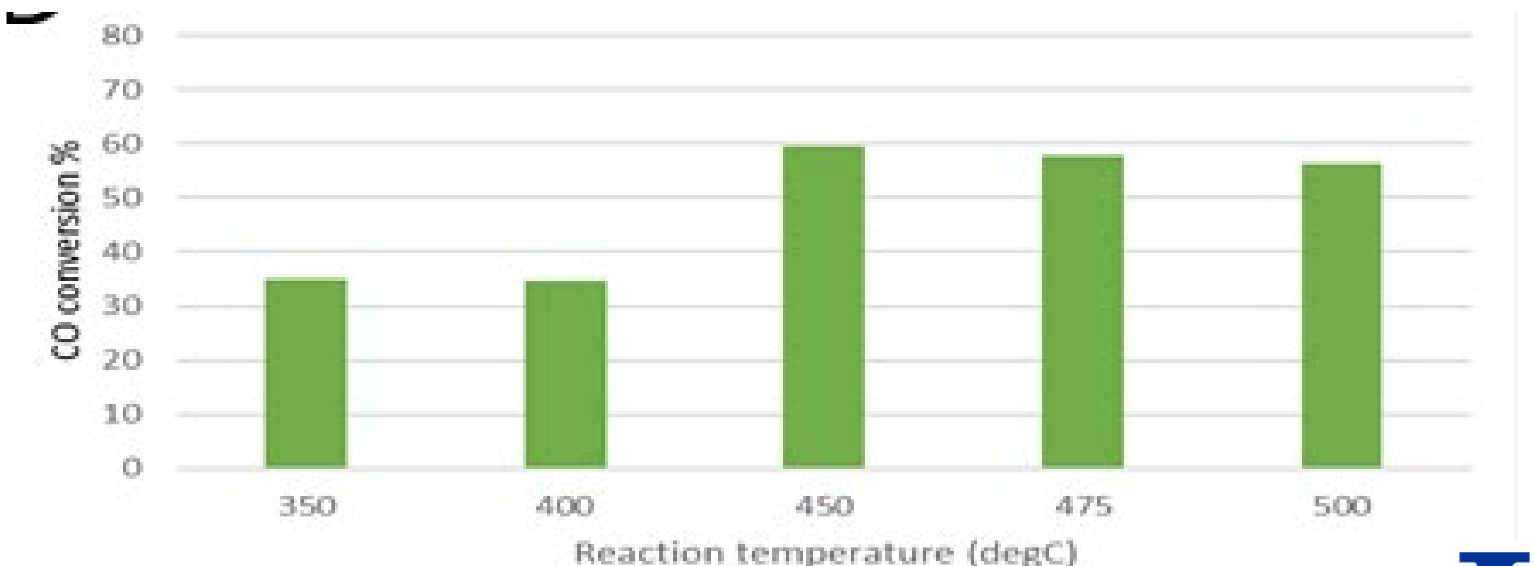




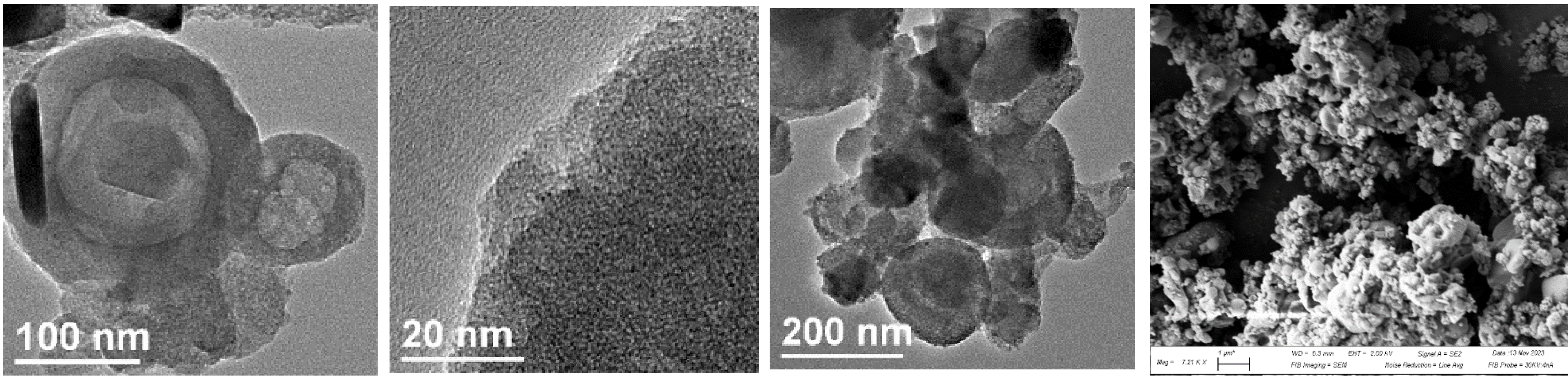
Small particle size and high porosity Lead to better performance

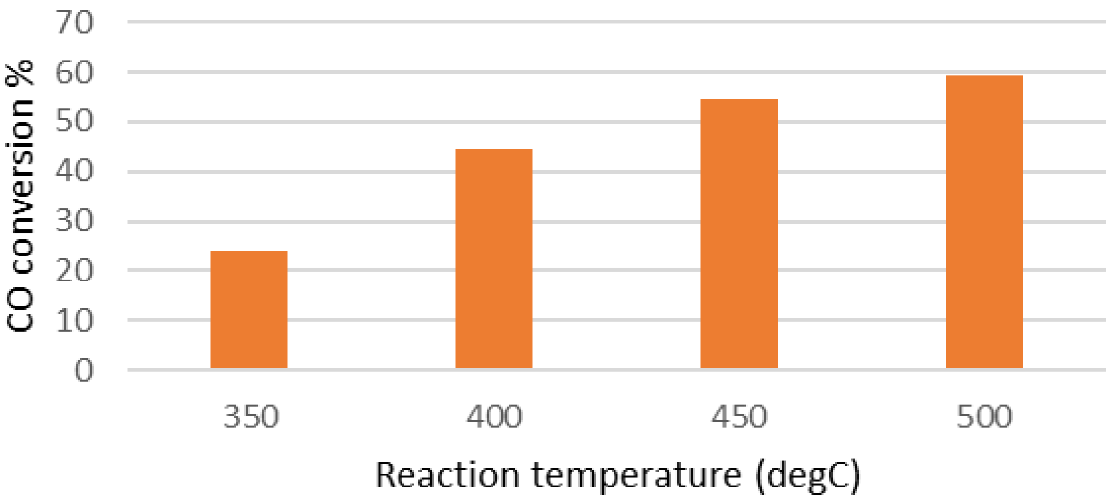
Layer Double Hydroxide-Derived Fe_2O_3





Cu Promoted Fe/SiO_2 Catalyst

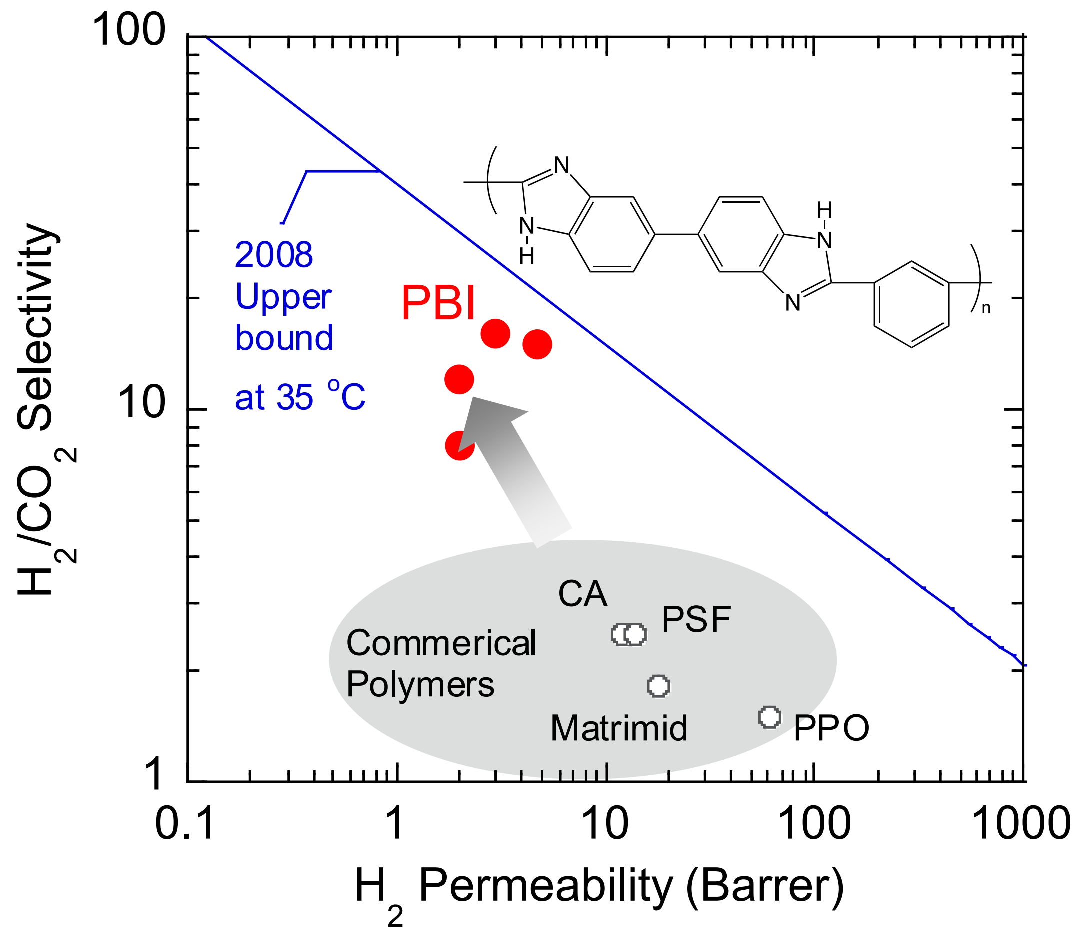




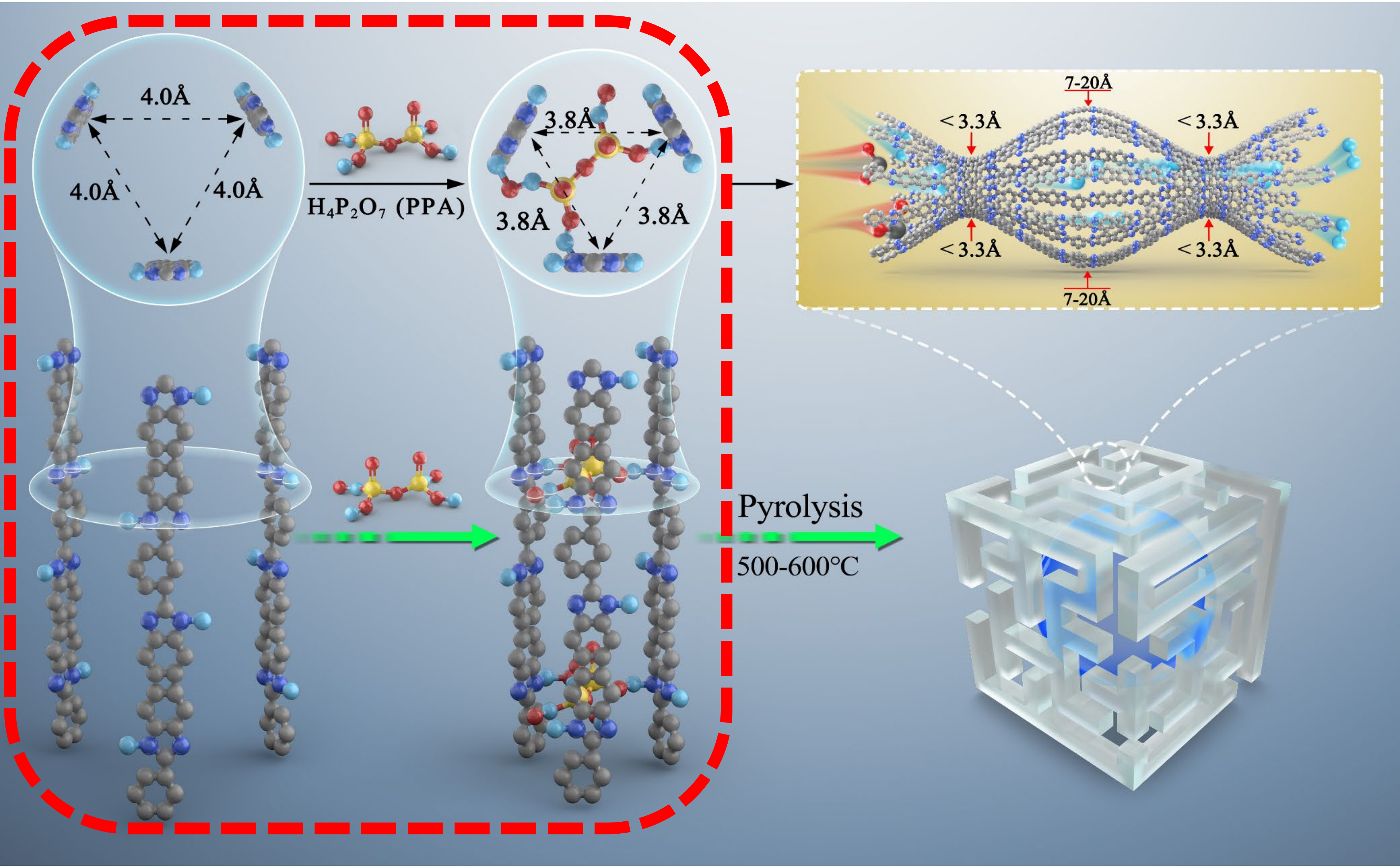
Permeability/Selectivity Tradeoff

	Critical temperature (K)	Kinetic diameter (Å)
H_2	33	2.89
CO_2	304	3.3

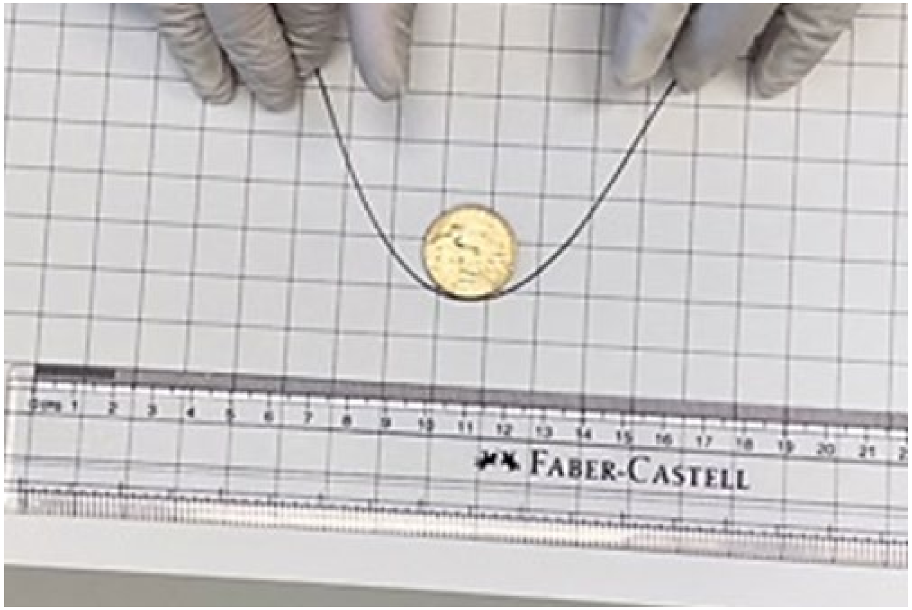
$$\frac{S_{H_2}}{S_{CO_2}} << 1 \quad \text{and} \quad \frac{D_{H_2}}{D_{CO_2}} >> 1$$

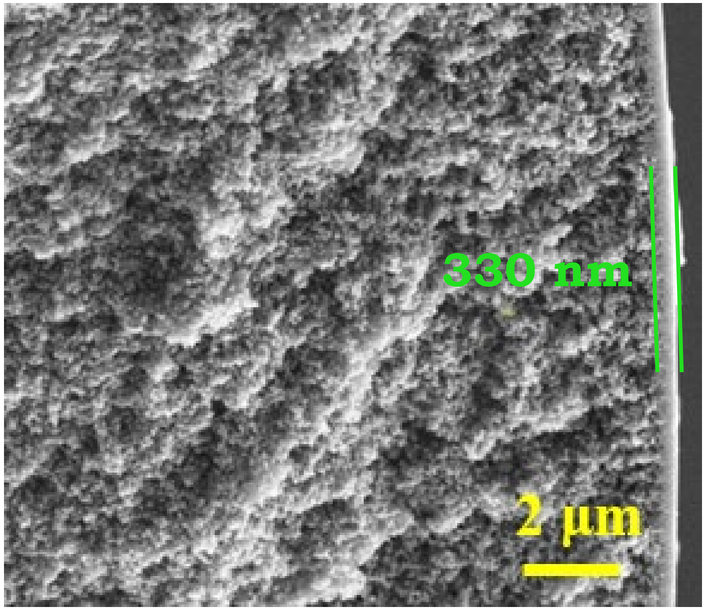


Our Approach: Carbonization of Pyrophosphoric Acid (PAA)-Doped PBI

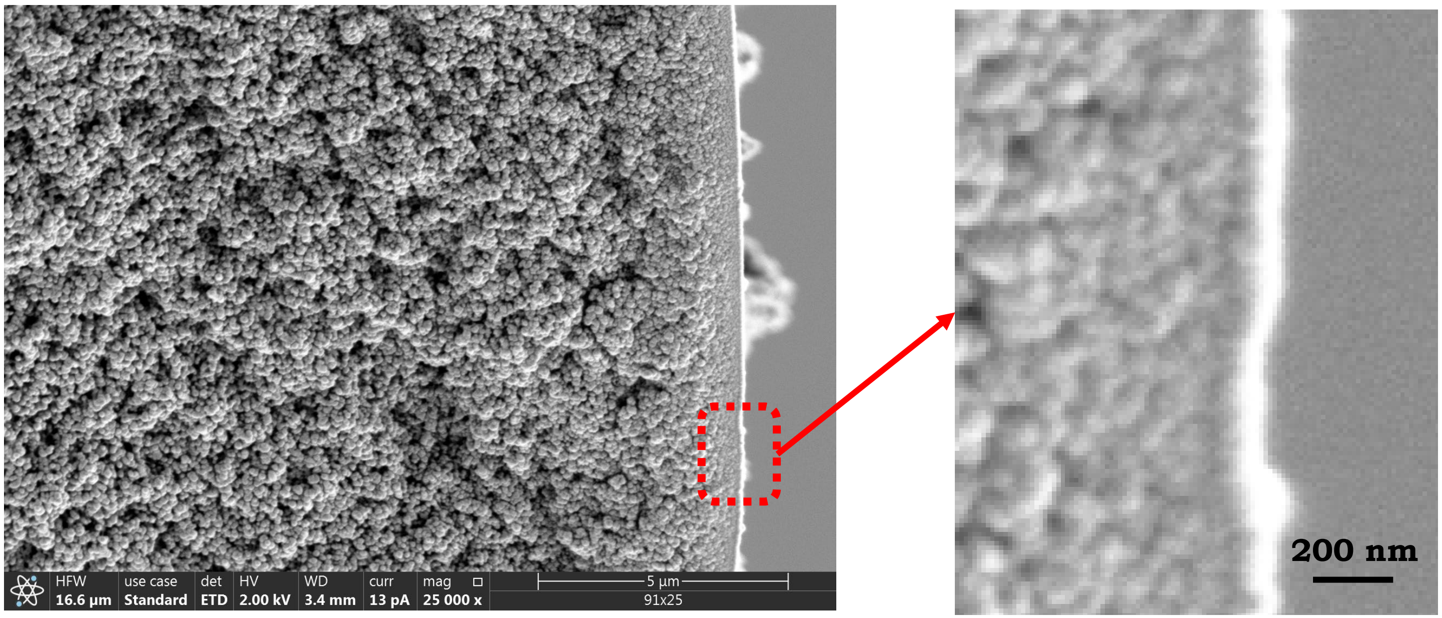


Carbonized PBI Hollow Fiber Membrane (HFM)



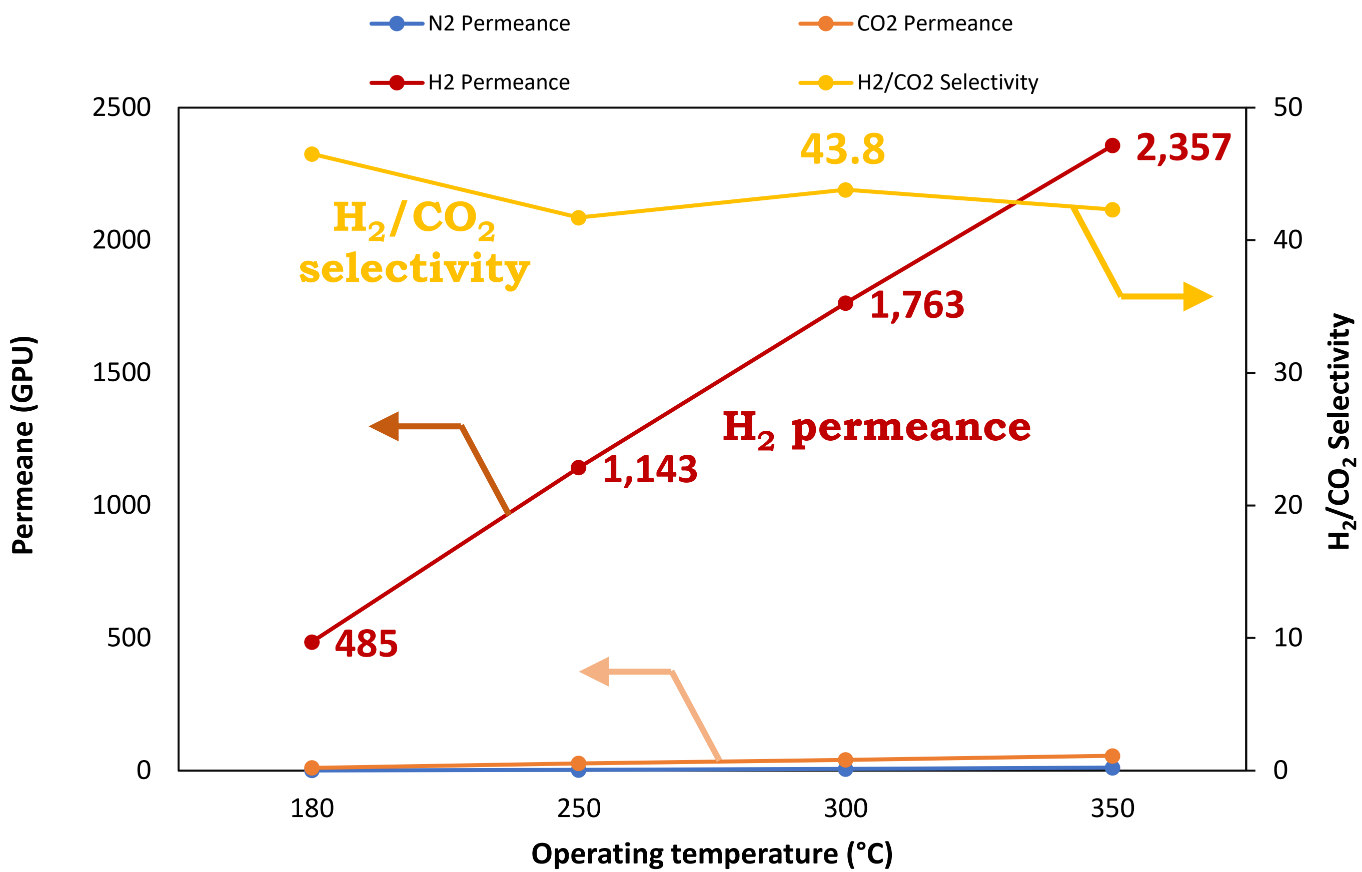


Robust Selective Layer after Carbonization



DBX crosslinked PBI HFM carbonized at 675 ℃

H_2/CO_2 Separation Properties



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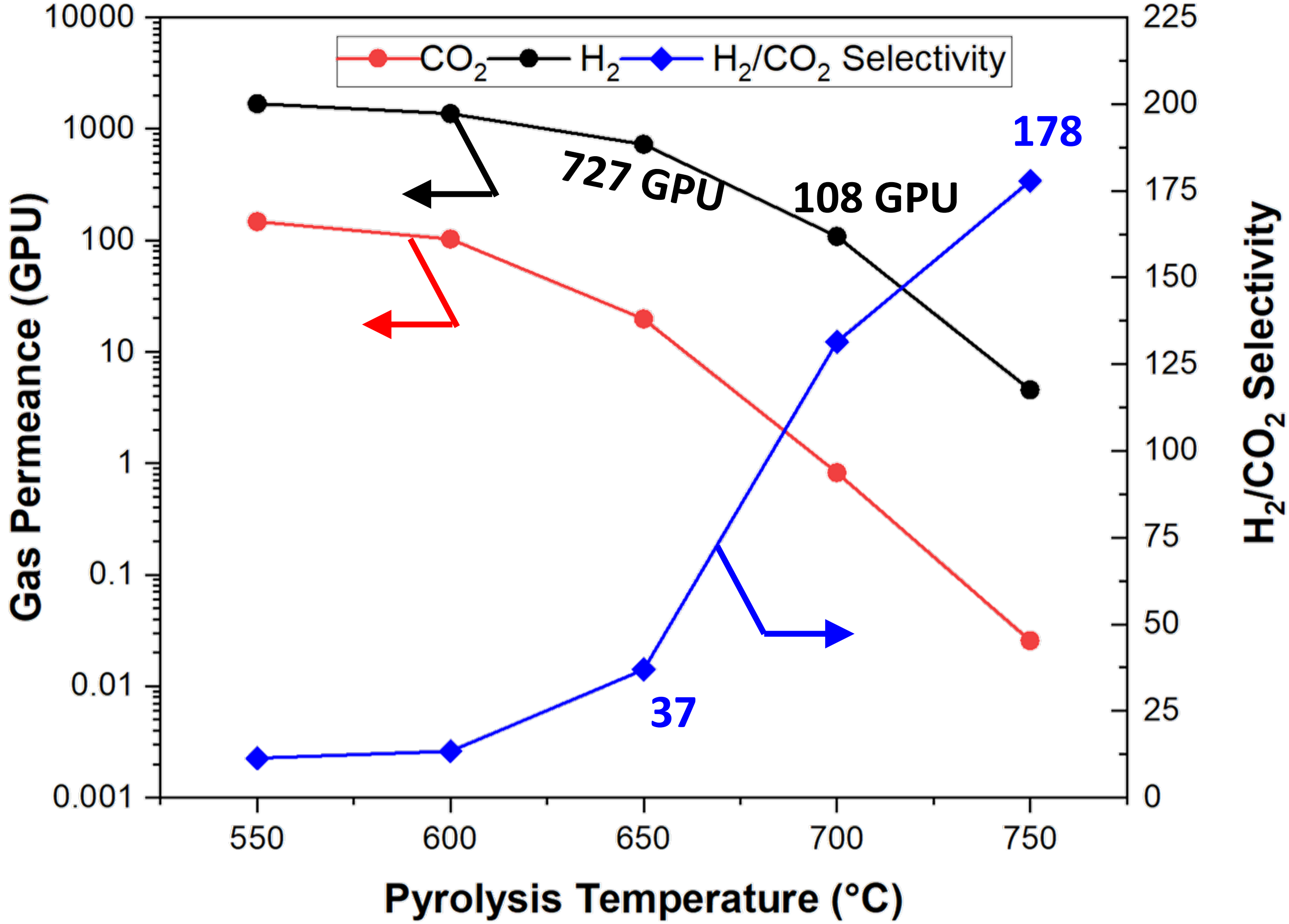
Carbonized Cross-linked PBI HFM

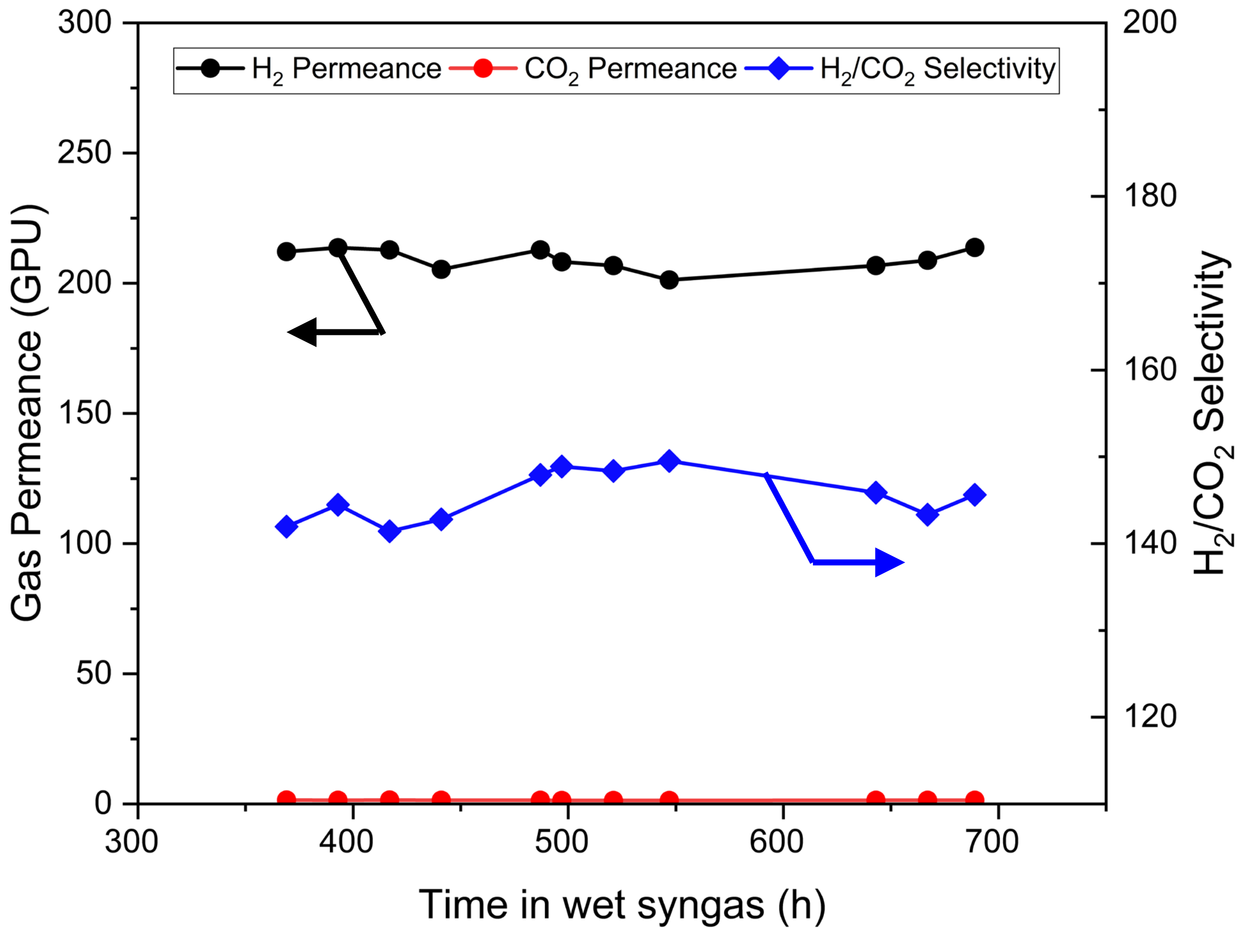
Dibromo-xylene (DBX) crosslinked PBI HFM



Testing at 180 °C

Long-Term Separation Properties

50 psia and 175°C, $H_2/CO_2/H_2O$ (35/35/30 vol.%) for 700 hours



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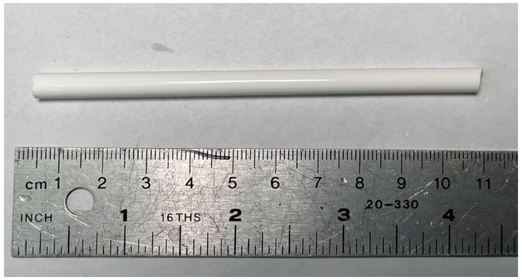
Tubular PBI CMS Membranes

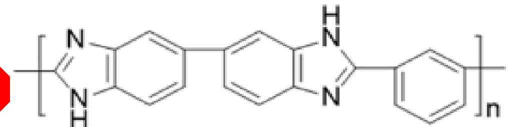
Ceramic tubing
(5.7 mm by 45 cm)



Dip coating

① **2.0 wt% PBI**

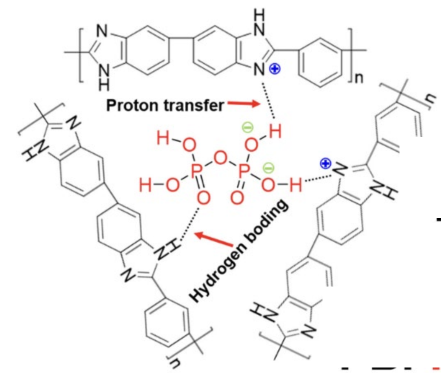
② **0.5 wt% PBI**



PBI

Acid doping

PBI - PPA



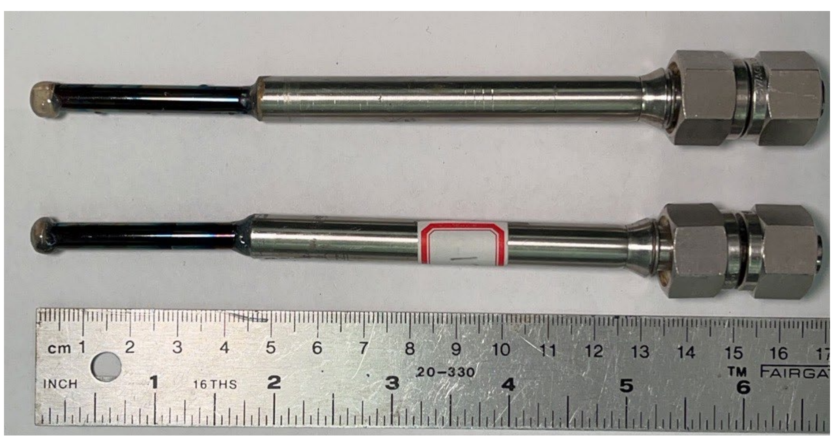
Carbonization

$$20° \xrightarrow{58\ min} 600°$$

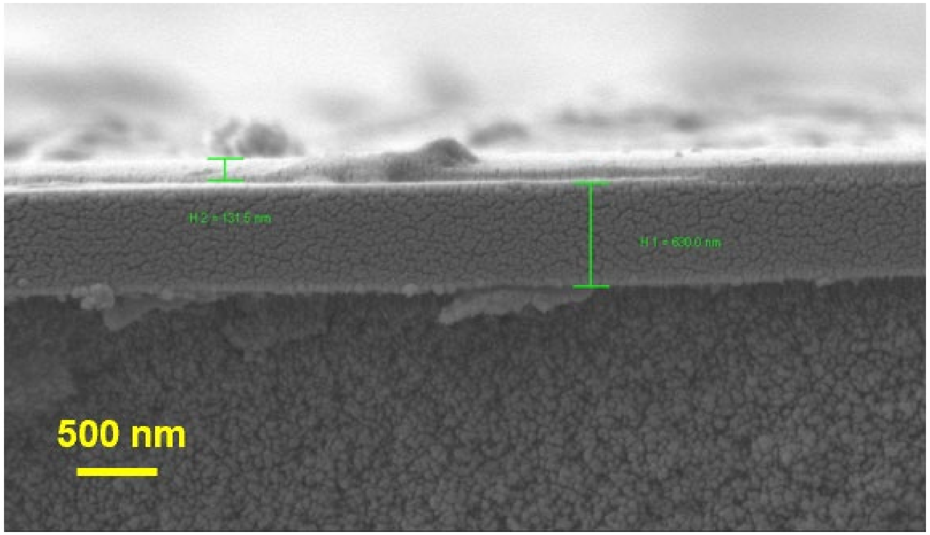
$$600° \xrightarrow{120\ min} 600°$$

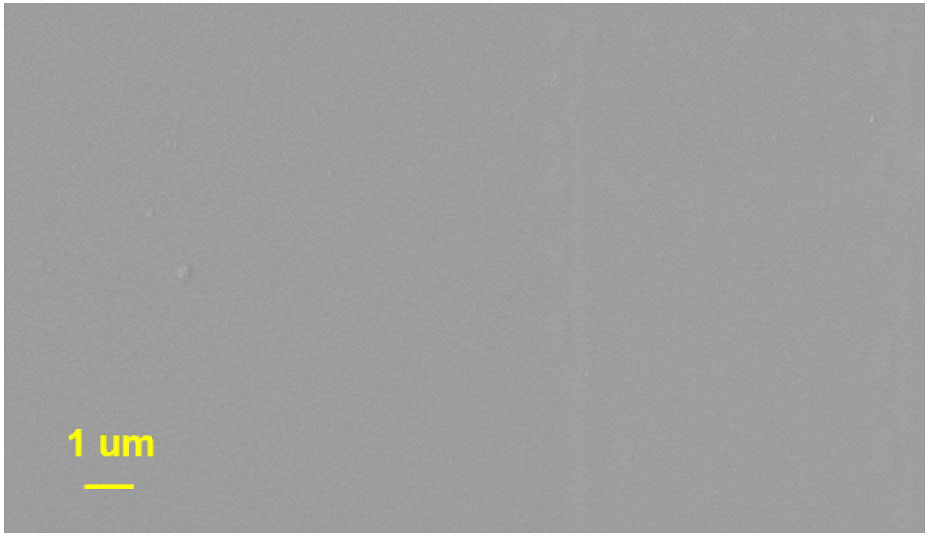
$$600° \rightarrow Room\ T$$

Ceramic-supported PBI CMS membrane

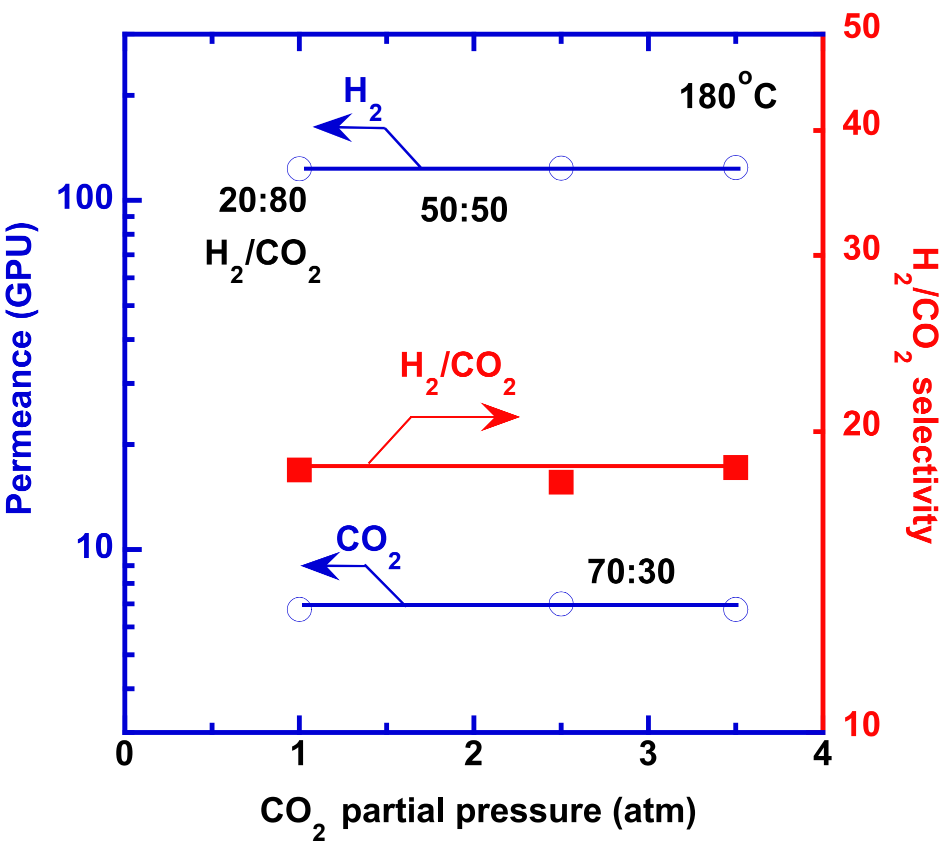


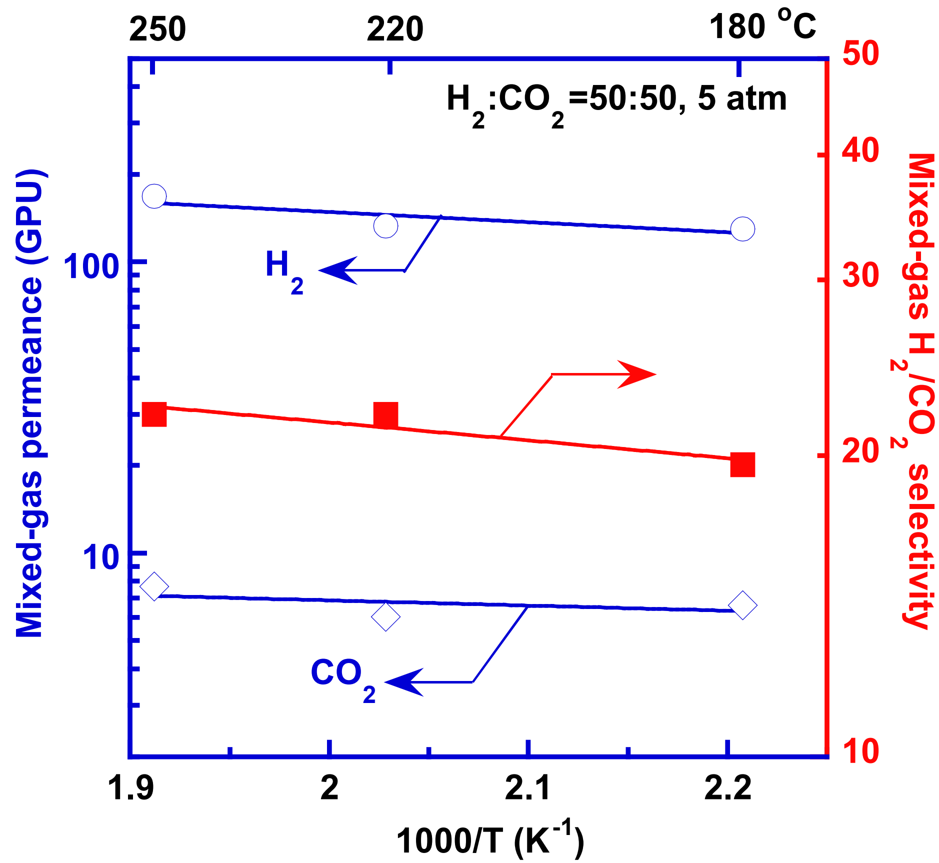
Morphology of Tubular CMS Membrane



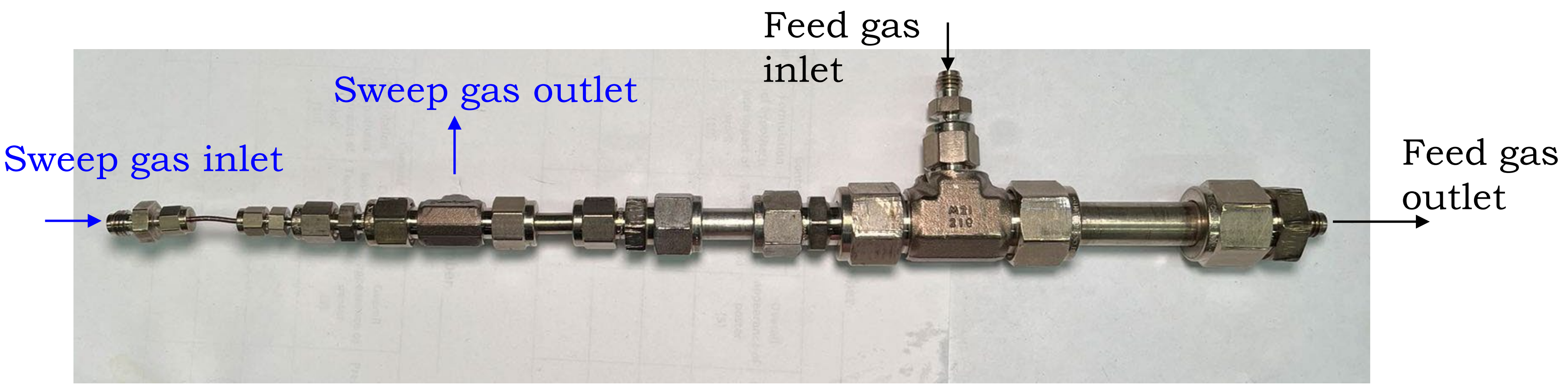


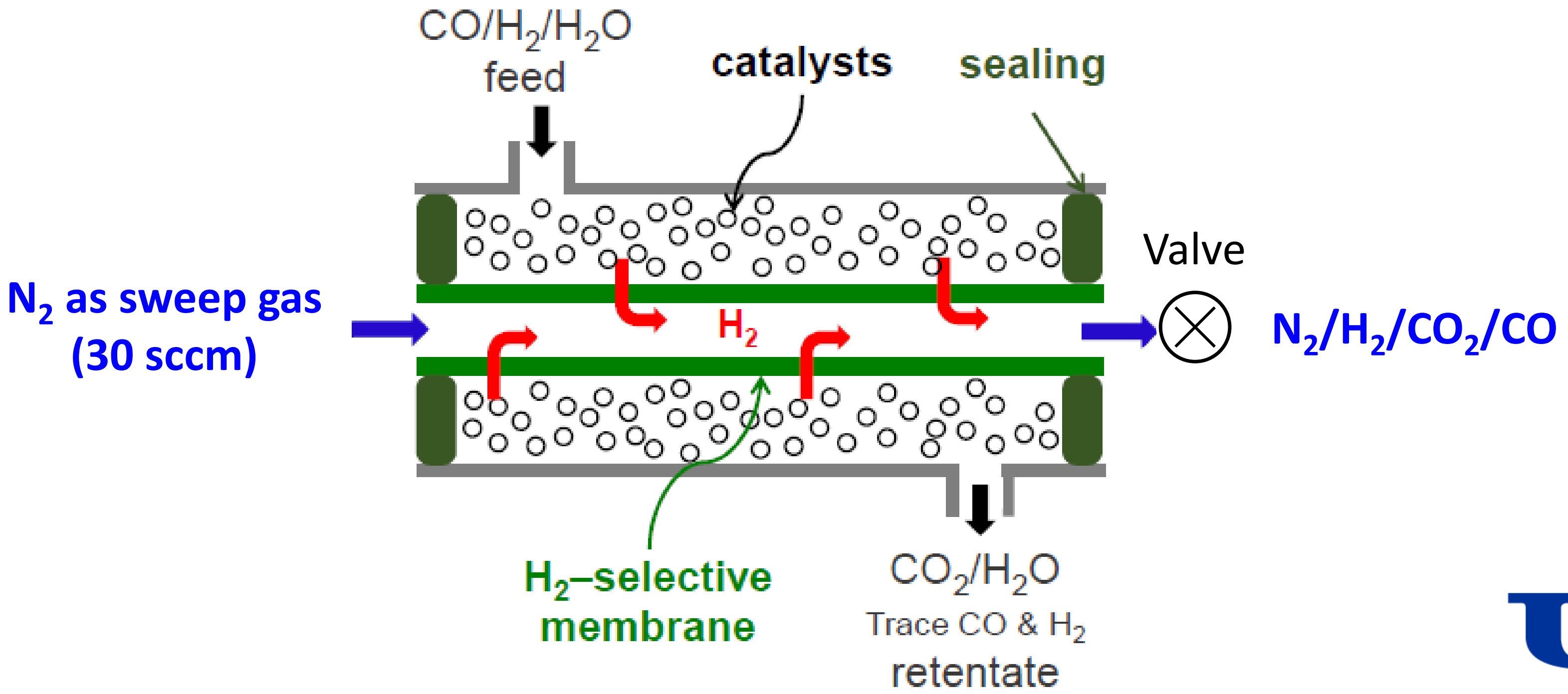
Good H_2/CO_2 Separation Performance





Base Case of Membrane Reactors





Advantage of CMRs

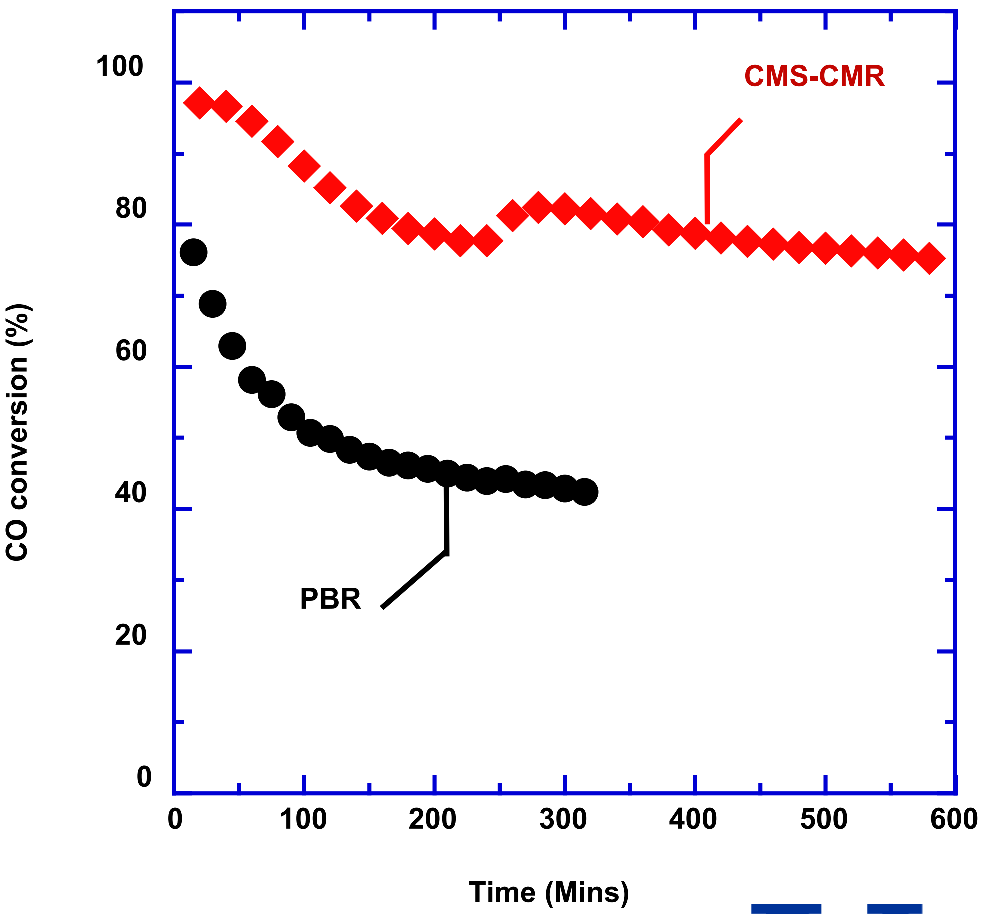
Catalyst: Cu/Zn/Al from Riogen Inc. (25 wt% diluted by SiC)

Feed CO: 50/50 CO/N_2

Temperature: 220 ^oC

Pressure: 30 psig

$\mathbf{H_2 : CO : H_2O}$ = 1 : 1 : 1.5



Status of Project Milestones

ID	Task	Description	Planned Completion Date	Actual Completion Date
M1	**1.1**	**Project Management Plan (PMP)**	**10/31/22**	**10/11/2022**
M2	**1.0**	**Project Kick-off Meeting**	**12/30/2022**	**10/11/2022**
M3	**1.2**	**Technology Maturation Plan (TMP)**	**12/30/2022**	**10/11/2022**
M4	1.4	Environmental Justice Questionnaire	12/29/2024	
M5	**2.0**	**Model for CMRs**	**09/30/2023**	**03/31/2024**
M6	**4.0**	**High-performance WGS catalysts with CO_2 reaction order less than -0.2**	**09/30/2023**	**03/31/2024**
M7	**5.0**	**Membranes with superior H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 100**	**09/30/2023**	**03/31/2024**
M8	**6.1**	**CMRs for the high-temperature WGS reaction with $(CO + CO_2)/H_2 < 0.02$ on the permeate side and $(CO + H_2)/CO_2 < 0.05$ on the retentate side**	**06/30/2024**	
M9	6.2	200-h continuous operation of the CMRs for WGS reaction	07/31/2024	
M10	7.0	Final Techno-Economic Analysis (TEA)	09/30/2024	

Summary

- Our simulation shows that the primary advantage of CMR is to increase DGHSV compared to PBRs
- Various Fe_2O_3-based nano-catalysts exhibit high CO conversion (~78%)
- CMS HFMs shows excellent H_2/CO_2 separation performance meeting the target
- Base case CMRs using tubular membranes demonstrate higher CO conversion than PBRs
- We will focus on the CMR demonstration and TEA study.

Acknowledgement

- DOE NETL
- Program managers
  - John Homer (current)
  - Evelyn Lopez (former)
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