Novel Zeolitic Imidazolate Framework/Polymer Membranes for Hydrogen Separations in Coal Processing

Inga H. Musselman, John P. Ferraris, Kenneth J. Balkus, Jr.

Department of Chemistry, The University of Texas at Dallas

UCR/HBCU Contractors Review Conference
Pittsburgh, PA
May 30-31, 2012

DE-NT0007636 Program Manager: Dr. Richard Dunst

Outline of Talk

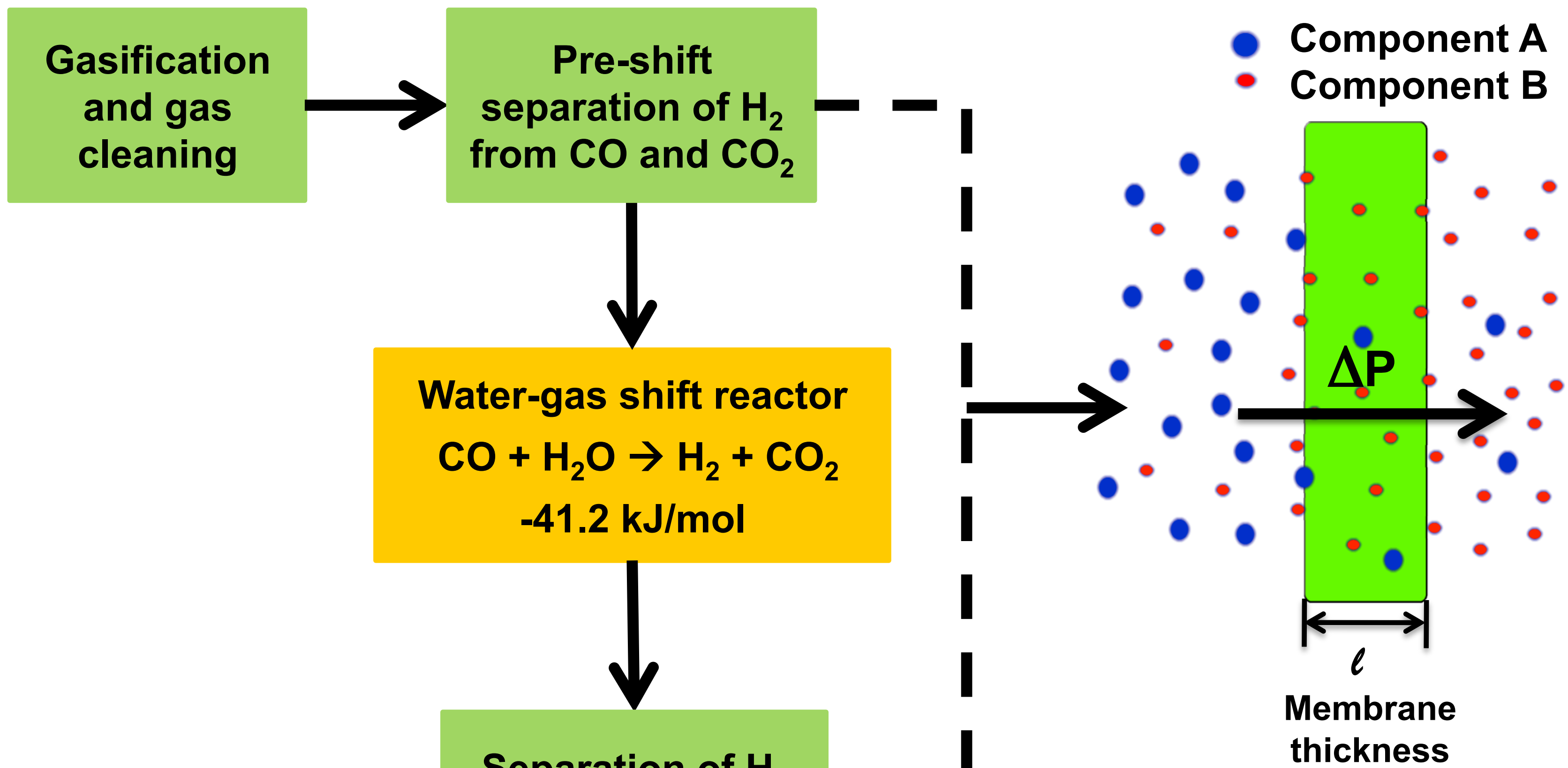
I. Introduction
  i. Hydrogen from coal: H_2 separations
  ii. Mixed-matrix membranes (MMMs)

II. UT-Dallas project objectives and capabilities

III. UT-Dallas results
  i. Polymers, zeolitic imidazolate frameworks (ZIFs), metal-organic frameworks (MOFs)
  ii. Mixed-matrix membrane studies
  iii. Permeability experiments at HPHT
  iv. Cross-linking of polyimides

IV. Summary / Future work

Coal Gasification



Permeability of A = $P_A = S_A D_A$

Selectivity = $\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{S_A}{S_B}\right)\left(\frac{D_A}{D_B}\right)$

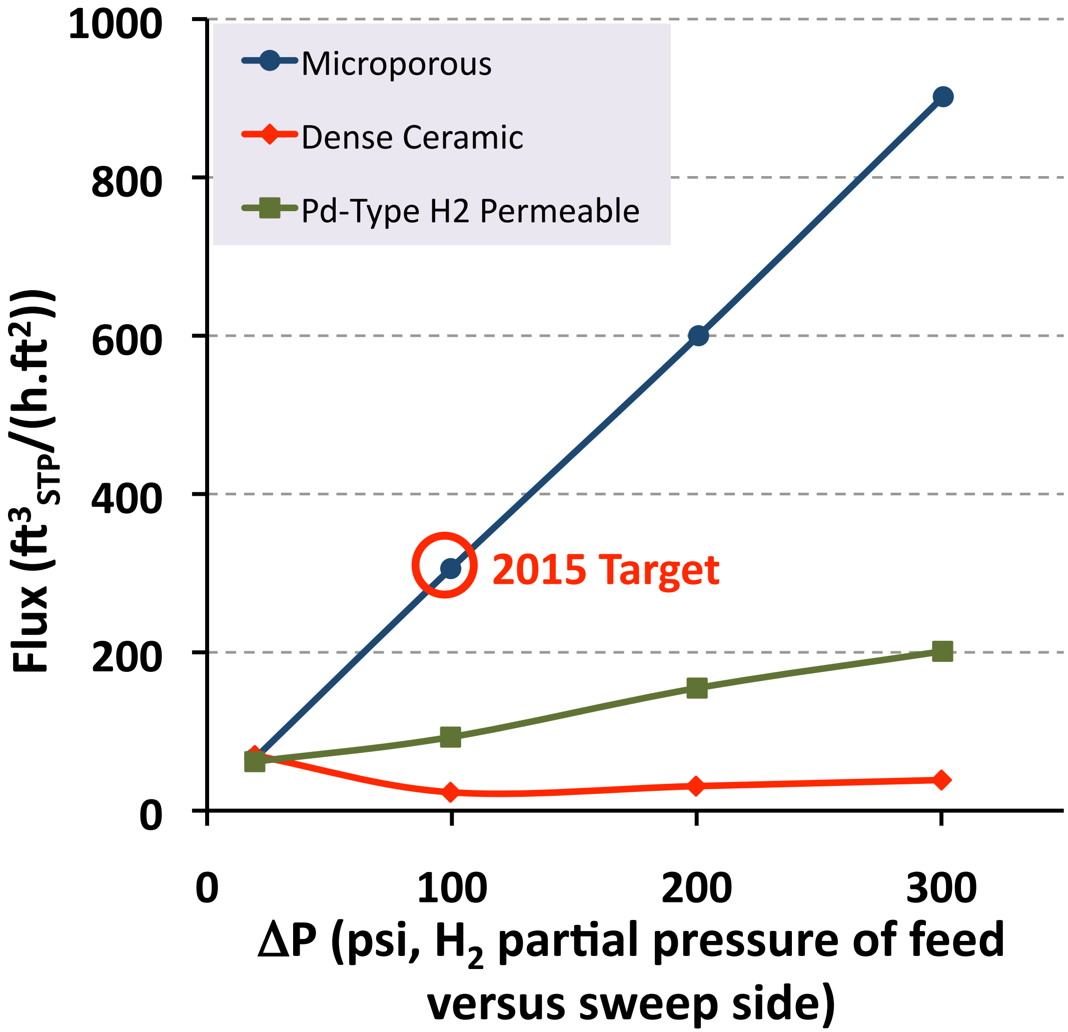
S_A = Solubility coefficient of A

D_A = Diffusion coefficient of A

Mixed-Matrix Membranes

2015 DOE Technical Targets

Microporous membranes show the potential to achieve high H_2 fluxes at low ΔP [1]

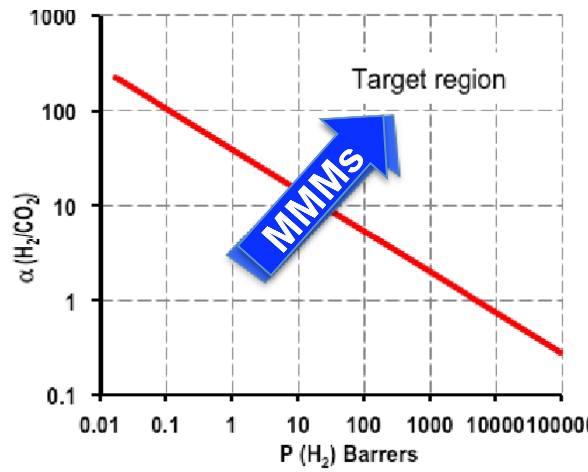


- Hydrogen flux: 300 $ft^3_{STP}/(h.ft^2)$ @ 100 psi ΔP H_2 partial pressure
- Temperature: 250 to 500 °C
- Pressure performance: ΔP 800 to 1000 psi
- Sulfur tolerance: >100 ppm
- CO tolerance
- Water Gas Shift (WGS) activity
- Hydrogen purity: 99.99%

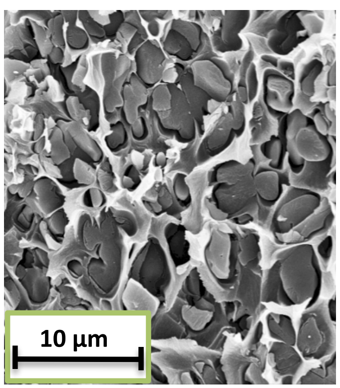
[1] Hydrogen from coal program: Research, development, and demonstration plan, U. S. DOE, 2009

Mixed-Matrix Membranes (Nanoparticle – Polymer Composites)

- **Combine separation properties of inorganic materials with the processability of polymers**
- **Possibility to test materials that would not form membranes themselves**
- **Embrittlement limits loading of inorganic material (~30% (w/w) zeolite)**
- **Matching of component diffusion properties in composites**
- **Challenges with inorganic – organic interface**

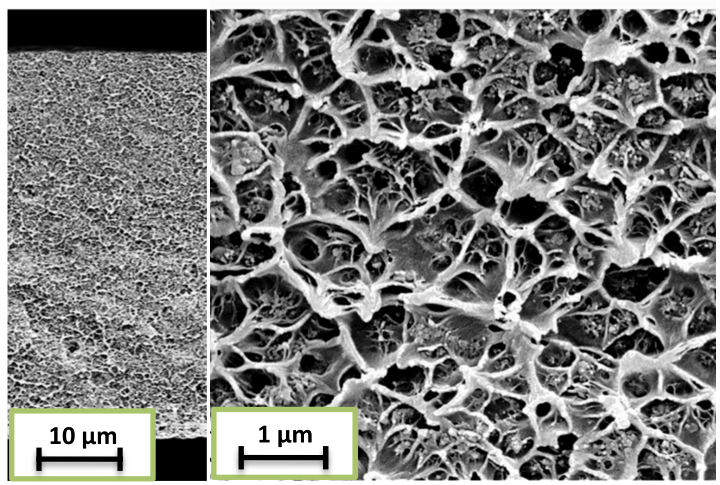


(sieve-in-a-cage problem)



ZIF-95/Matrimid®
Musselman, I.H. *et al.*, **2009**

(good particle/polymer wetting)



MOF-5/Matrimid®
Perez, E.V., *J. Membr. Sci.* **2009**, *328*, 165

UT-Dallas Project Objectives and Capabilities

UT-Dallas project objectives (DE-NT0007636)

- Prepare novel MMMs based on polymer composites with nanoparticles of zeolitic imidazolate frameworks (ZIFs)
  - Synthesis or acquisition of ZIFs
  - Synthesis or acquisition of high performance polymers
  - Fabrication of MMMs
- Evaluate MMMs for separations important to coal gasification (e.g. H_2, CO, O_2, CO_2)
- Test performance of MMMs under operating conditions defined by 2015 DOE targets
  - Construction of high pressure-high temperature permeameter

UT-Dallas Membrane Team

Dr. Inga H. Musselman, Professor

Ph.D. Analytical Chemistry, U. of North Carolina

imusselm@utdallas.edu

http://www.utdallas.edu/chemistry/faculty/musselman.html

Dr. John P. Ferraris, Professor

Ph.D. Organic Chemistry, The Johns Hopkins University

ferraris@utdallas.edu

www.utdallas.edu/~ferraris

Dr. Kenneth J. Balkus, Jr., Professor

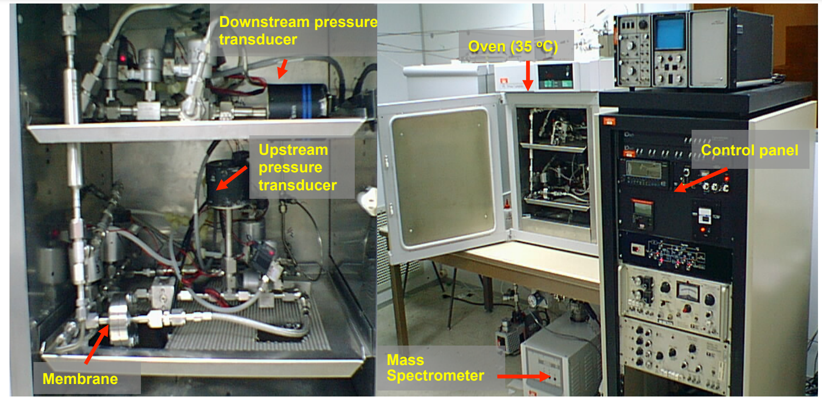
Ph.D. Inorganic Chemistry, University of Florida

balkus@utdallas.edu

www.utdallas.edu/~balkus

UTD Mixed-Matrix Membranes

UT-Dallas Membrane Lab



4 Custom-built permeameters

- 35 °C and 3 bars
- Flat, hollow fiber, and tubular membranes

Custom-built high pressure, high temperature permeameter (HPHT)

- ≤ 300 °C and ≤ 30 bars
- Flat and hollow fiber membranes

High pressure volumetric analyzer (adsorption studies)

- ≤ 350 °C and ≤ 100 bars

Tools for membrane preparation

- Resodyn LabRam® Acoustic Mixer
- Automatic Film Applicator

Characterization instrumentation:

- X-Ray Diffractometer (XRD)
- Atomic Force Microscope (AFM)
- Scanning Electron Microscope (SEM)
- Thermal Gravimetric Analyzer (TGA)
- Differential Scanning Calorimeter (DSC)

A 1,000 ft^2 membrane facility is currently under construction.

UT-Dallas Results

Polymers
Zeolitic Imidazolate Frameworks
Metal Organic Frameworks

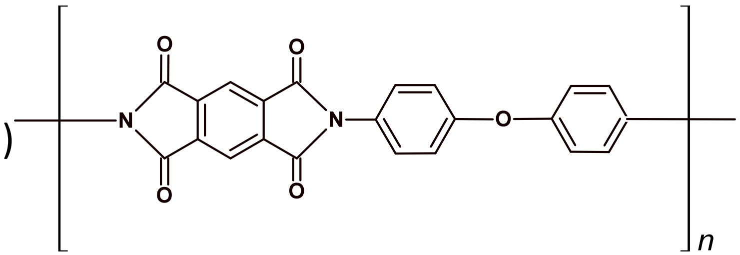
UTD Mixed-Matrix Membranes

Polymers for MMMs

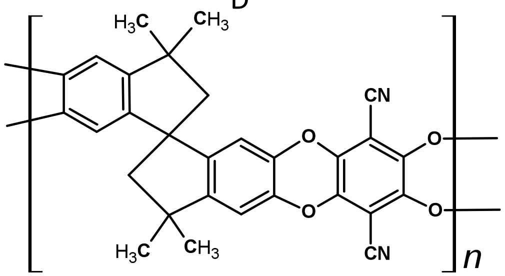
Polymers

- Stable above 300 °C
- Processable
- Separation properties close to upper bound (H_2/CO_2 separation)
- Stability to H_2O (steam), CO, and H_2S

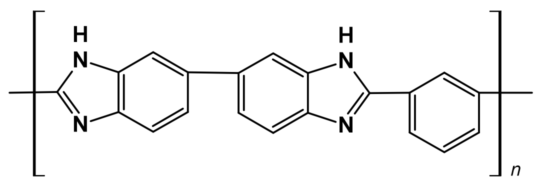
VTEC (similar to Kapton): T_g > 500 °C



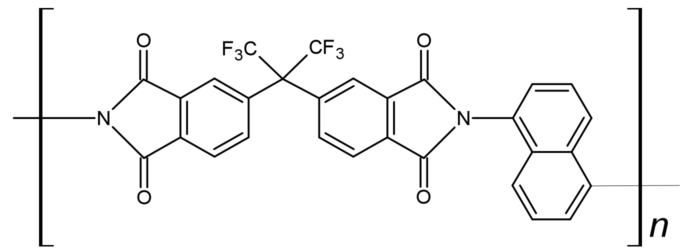
PIM-1: T_D > 600 °C



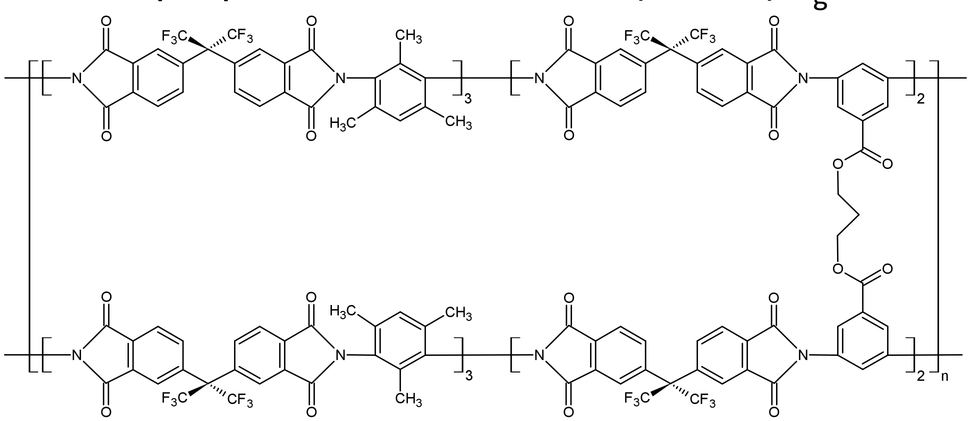
PBI: T_g > 450 °C



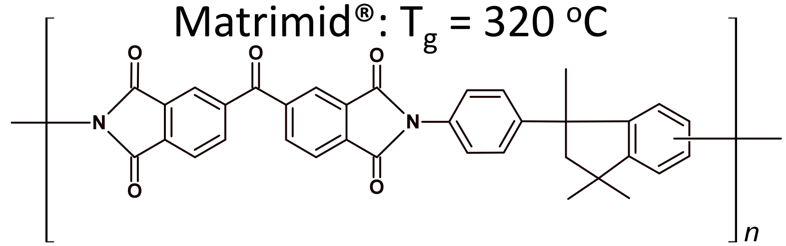
6FDA-NDA: T_g = 430 °C



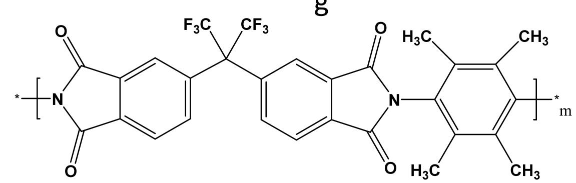
Cross-linked propane diol monoester (CPDM) T_g = 360 °C



Matrimid®: T_g = 320 °C



6FDA-durene: T_g = 425 °C



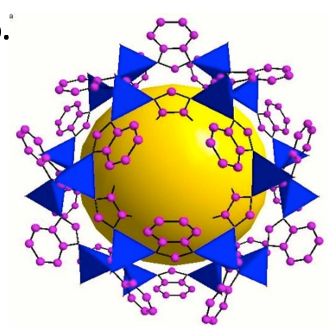
ZIFs/MOFs for H_2 Separations

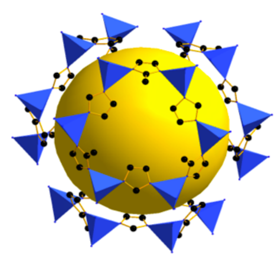
Inorganic Additive

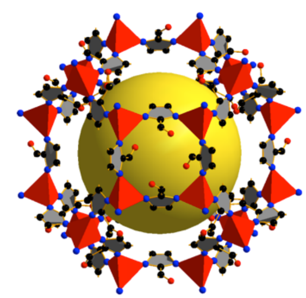
- Stable above 300 °C
- Stable to H_2O (steam), CO, and H_2S
- Fabricated as nanoparticles
- Controlled pore size
- Have strong interaction with polymer

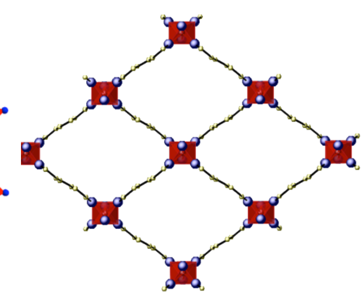
ZIF	Pore Size (nm)	Pore Aperture (nm)	Sieving
ZIF -7	0.90	0.30	H_2
ZIF-8	1.10	0.34	H_2
ZIF-90	1.12	0.35	H_2
MIL-53-lt	n/a	0.28	H_2
SIM-1	0.80	<0.34	H_2

	Kinetic Diameter	Critical Temp.
N_2	0.36 nm	-147 °C
O_2	0.34 nm	-118.4 °C
CH_4	0.38 nm	-82.1 °C
CO_2	0.33 nm	31 °C
H_2	0.28 nm	-232.6 °C


ZIF-7


ZIF-8

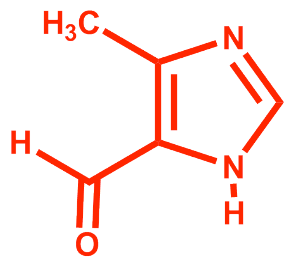

ZIF-90

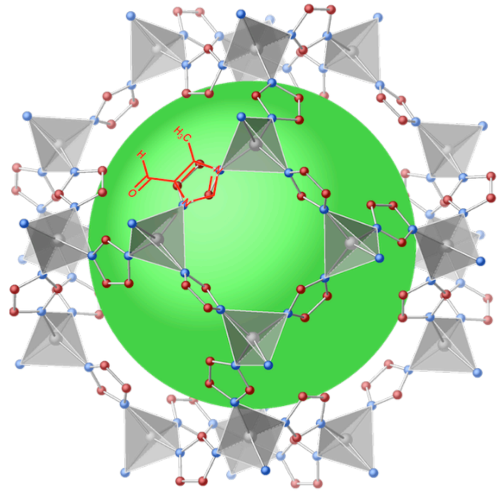

MIL-53

UTD Mixed-Matrix Membranes

Substituted Imidazolate-based MOF (SIM-1)

+

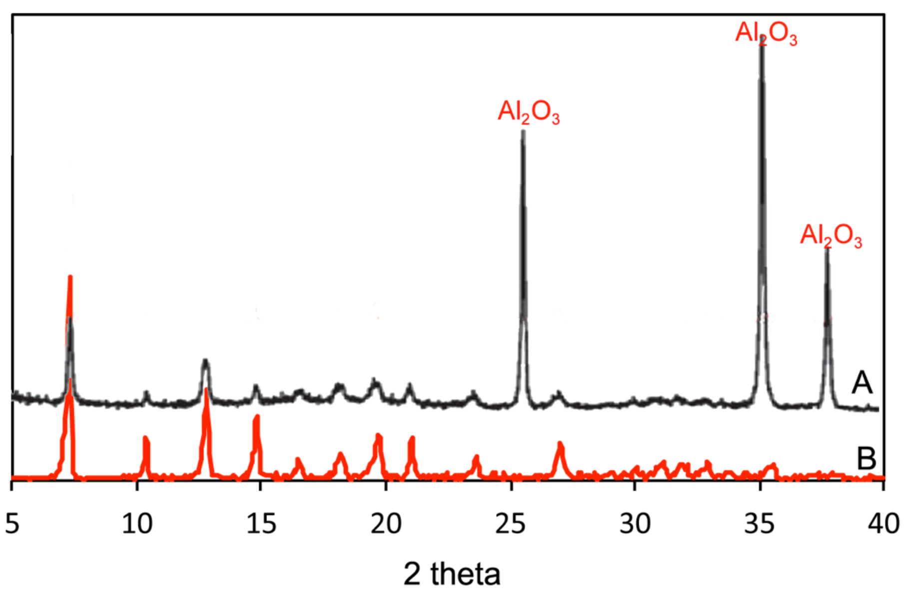


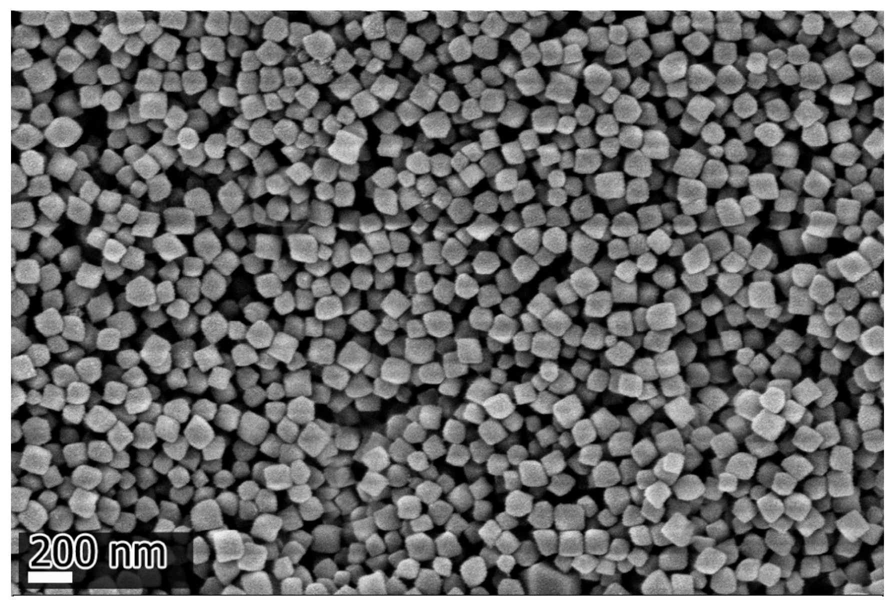


- cage size: 8.0 Å
- pore aperture: < 3.4 Å
- surface area: 450 m^2/g
- stable to 400 ^oC

Zn cluster

4-methyl-5-imidazole carboxaldehyde

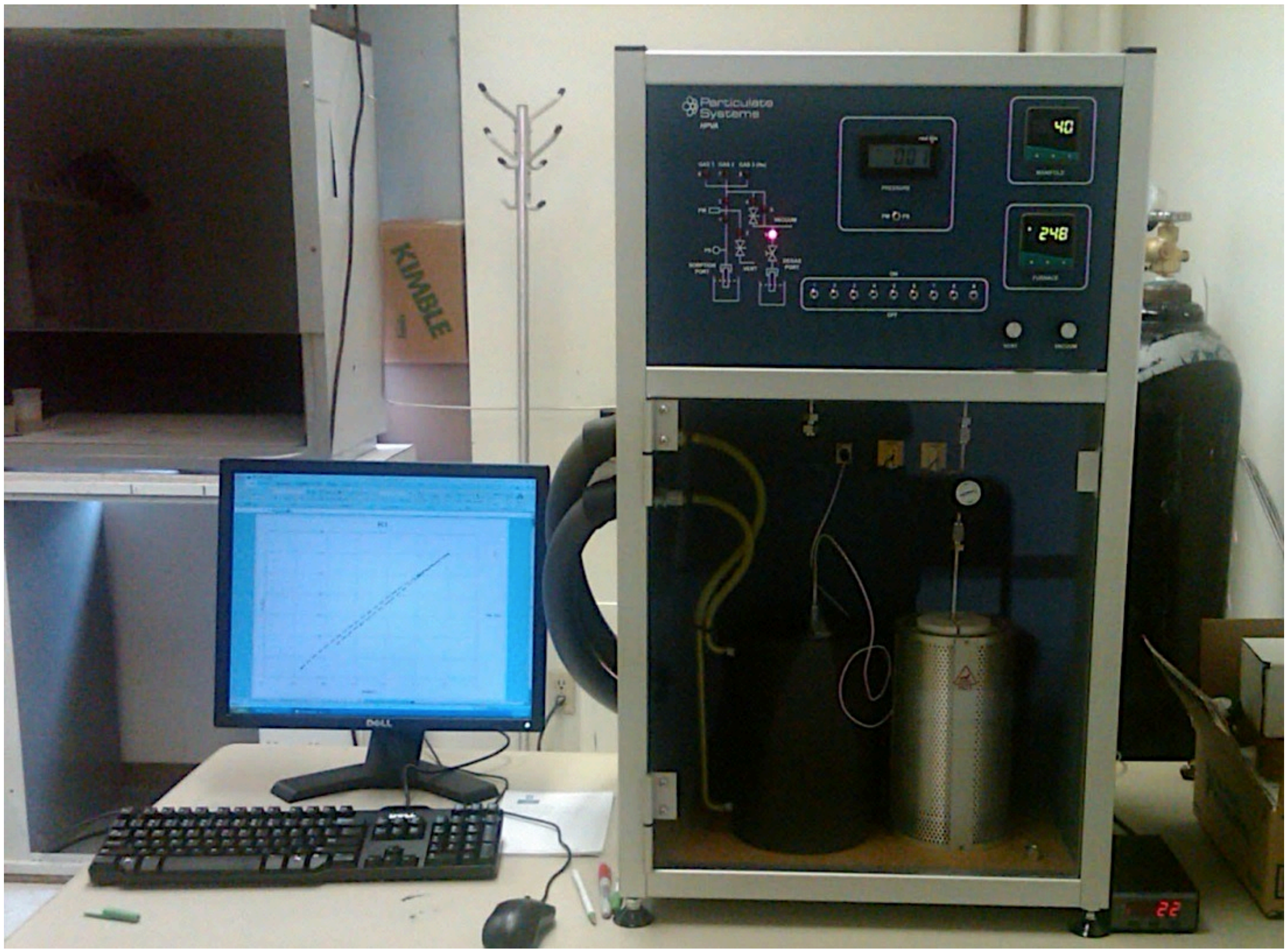




Aguado, S.; Canivet, J.; Farrusseng, D., *Chem. Commun.* **2010,** *46* (42), 7999-8001

Adsorption Studies of ZIFs

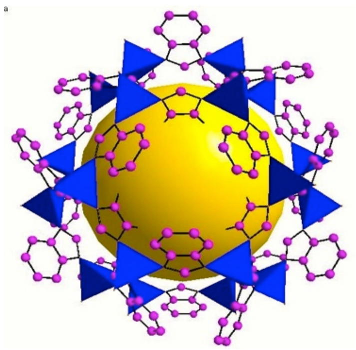
High Pressure Volumetric Analyzer (HPVA-100, Micromeritics)

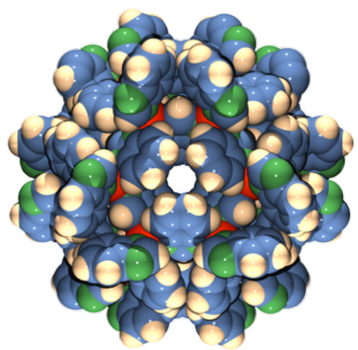


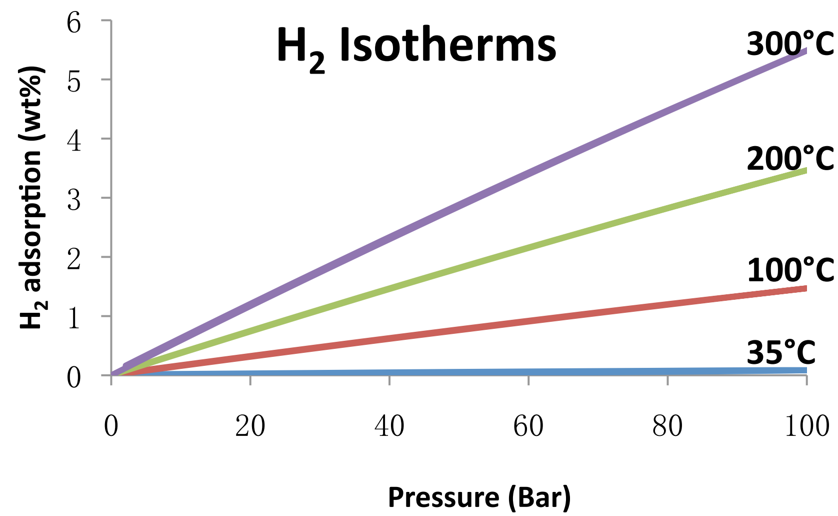
Temp. 0 - 300 ^{o}C

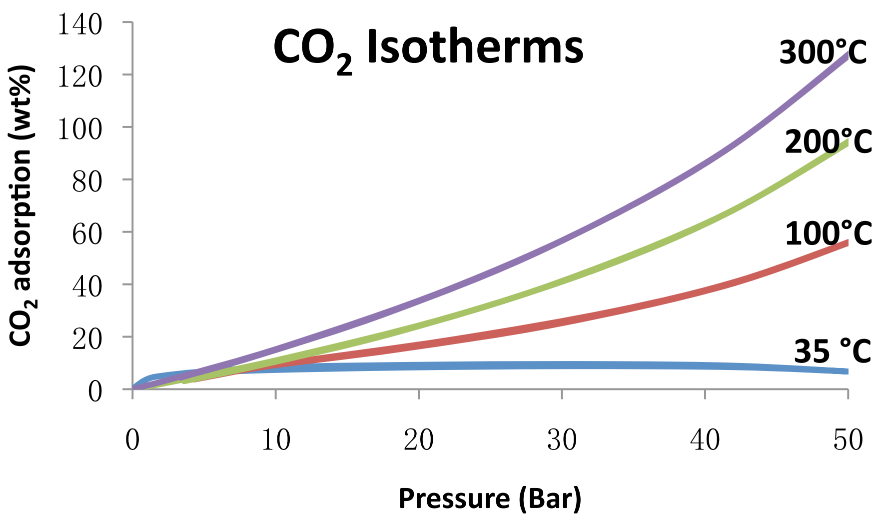
Pressures 3 - 100 bars

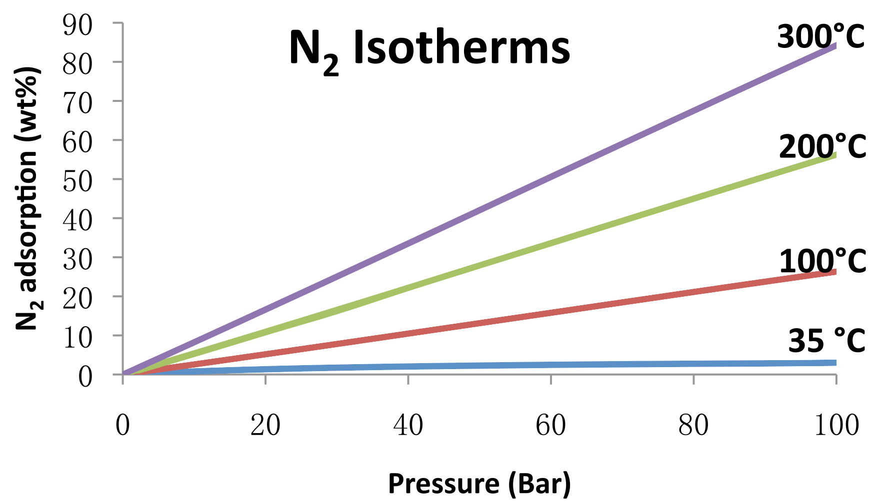
Gas Sorption in ZIF-7





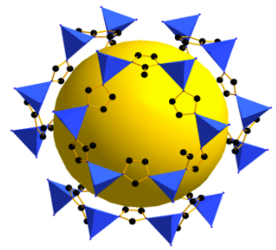






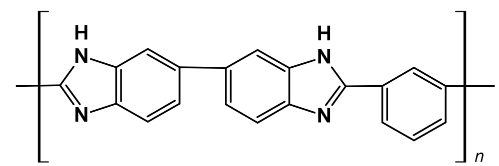
UT-Dallas Results

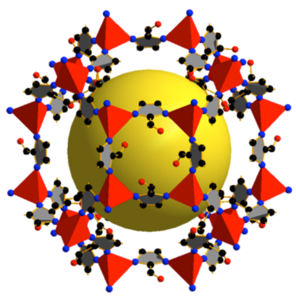
Mixed-Matrix Membrane Studies



ZIF-8

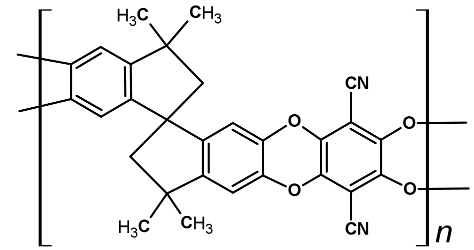
MIL-53/PBI
ZIF-8/PBI
SIM-1/PBI



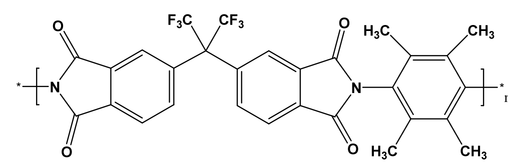


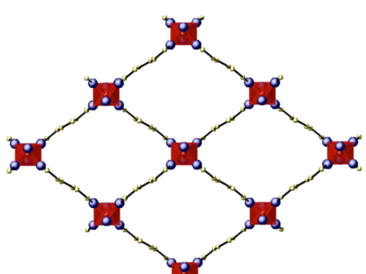
ZIF-90

MIL-53/PIM-1
ZIF-8/PIM-1
ZIF-90/PIM-1



ZIF-8/6FDA-durene
Cross-linked ZIF-8/6FDA-durene

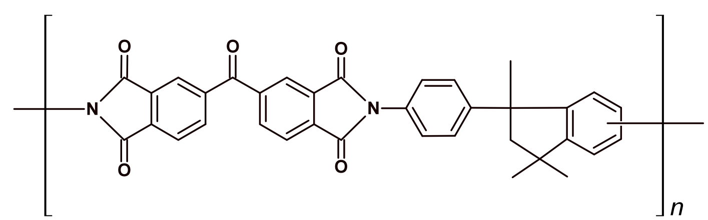




MIL-53 ht

ZIF-8/CPDM
ZIF-8/PDMC

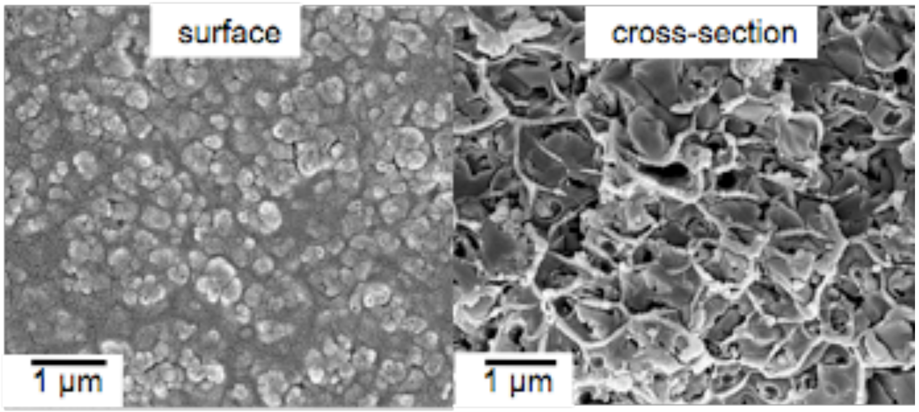
MIL-53/Matrimid
ZIF-8/Matrimid
Cross-linked ZIF-8/Matrimid



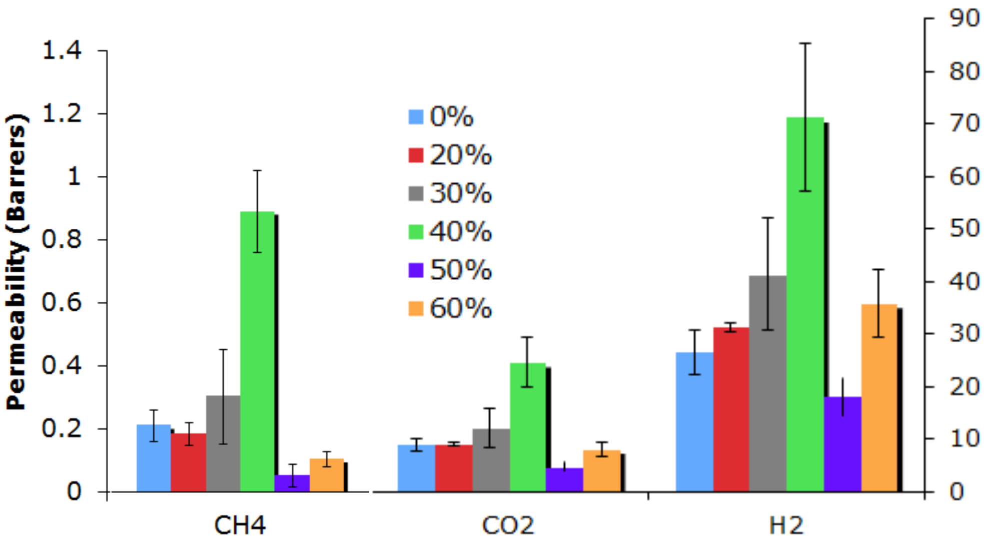
ZIF-8/Matrimid® MMMs

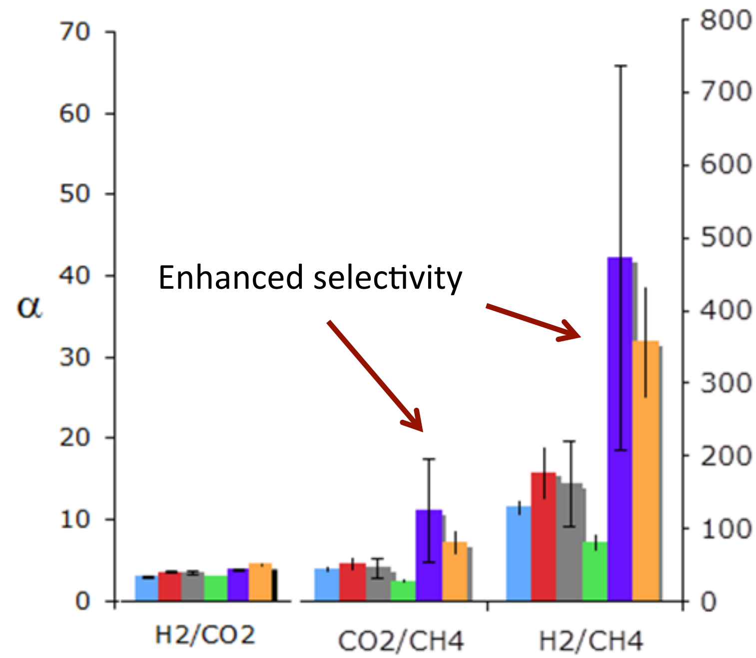
ZIF-8/Matrimid® MMM

60% (w/w)



- Good dispersion of ZIF-8 in Matrimid®
- Strong interaction between ZIF and polymer
- Enhanced selectivity observed in ZIF-8/Matrimid® MMMs.





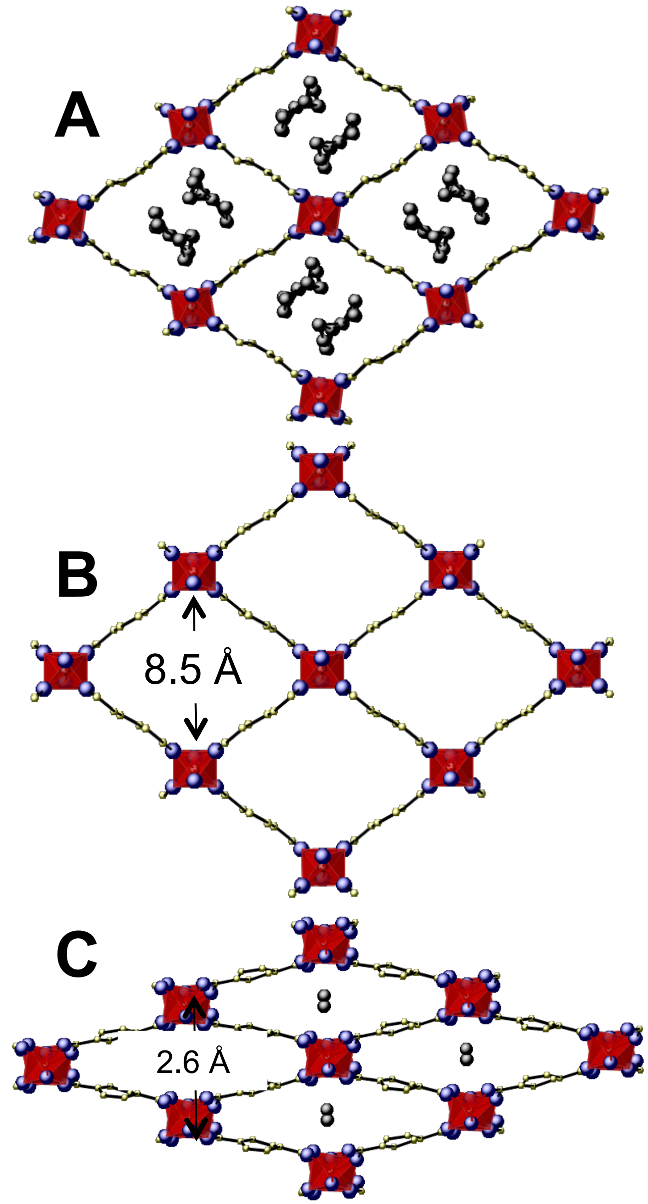
Ordoñez, J.; Balkus, K.; Ferraris, J.; Musselman, I., *J. Membrane Sci.*, 2010, 362, 28-37.

MIL-53/Matrimid® MMMs

UTD Mixed-Matrix Membranes

MIL-53

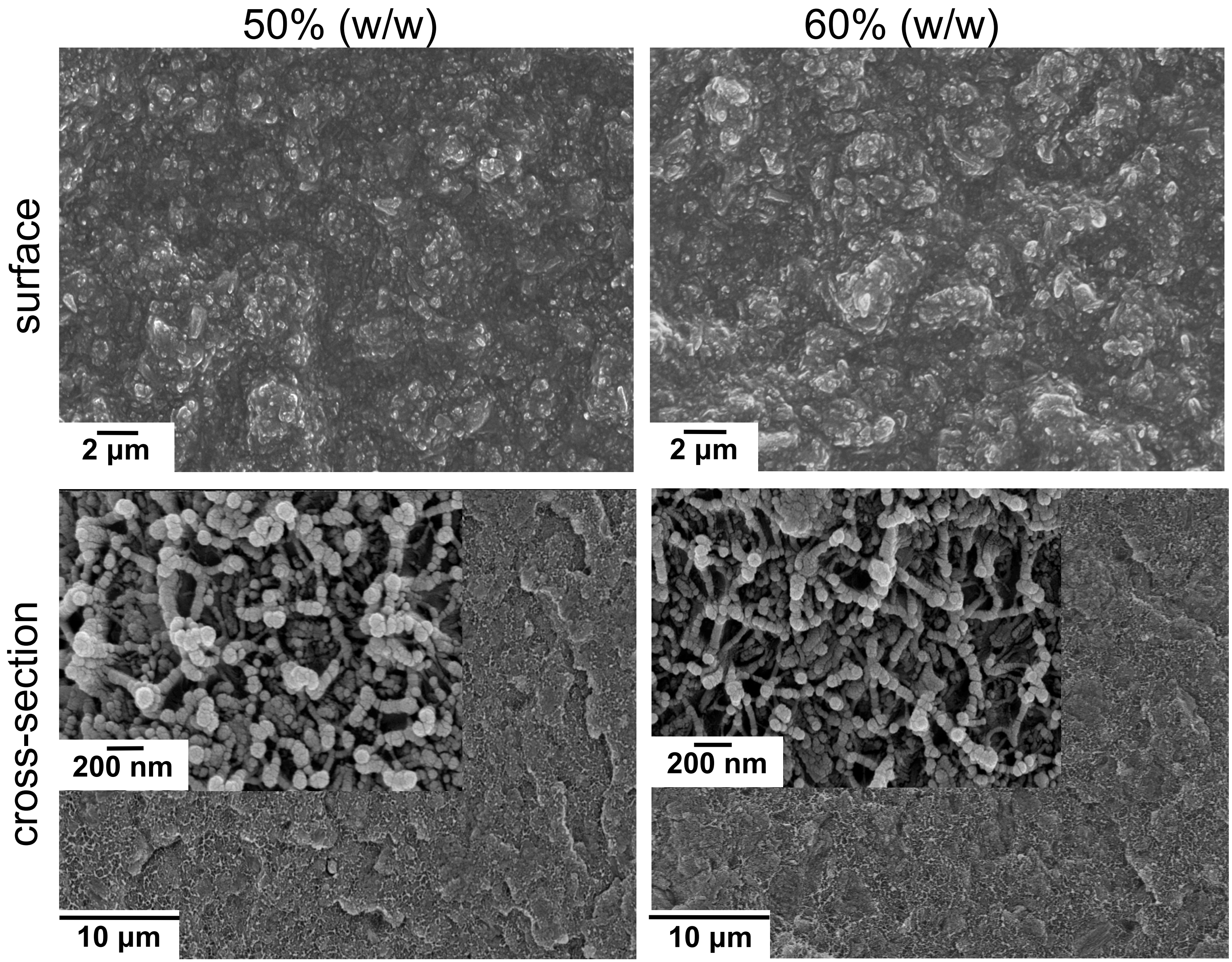
- 3D framework of aluminum octahedral clusters interconnected by 1,4-benzenedicarboxylate (BDC) groups
- Breathing effect induced by pressure, temperature, absorption of molecules
- **(A)** As synthesized – excess BDC in pores
- **(B)** Calcined form – BDC is expelled
  - high temperature (ht) framework
  - open-pore (8.5 Å)
- **(C)** Room temperature form - contraction of framework
  - low temperature (lt) framework
  - closed-pore (2.6 Å)



Loiseau, T.; Serry, C.; Ferey, G., *Chem. Eur. J.*, **2004**, 10, 1373-1382

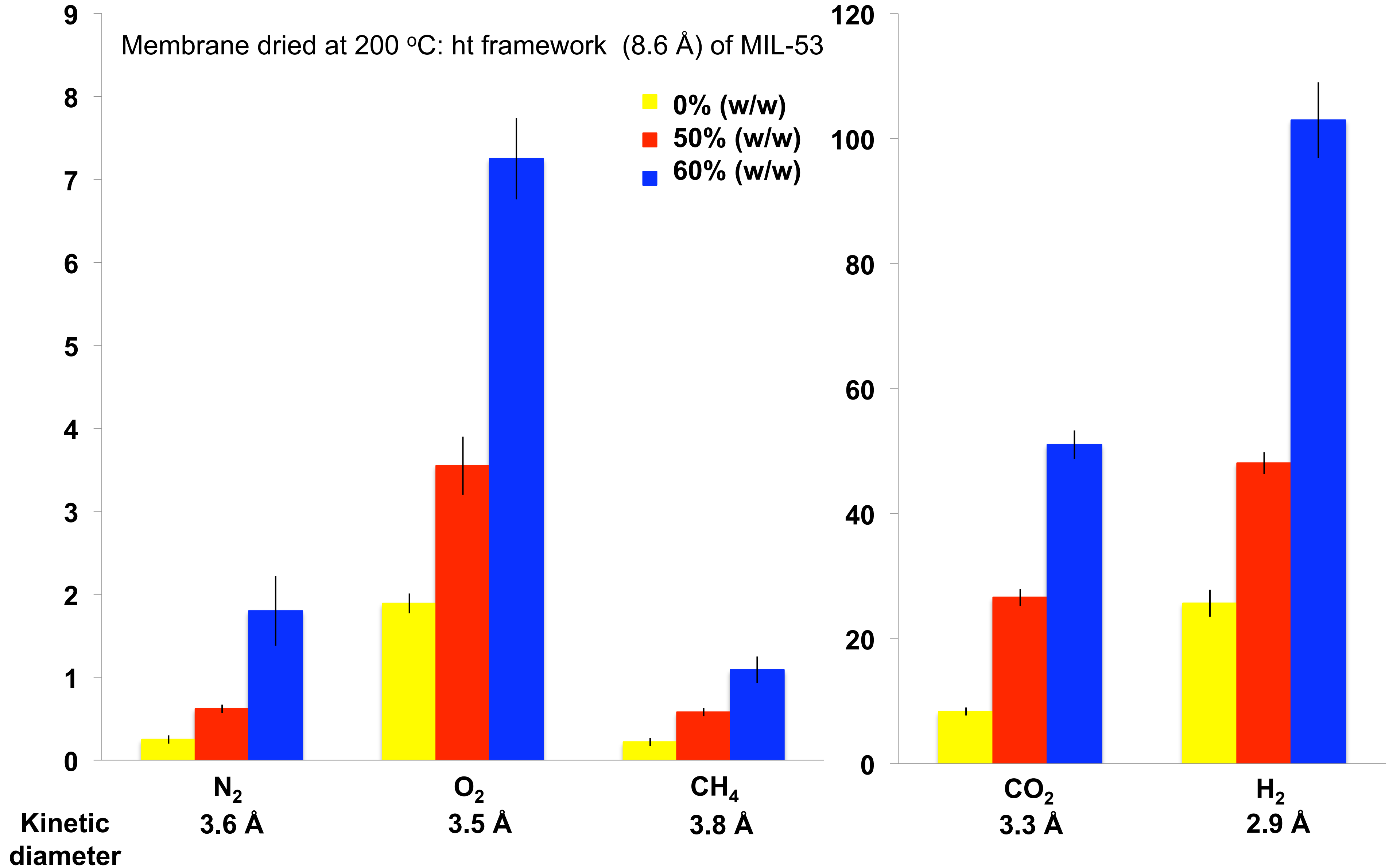
Llewellyn, P.; Maurin, G.; Ferey, G., *J. Am. Chem. Soc.*, **2008**, 130, 12808-12814

SEM of MIL-53-ht MMMs



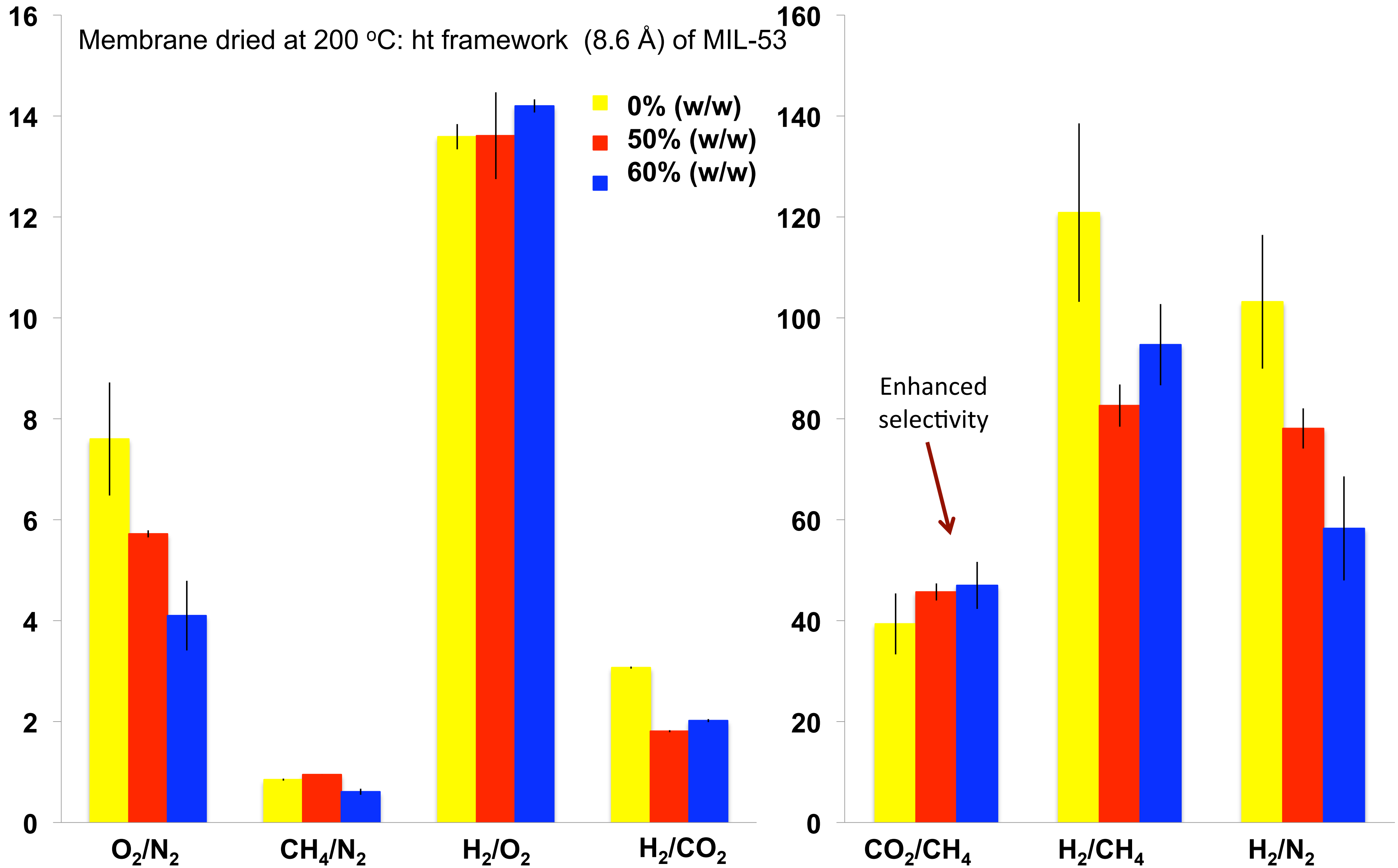
UTD Mixed-Matrix Membranes

Permeability



UTD Mixed-Matrix Membranes

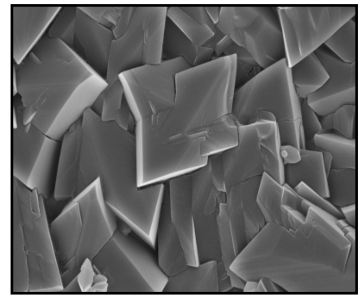
Selectivity

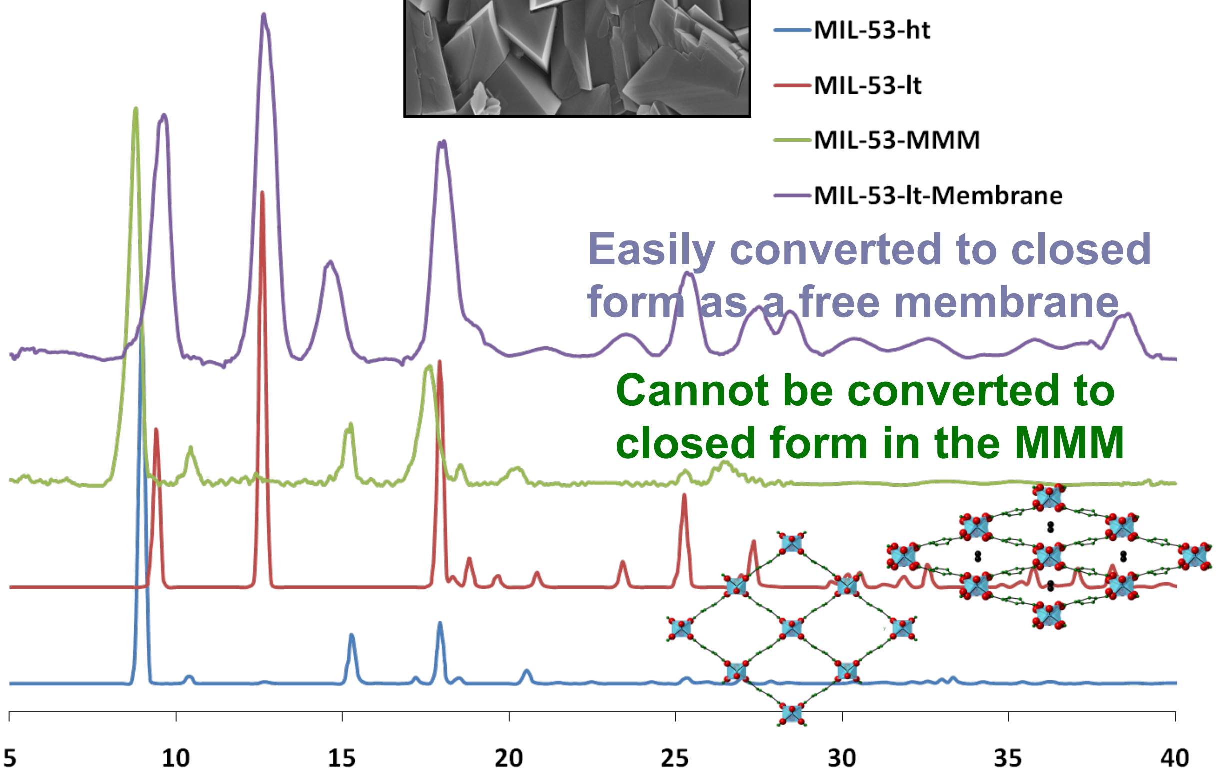


MIL-53/Matrimid® MMM

- MIL-53 gate-opening altered in MMMs
- XRD shows that constrained environment of polymer suppresses structural changes of MIL-53 framework in MMM
- In contrast, reversible gate opening occurs in pure MIL-53 membrane

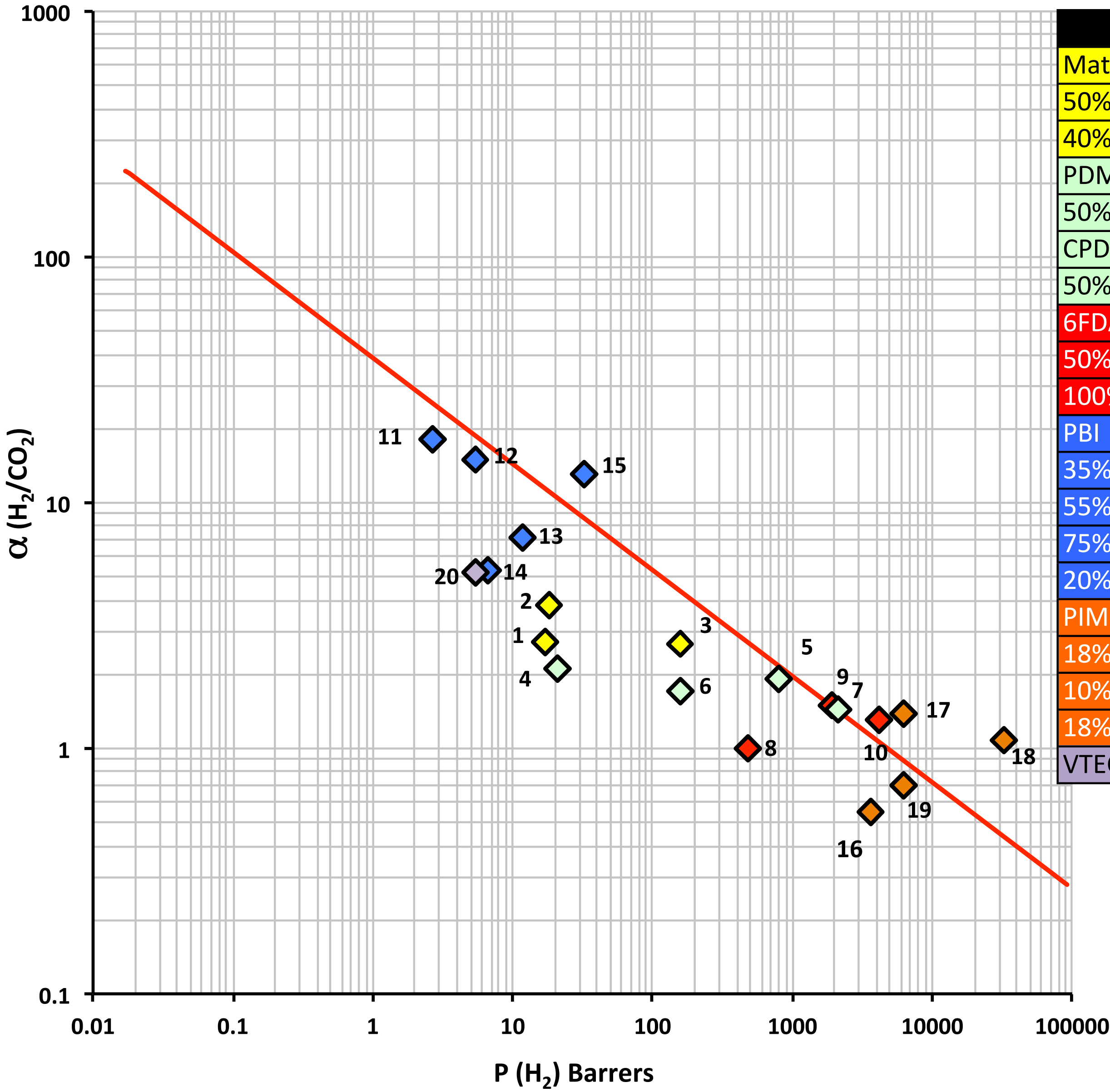
SEM image of MIL-53 crystals





UTD Mixed-Matrix Membranes

Robeson Upper Bound for H_2/CO_2



Membrane	Label
Matrimid	1
50% (w/w) ZIF-8/Matrimid MMM	2
40% (w/w) ZIF-8/Matrimid MMM	3
PDMC	4
50% (w/w) ZIF-8/PDMC MMM	5
CPDM	6
50% (w/w) ZIF-8/CPDM	7
6FDA-durene	8
50% (w/w) ZIF-8/6FDA-durene MMM	9
100% (w/w) ZIF-8/6FDA-durene MMM	10
PBI	11
35% (w/w) ZIF-8/PBI MMM	12
55% (w/w) ZIF-8/PBI MMM	13
75% (w/w) ZIF-8/PBI MMM	14
20% (w/w) MIL-53/PBI MMM	15
PIM-1	16
18% (w/w) ZIF-8/PIM-1 MMM	17
10% (w/w) MIL-53/PIM-1 MMM	18
18% (w/w) ZIF-90/PIM-1 MMM	19
VTEC	20

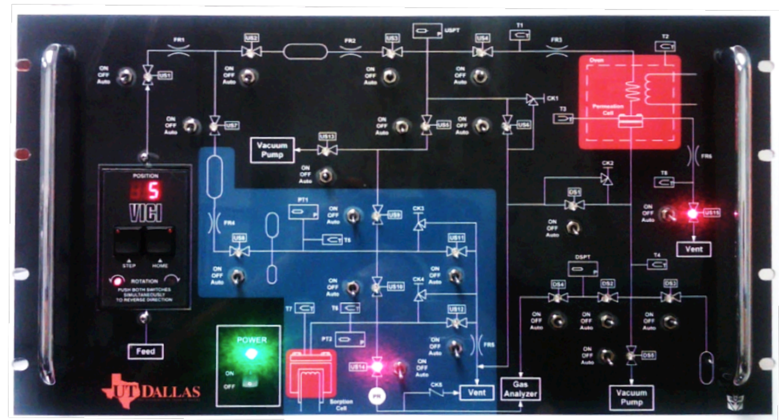
UT-Dallas Results

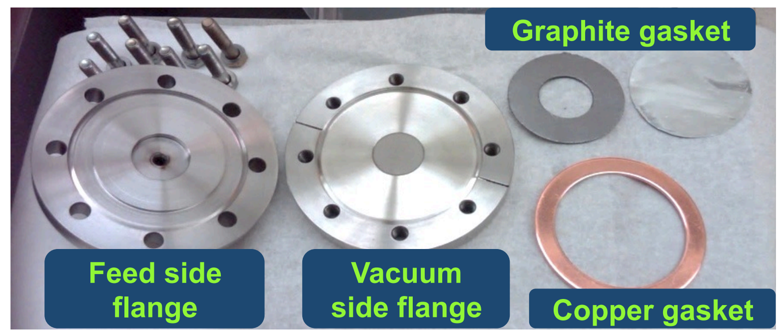
Strategies to Improve MMMs

Permeability Experiments at High Temperature and High Pressure

UTD Mixed-Matrix Membranes

High Pressure-High Temperature Permeameter





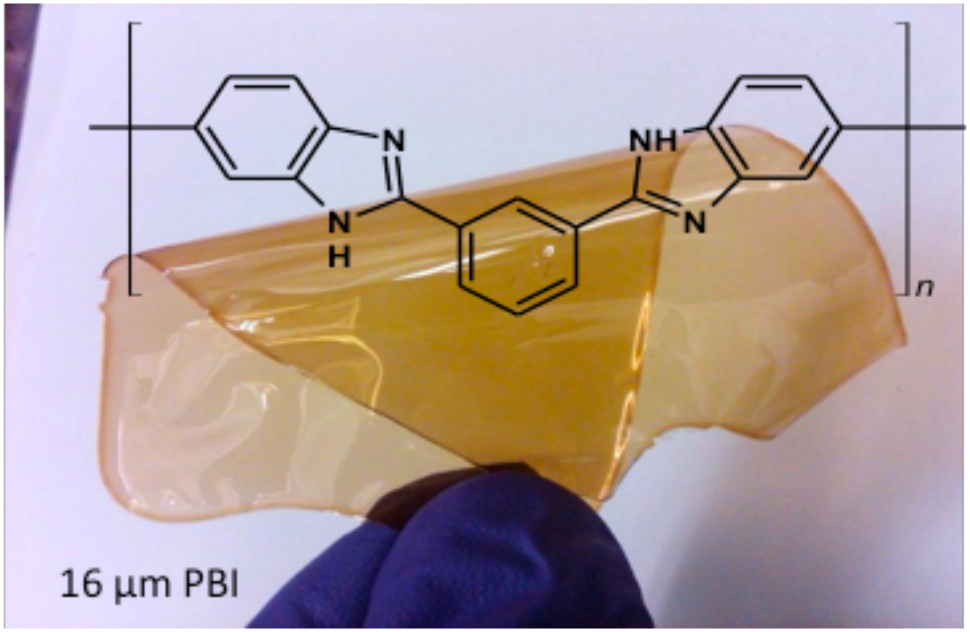
USB data acquisition units provide a fast and easy-to-configure interface

Operates using LabView software

In-line thermocouples provide accurate and fast measurements of gas and cell temperatures

UTD Mixed-Matrix Membranes

High Temperature and High Pressure Testing of PBI



Polybenzimidazole (PBI)

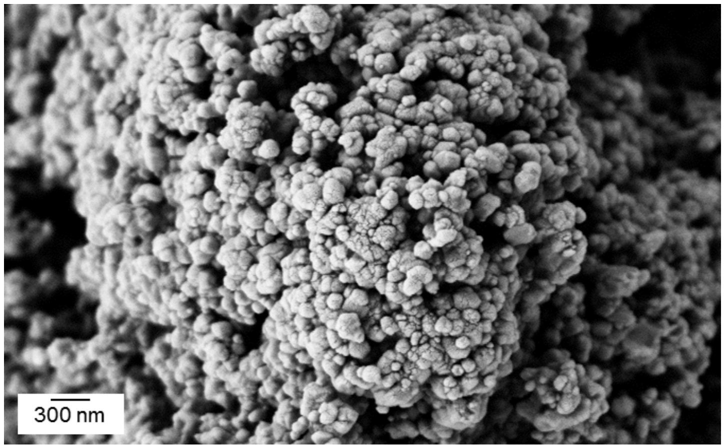
Permeability (Barrers) of a pure PBI film at 35 °C and 300 °C and up to 15 bars

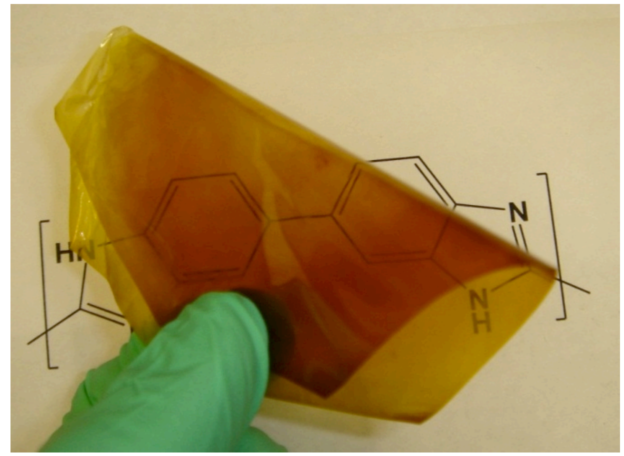
Temperature	35 °C	300 °C	
Pressure (atm)	*3*	*10*	*15*
H_2	2.59 ± 0.02	73.08 ± 0.84	73.15 ± 0.29
CO_2	0.11 ± 0.02	2.79 ± 0.13	2.63 ± 0.01
α	23.09	26.18	27.81

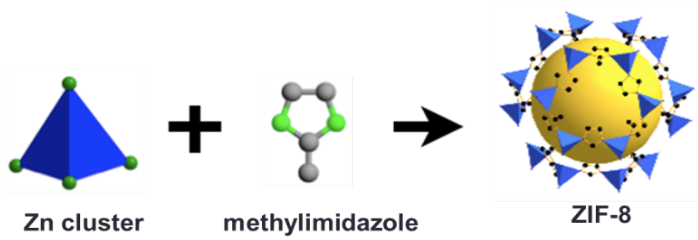
Testing PBI at 300 °C increased H_2 permeability while maintaining selectivity

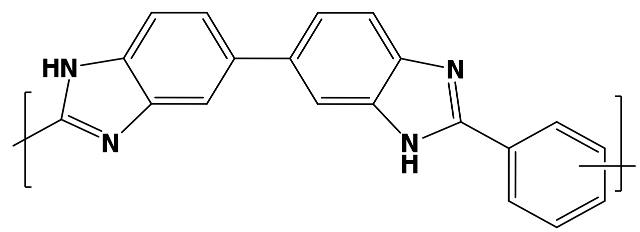
UTD Mixed-Matrix Membranes

ZIF-8/PBI MMMs









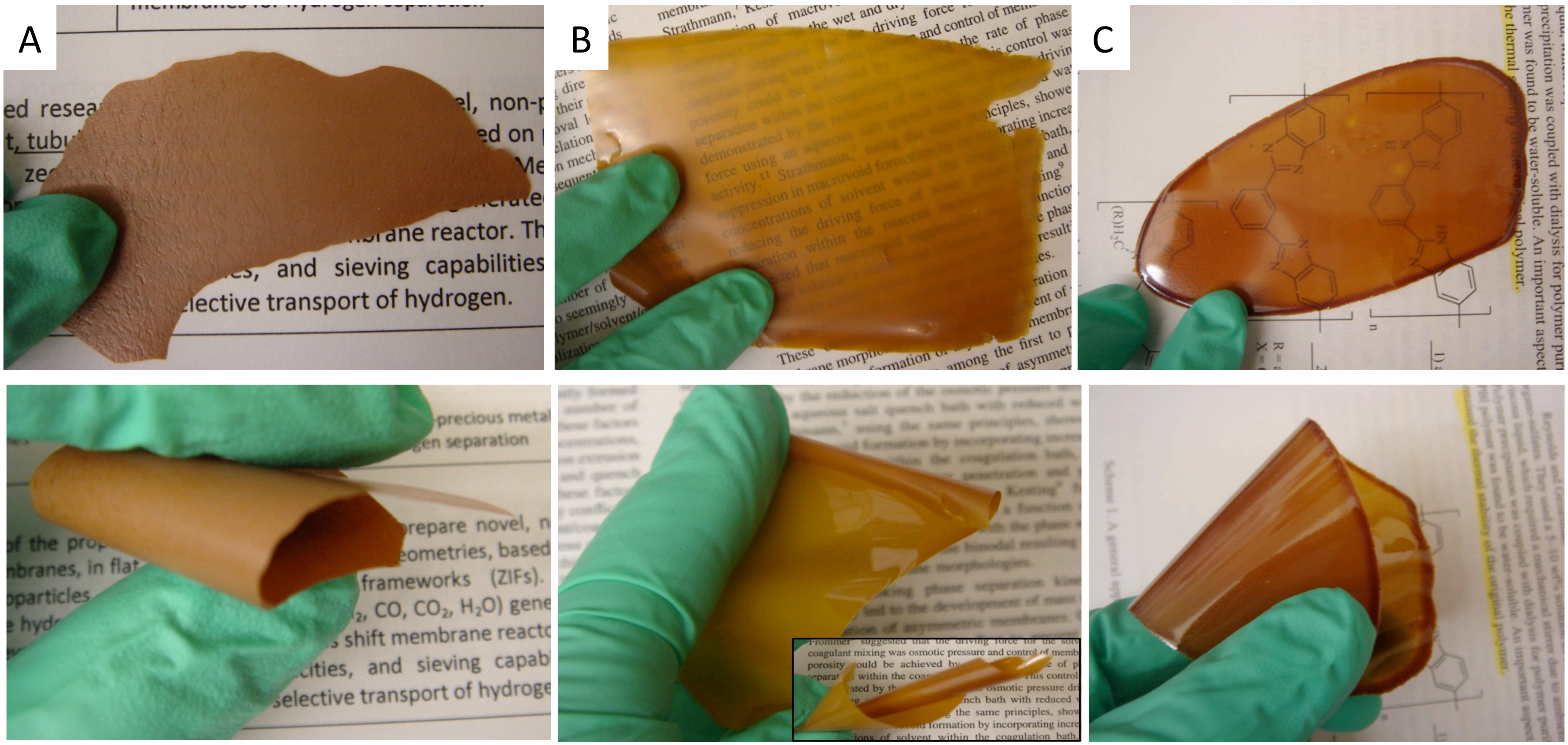
- Thermally stable up to 400 °C
- H_2/CO_2 selectivity = 4.5
- H_2 permeance = 0.5 $m^3_{(STP)}$ /m^2•h•bar
- Pore size: 3.4 A
- Nanocrystalline
- Sigma Aldrich ($100/10g)

- T_g = 427-512 °C
- Onset of thermal degradation = ~600 °C
- H_2/CO_2 selectivity = 5.4
- Rigid polymer backbone
- PBI Performance Products, Inc. ($200/lb)

UTD Mixed-Matrix Membranes

ZIF-8/PBI MMMs

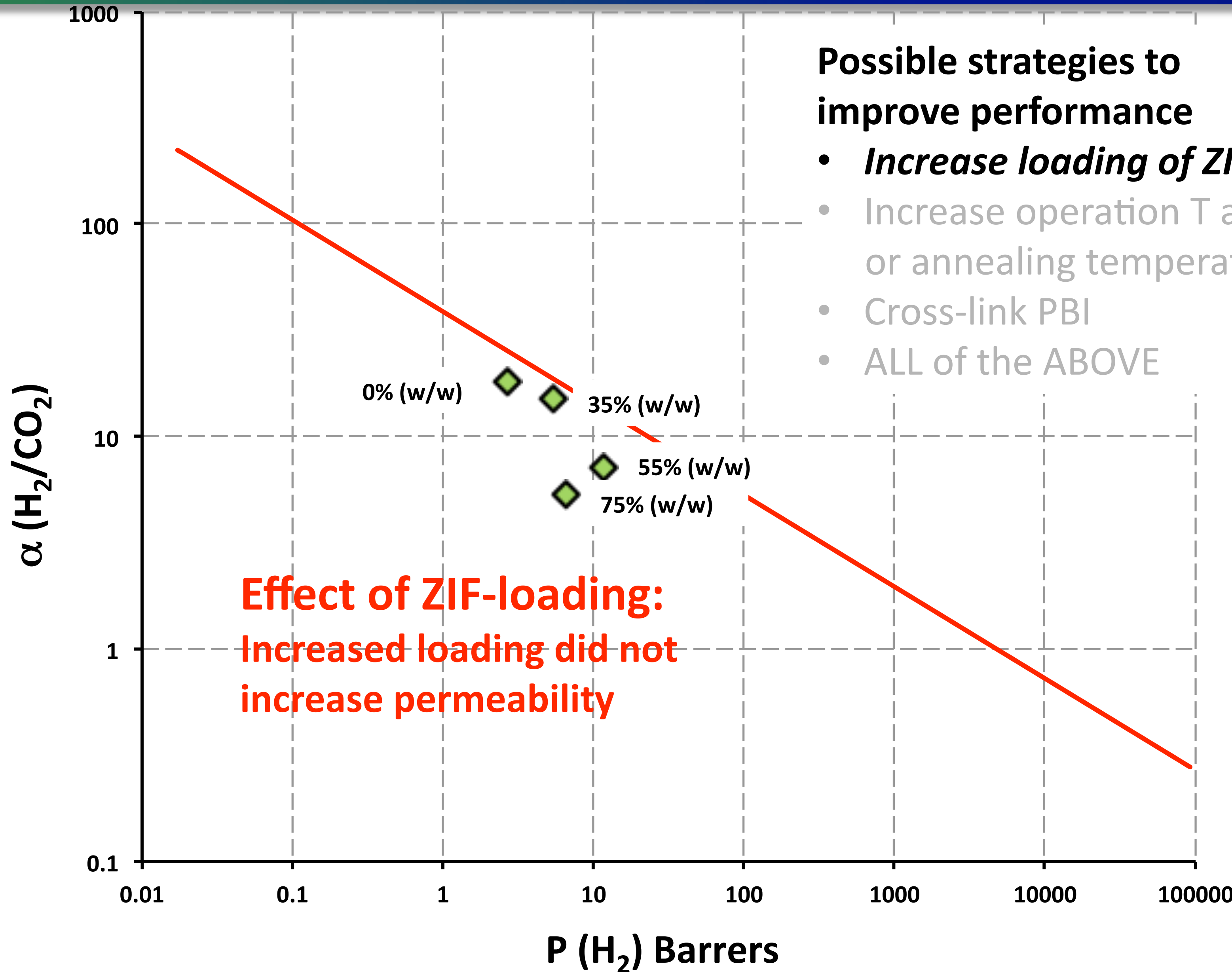
75% (w/w) **55% (w/w)** **35% (w/w)**



ZIF-8 loadings up to 75% (w/w) in PBI resulted in flexible films

UTD Mixed-Matrix Membranes

ZIF-8/PBI MMMs
Performance at 35 °C and 3 atm

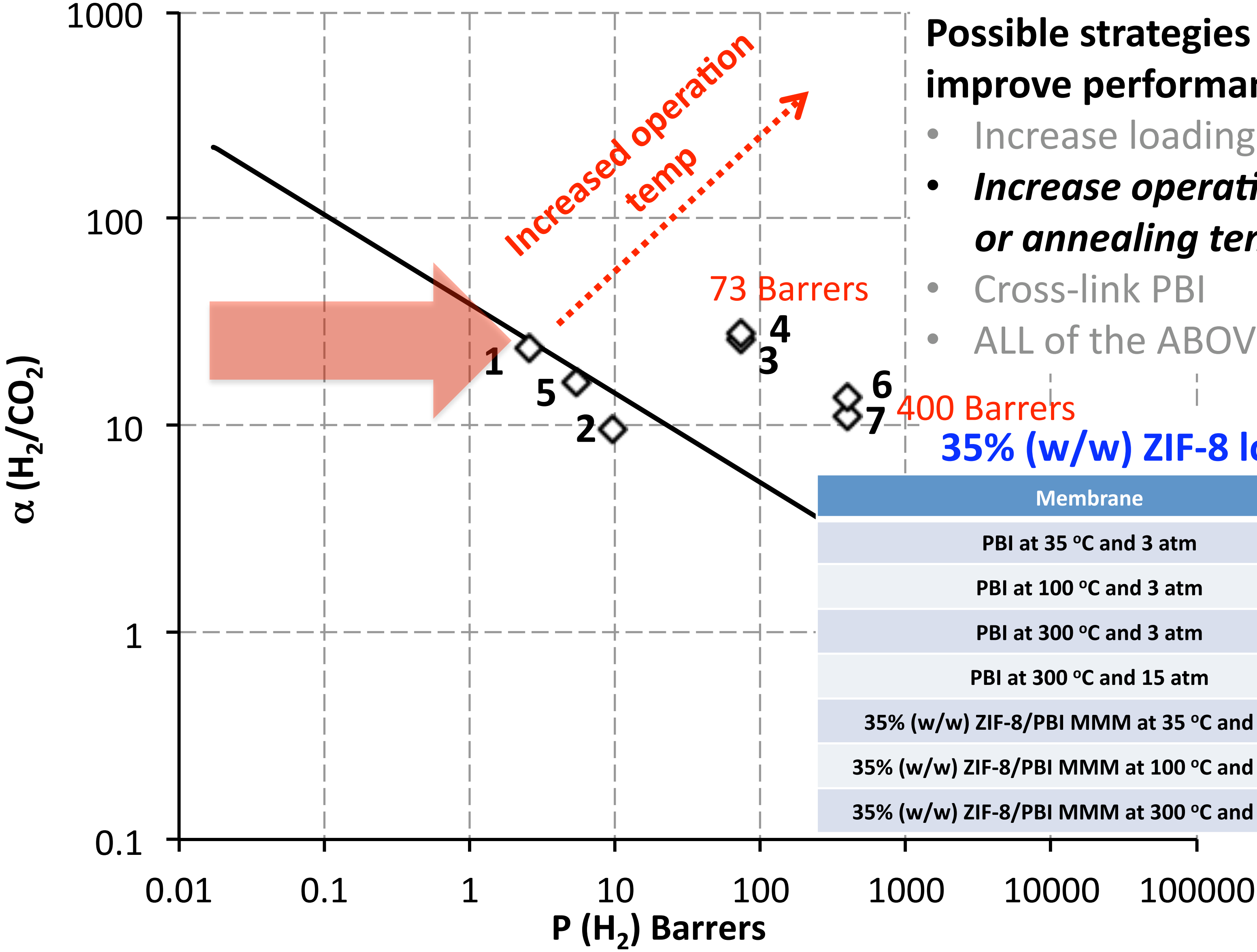


Possible strategies to improve performance

- ***Increase loading of ZIF***
- Increase operation T and/ or annealing temperature
- Cross-link PBI
- ALL of the ABOVE

UTD Mixed-Matrix Membranes

ZIF-8/PBI MMMs Performance at HPHT



Possible strategies to improve performance

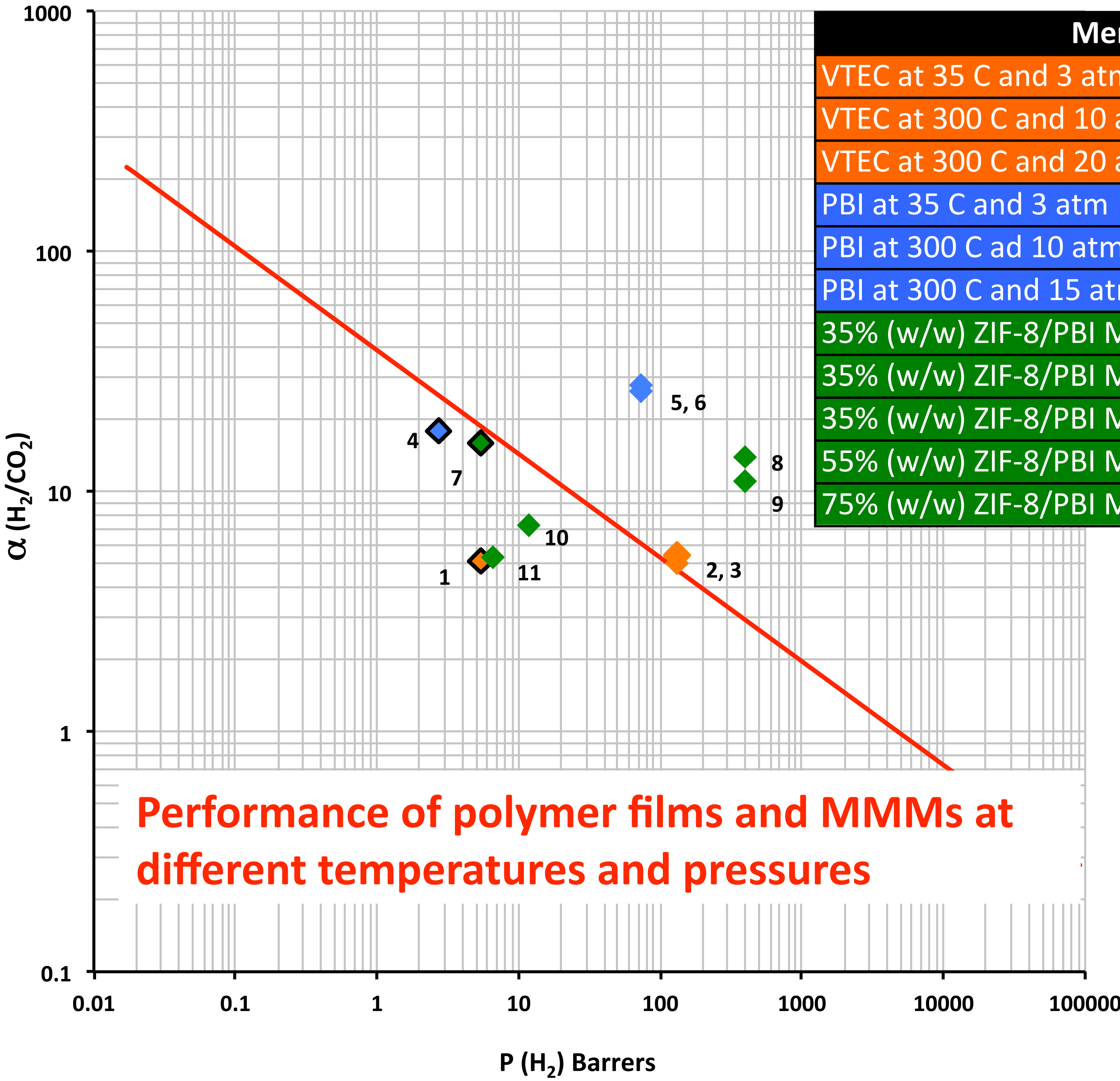
- Increase loading of ZIF
- ***Increase operation T and/ or annealing temperature***
- Cross-link PBI
- ALL of the ABOVE

35% (w/w) ZIF-8 loading only

Membrane	Label
PBI at 35 °C and 3 atm	1
PBI at 100 °C and 3 atm	2
PBI at 300 °C and 3 atm	3
PBI at 300 °C and 15 atm	4
35% (w/w) ZIF-8/PBI MMM at 35 °C and 3 atm	5
35% (w/w) ZIF-8/PBI MMM at 100 °C and 10 atm	6
35% (w/w) ZIF-8/PBI MMM at 300 °C and 10 atm	7

UTD Mixed-Matrix Membranes

High Pressure-High Temperature Permeability Results



Membrane	Label
VTEC at 35 C and 3 atm	1
VTEC at 300 C and 10 atm	2
VTEC at 300 C and 20 atm	3
PBI at 35 C and 3 atm	4
PBI at 300 C ad 10 atm	5
PBI at 300 C and 15 atm	6
35% (w/w) ZIF-8/PBI MMM at 35 C and 3 atm	7
35% (w/w) ZIF-8/PBI MMM at 300 C and 10 atm	8
35% (w/w) ZIF-8/PBI MMM at 300 C and 15 atm	9
55% (w/w) ZIF-8/PBI MMM	10
75% (w/w) ZIF-8/PBI MMM	11

Performance of polymer films and MMMs at different temperatures and pressures

UT-Dallas Results

Strategies to Improve MMMs

Cross-linking Polyimides with Diamines

Spin coating and EDA cross-linking

50% (w/w) ZIF-8/6FDA-durene MMM

Annealed at 210 °C for 24 h

Spin coat 3 wt% 6FDA-durene in 1:1 CH_2Cl_2:THF
Air dry for 6 h

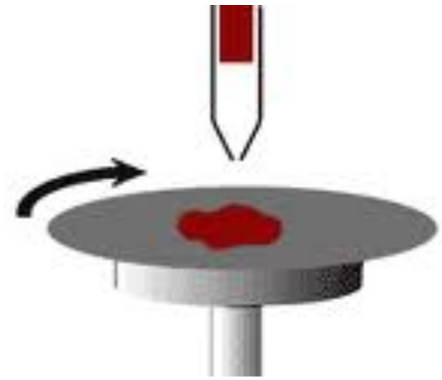
Anneal at 50 °C 12 h, 100 °C 6 h, 150 °C 6 h, 210 °C 12 h

MMM with a 6FDA-durene layer on 1 side

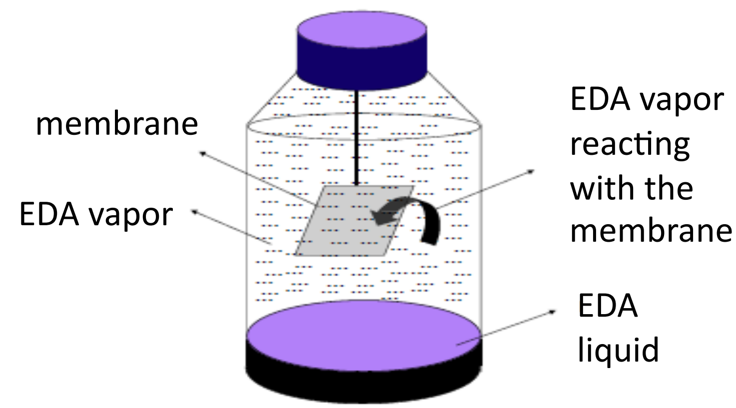
Expose to EDA vapor 3 min
Immediately wash with water

Anneal at 70 °C for 24 h

Spin coated MMM



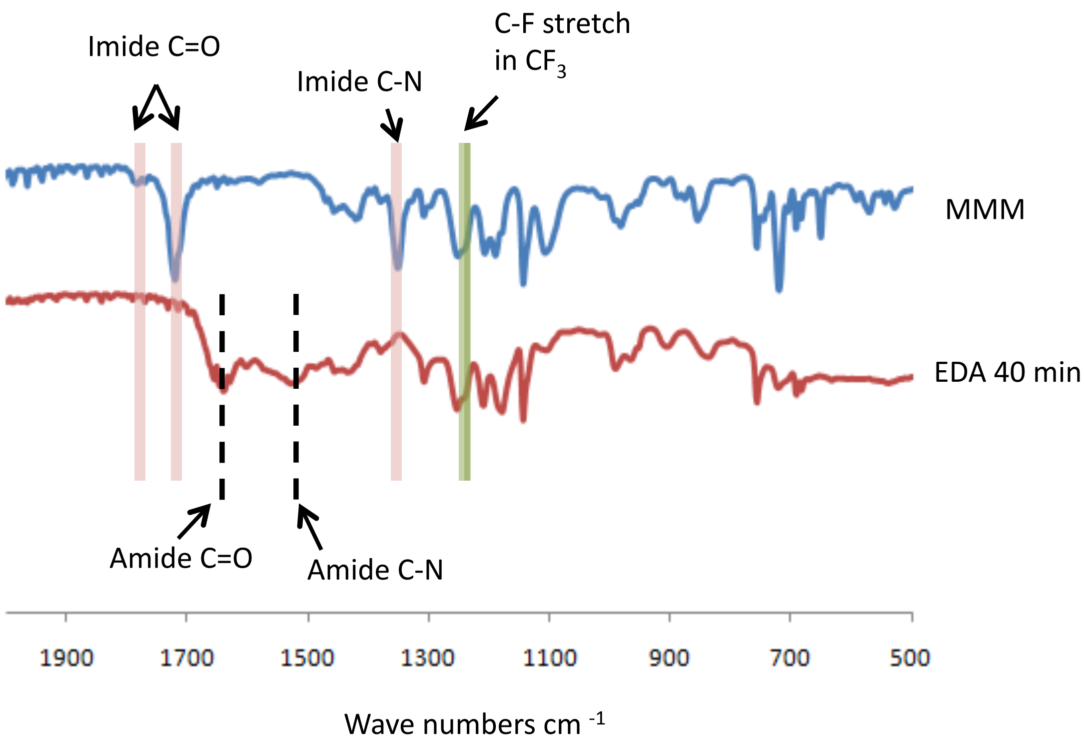
Cartoon of a spin coater

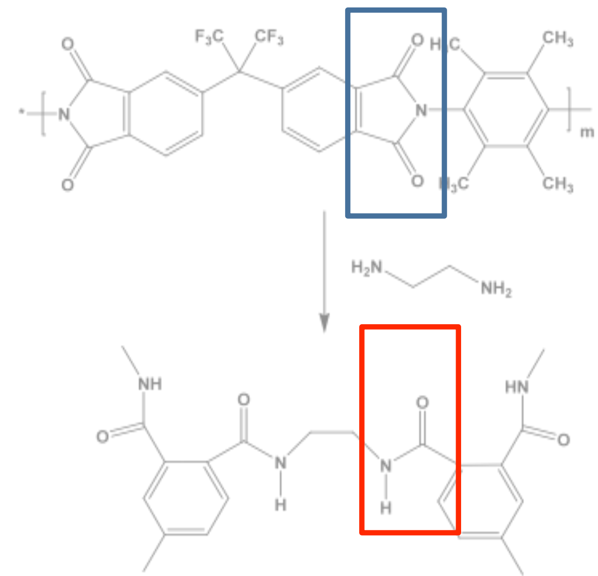


Set up for EDA cross-linking

UTD Mixed-Matrix Membranes

ATR-FTIR analysis of EDA cross-linking





Chemical reaction occurring during EDA treatment

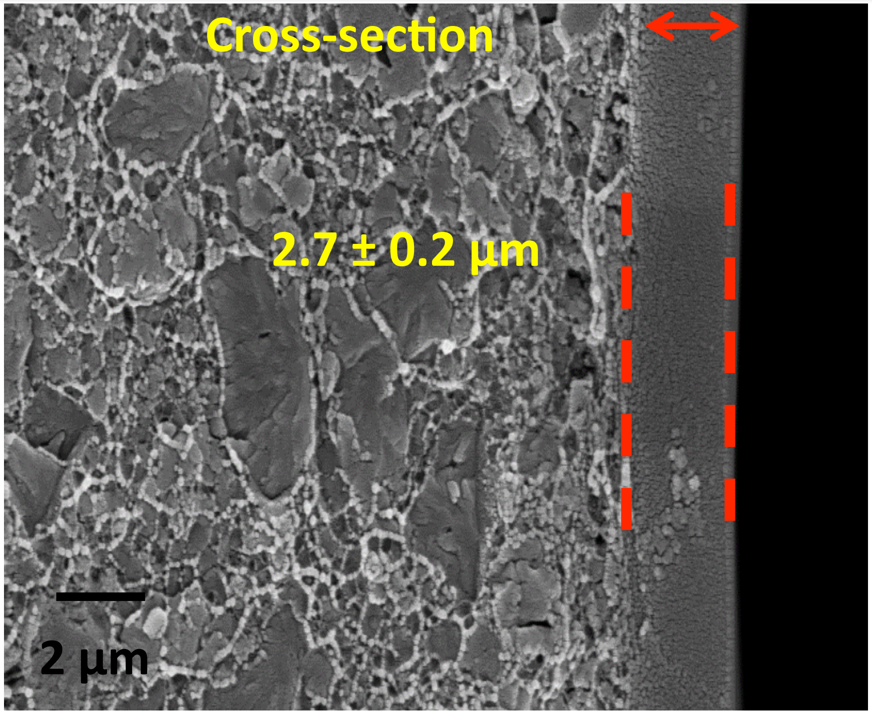
Top - 50% (w/w) ZIF-8/6FDA-durene MMM
Bottom - 50% (w/w) ZIF-8/6FDA-durene MMM reacted with EDA for 40 min

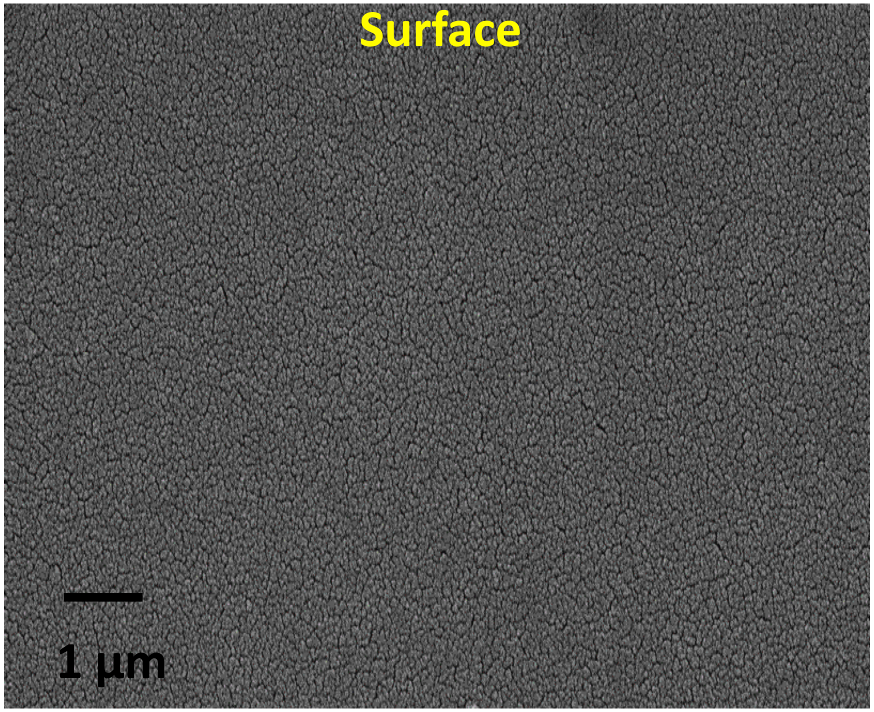
- **ZIF-8/6FDA-durene** 1785 cm^{-1} (imide C=O asymmetric stretch), 1718 cm^{-1} (imide C=O symmetric stretch), 1352 cm^{-1} (imide C-N stretch)
- **ZIF-8/6FDA-durene-EDA** 1644 cm^{-1} (amide C=O stretch), 1520 cm^{-1} (amide C-N stretch), 1240 c m^{-1} (C-F reference)

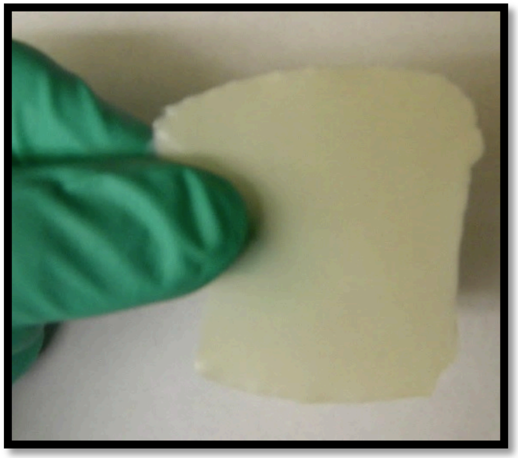
Shao, L.; Lau, C.-H.; Chung, T.-S. *International Journal of Hydrogen Energy* **2009,** *34*, 8716-8722.

UTD Mixed-Matrix Membranes

6FDA-durene spin-coated on MMMs

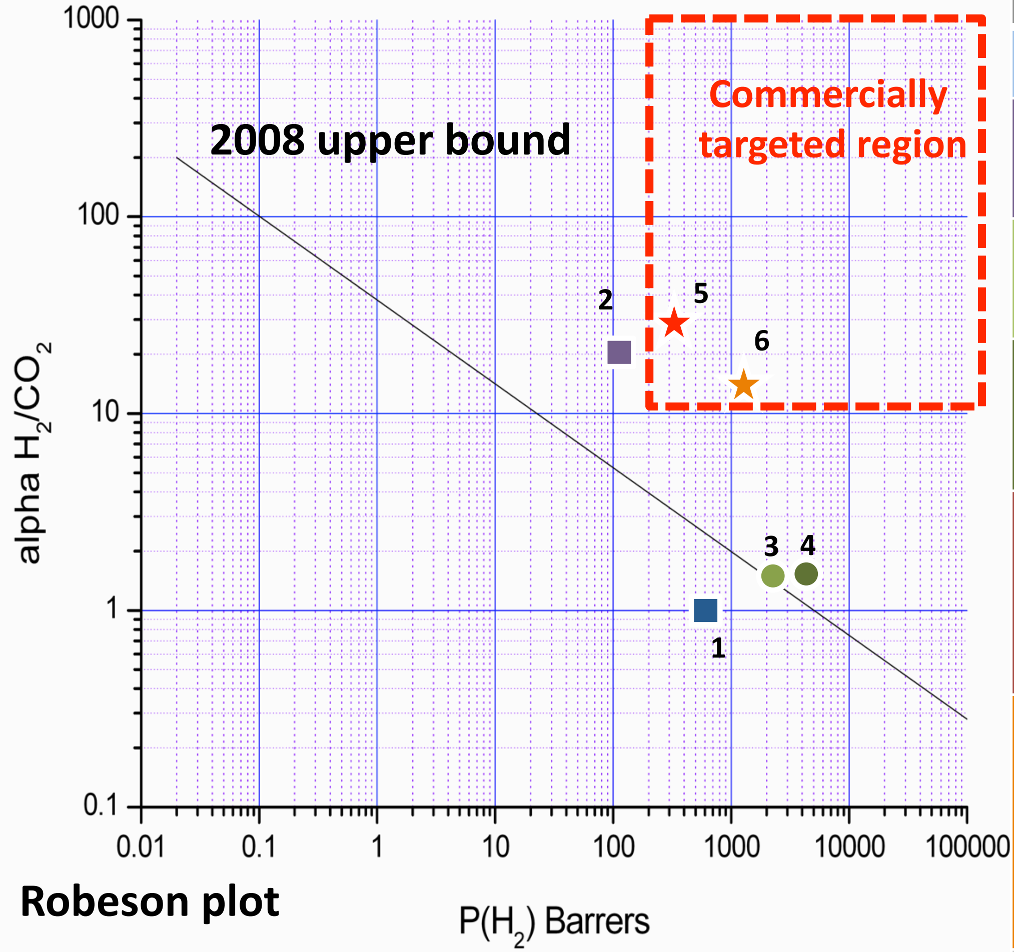






UTD Mixed-Matrix Membranes

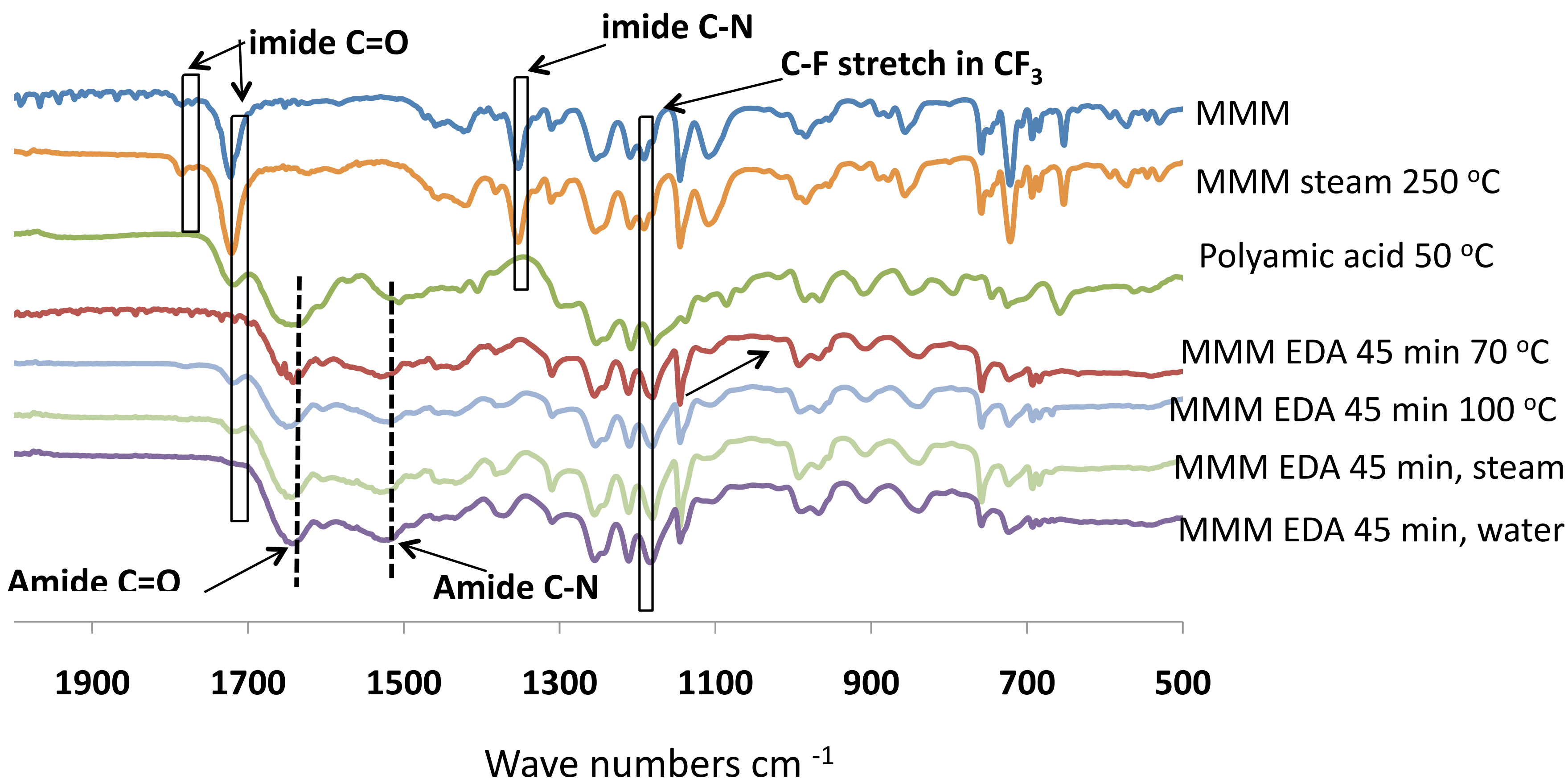
H_2/CO_2 separation



Robeson plot

Membrane	H_2 (Barrer)	H_2/CO_2
(1) 6FDA-durene	480.4	1.0
(2) 6FDA-durene (EDA 3min)	112.3	19.0
(3) 50% (w/w) ZIF-8/6FDA-durene	2137 ± 190	1.4 ± 0.0
(4) 100% (w/w) ZIF-8/6FDA-durene	4157	1.3
(5) 6FDA-durene spin coated 50% (w/w) ZIF-8/6FDA-durene MMM (EDA 3 min)	395.6 ± 190	27.9± 3.1
(6) 6FDA-durene spin coated 100% (w/w) ZIF-8/6FDA-durene MMM (EDA 3 min)	1369 ± 334	13.2 ± 2.2
Knudsen value		4.7

Hydrothermal Stability



Hydrothermal stability of 50% (w/w) ZIF-8/6FDA-durene MMMs before and after EDA treatment

Mixed-Matrix Membranes

Results to Date

- **Synthesized ZIFs and related frameworks; Tested gas sorption (H_2, CO_2, N_2) up to 300 °C and 100 bars**
- **Synthesized high performance polymers capable of withstanding high temperature environments**
- **Prepared and characterized MMMs for H_2/CO_2 separations at 35 °C and 3 bars**
- **Constructed HPHT permeameter that operates up to 30 bars and up to 300 °C**
- **Measured H_2 and CO_2 permeability in VTEC PI-1388, PBI, and ZIF-8/PBI MMMs at 300 °C and 10/15 bars**

Future Work

- **Prepare and characterize additional MMMs for H_2 separations at NETL test protocol conditions**
- **Continue testing these membranes at DOE 2015 test conditions**
- **Work with DOE-NETL Pittsburgh to test H_2S resistance of most promising MMMs**

UTD Mixed-Matrix Membranes

UT-Dallas Membrane Team

ZIF-containing MMMs offer exciting opportunities in hydrogen separations

Postdocs

Dr. Grace Kalaw
Dr. Edson Perez
Dr. Chalita Ratanatawanate

Graduate students

David Bushdiecker II*
Yu (Tony) Huang
Jing Liu
Josephine Ordoñez Hsieh*
Nimanka Panapitiya
Sumudu Wijenayake
Zhen Zhang*

Undergraduate students

Catherine Eckert
Mishelle Kochumuttom*
Pauras Memon*
Kelsey Musselman
Bao Nguyen
Cindy Nguyen
Do Nguyen
William Regner
Natasha Varughese*
Saskia Versteeg

*Research assistantship/summer pay from DE-NT0007636