Microporous Zeolite Membranes and Their Potential for H_2 Production

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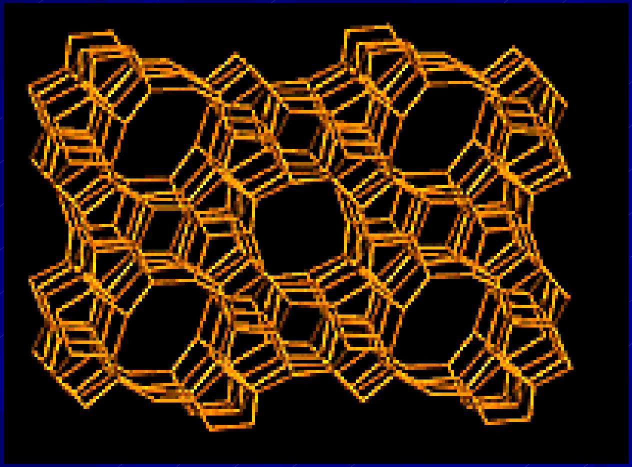
NNSA National Nuclear Security Administration

Zeolites and Zeotypes

- Zeolite – A crystalline alumino-silicate made up of a 3D framework that forms uniformly sized pores of molecular dimensions (2-20 Å).

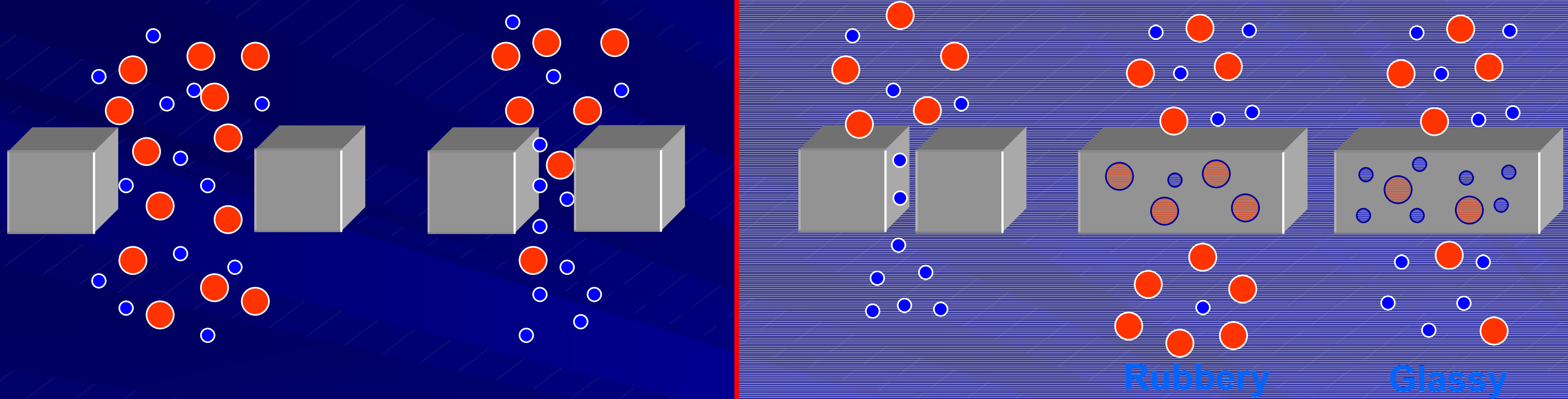


MFI Zeolite

- Zeotype – Any other crystalline material (e. g. aluminophosphates, titanosilicates) with a 3D framework in which one of the tetrahedral sites occupied by Si is replaced with another element. Many zeotypes have the same structure as known zeolites.

Membrane Materials Separation Mechanisms

1,000 – 100,000 Å | 20 – 1,000 Å | 2 - 20 Å | Dense Membrane



Poiseuille Flow
No Separation

Knudsen Diffusion
$P \propto (MW)^{-1/2}$
$\alpha_{A/B} = (MW_A/MW_B)^{1/2}$

Molecular Sieve
$P \propto KD$
$\alpha_{A/B} = P_A/P_B$

Solution Diffusion
$P = DS$
$\alpha_{A/B} = P_A/P_B$

Kinetic Diameter (Å)

He	H_2	CO_2	O_2	N_2	CH_4
2.60	2.89	3.30	3.46	3.64	3.80

* *W. D. Breck, Zeolite Molecular Sieves, John Wiley & Sons, Inc., New York, 1974, p 636.*

Small Pore Zeolites & Zeotypes

Zeolites: (pore sizes, Å)

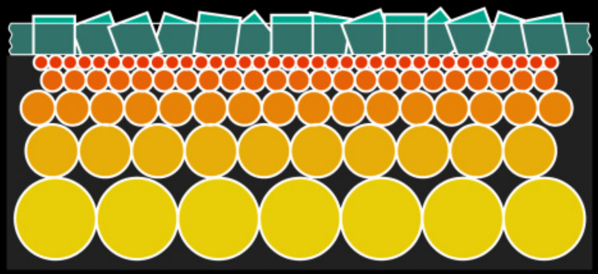
- MFI Zeolites (5.4)
  - Silicalite-1
  - ZSM-5
- LTA (4.1)
  - Zeolite A
- GIS (4.5)
- CHA (3.8)
- ABW (3.8)
- Analcime (2.6)

Zeotypes: (pore sizes, Å)

- ETS-4 and Zorite (3-4)
- ETS-10 (8)
- SAPO-34 (3.8)
- AlPO
  - AlPO-52 (3.6)
  - AlPO-16 (3.0)
- Many others!

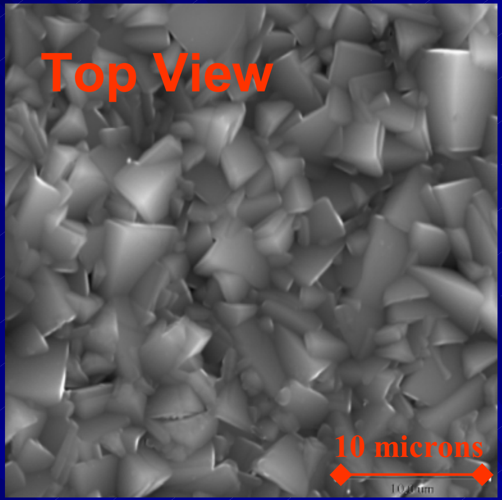
Zeolite Membranes - Fabrication

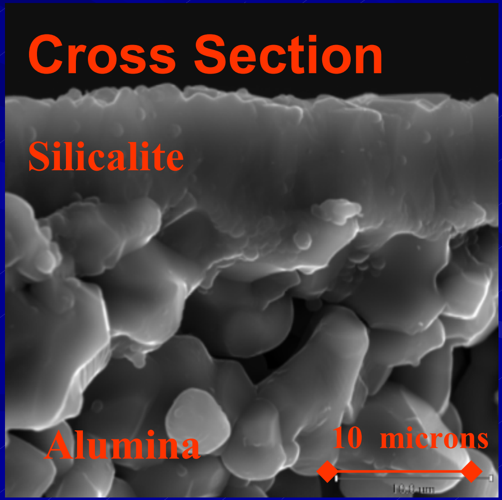
- Two step growth mechanism – support seeding followed by membrane formation
- May use a templating agent
- Supported crystalline membranes
- Single or double sided
- Tubes or disks



Zeolite Membranes – Typical Properties

- Thickness: 10 µm – 300 µm
- Permeance: 10^{-5} to 10^{-9} mol/(m^2*Pa*s)
  - Translates to fluxes: 1 to 120 scfh/ft^2.
- H_2 Selectivity vs. CO_2: ≤80
  - At room temperature and 1 bar.
  - A 50/50 feed stream results in a 98% H_2 outlet stream.
- Operating Pressures: beyond 6 bar
- Operating Temperatures: up to 1000 °C
  - Depends on zeolite type.





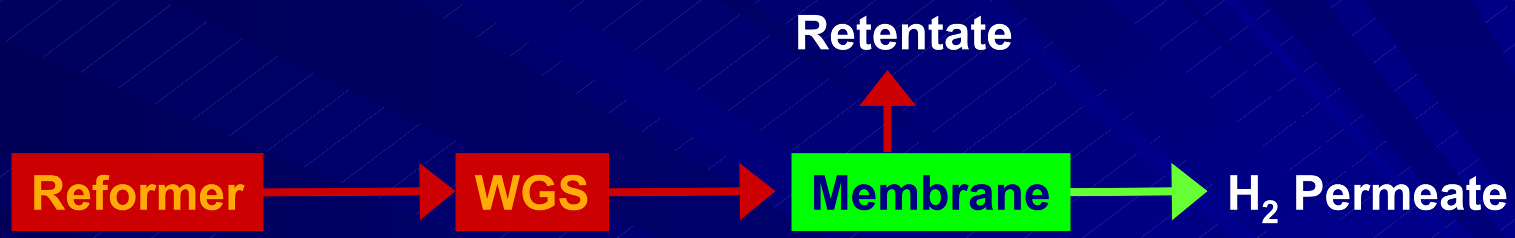
*Bonhomme, F.; Welk, M. E.; Nenoff, T. M. *Microp. Mesop. Mat.* **2003**, *66*, 181.

Current Industrial Uses

- Sodium Zeolite A for pervaporation separations*
  - From Mitsui Co.
    - 20 cm tubes, ID 9 mm. Used in alcohol separation from H_2O, for instance, isopropanol/water. Cost savings of 49%.
- Advantages:
  - Can separate azeotropes - "defect –free" not necessary for this application
  - Cost savings vs. distillation
  - Better solvent and temp. stability than polymer membranes
  - Easy 'fouling' remediation
  - Small space requirements
- Limitations:
  - Higher replacement costs than polymer membranes
  - Lifetimes (3.3 yrs.) could be improved, but are on the order of polymer membranes.

*Van Hoof, V. et. al. *Separation and Purification Technology* **2004**, *37*, 33.

Membrane Use in Reformers



<u>Potential End Users</u>

- Onboard reformers
  - Intelligent Energy, Ltd.
- Skid reforming stations
- Plant scale reforming

Permeate can theoretically be > 99% H_2. H_2 recovery from the feed stream through the membrane may be higher (as much as 90%) than the 50-60% recovered in the PSA units. Membrane could eliminate the need for PSA beds.

Suitable H_2 Feedstocks

Reformate streams from:

- Methane
- Kerosene
- Propane
- Natural Gas
- Biomass
- Diesel fuel

As a result of their chemical and thermal robustness, zeolite membranes may find use in any number of separation arenas.

Initial results at SNL show that neither H_2S nor H_2O degrade the zeolite membranes.

Current & Expected Level of H_2 Purity

- Ongoing experimental work at SNL shows that the H_2 purity from a 50/50 H_2/CO_2 mix after a single pass through a ZSM-5 membrane can be > 95%. Just as with PSA units, an enriched feed increases the final purity.
  - At room temperature, at 1 Bar (16 PSI)
  - A single pass through a zeolite membrane
  - No pre- or post-treatment
- **Expected improvements would result from:**
  - Higher temperatures
  - Higher pressures
  - A smaller pore zeolite
  - Use of multiple membranes in sequence
  - Incorporation of theory results
  - Use of a catalytic membrane

Key Hurdles to Overcome

- Currently, membranes cannot withstand rapid thermal cycling – cold start times are too long.
  - New support materials may alleviate thermal expansion mismatch between support and zeolite.
- Membranes show promising selectivity and flux. Both need improvement to reach the DOE targets, flux in particular. Must optimize the trade-off.
  - Further high temperature testing will narrow the gap to the DOE target; further improvements may be realized by the incorporation of theoretical conclusions.
- Synthesis is time-consuming, with a long calcination step at high temperatures.
  - Microwave synthesis has been introduced, may be able to apply more broadly.
- Sealing of membrane to module may require new sealant materials.
  - SNL has a patented ceramic to metal end seal material.

Zeolite Membrane Research Efforts

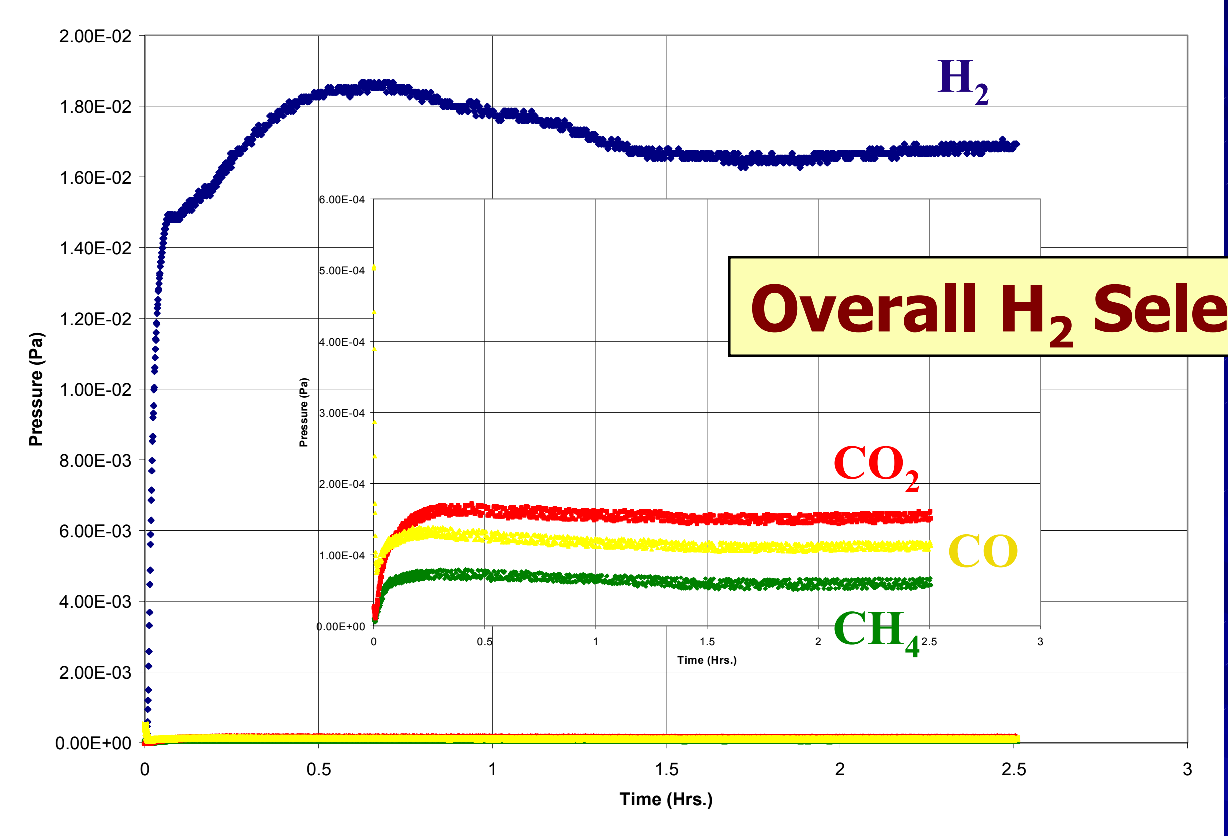
Increase Flux / Selectivity

- Grow oriented membranes
- Grow thin membranes
- Engineered zeolite heterostructures
- Model permeation through zeolites
- Minimize intergrowth of membrane with support
- Modify zeolite pore structure
- Synthesize new zeolites and first membrane growths of known zeolites.
- Minimize grain boundaries

Improve Industry Compatibility

- Optimize synthesis for time and cost
- Study methods to heal cracks
- Test permeation of reformate streams, at high T and P
- Grow membranes on industrially compatible supports
- Test membrane robustness vs. steam and contaminants
- Investigate coking
- Study membrane durability
- Investigate end seal materials
- Investigate catalytic membrane for desulfurization, etc.

Permeation of Reformate Stream



Overall H_2 Selectivity = 16.60

Feed Gas Mixture:
76% H_2
14% CO_2
7% CO
3% CH_4

Total Permeance= 6.90 x 10^{-7} mol/(Pa· s ·m^{2}) Total Pressure = 0.0190 Pa

H_2 Permeance = 6.78 x 10^{-7} P **H_2** = 1.87 x 10^{-2} Pa

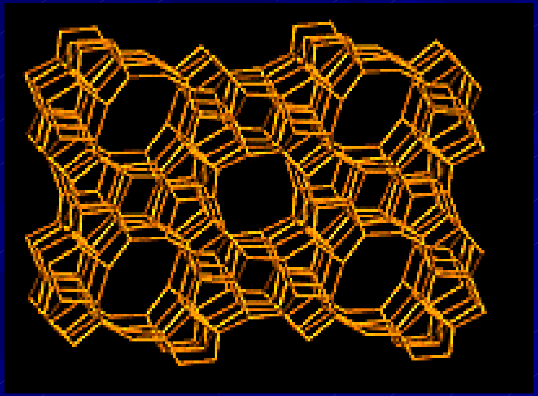
CO_2 Permeance = 5.79 x 10^{-9} P **CO_2** = 1.60 x 10^{-4} Pa

CO Permeance = 4.62 x 10^{-9} P **CO** = 1.28 x 10^{-4} Pa

CH_4 Permeance = 2.35 x 10^{-9} P **CH_4** = 6.40 x 10^{-5} Pa

Oriented Membranes

- To improve permeance and retain high selectivity, synthetic pathways to oriented membranes have been developed.
  - The straight pore channels in MFI Zeolite run along the *b*-axis. Thin *b*-axis oriented membranes have higher permeances, $5*10^{-4}$ mol/(m^2*Pa*s).



MFI Zeolite

- Drawbacks:
  - The straight pore channels in the oriented MFI Zeolite reduce the selectivity for H_2 over N_2. even though the membrane is "defect-free"
  - Oriented membrane growth necessitates synthesis of a specialized organic template; synthesis is overall more lengthy.

*Tsapatsis, M. et. al. *Science* **2003**, *300*, 456.
*Yan, Y. *J. Am. Chem. Soc.* **2004**, In press.

Ultra-thin Membranes

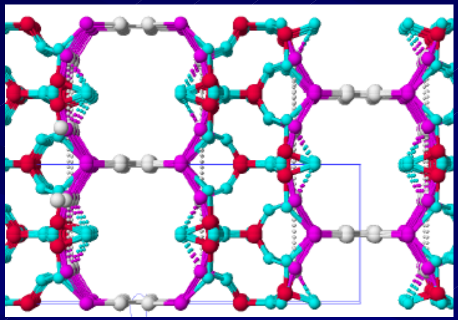
- To increase permeance through the membranes, membrane thickness can be reduced from as much as 300 μm to 1 μm.
  - Intergrowth with support was also minimized to increase permeance to ~10^{-6} mol/(m^2*Pa*s)
  - Uses less reactant material

*Verweij, H. et. al. *J. Membr. Sci.* **1998**, *144*, 65.
*Hedlund, J. et. al. *Microp. Mesop. Mat.* **2002**, *52*, 179.
*Algieri, C. et. al. *J. Membr. Sci.* **2003**, *222*, 181.

- Drawbacks:
  - Process requires additional 'masking step'
  - Thinness increases membrane fragility, which hinders potential incorporation into a module

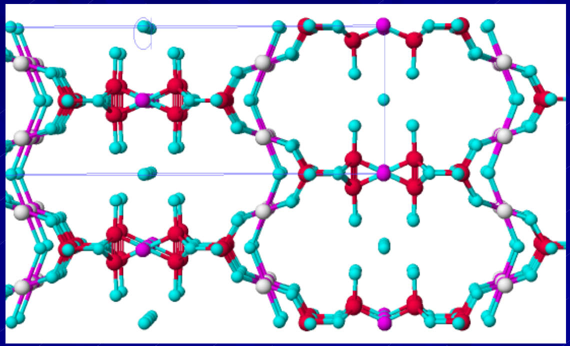
Computational Simulation of Gas Permeation in Pores of Silicotitanates

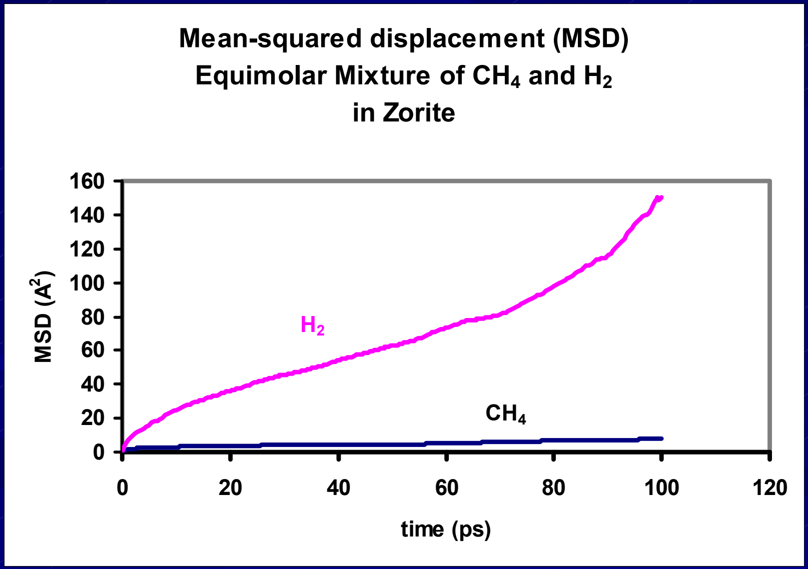
Zorite

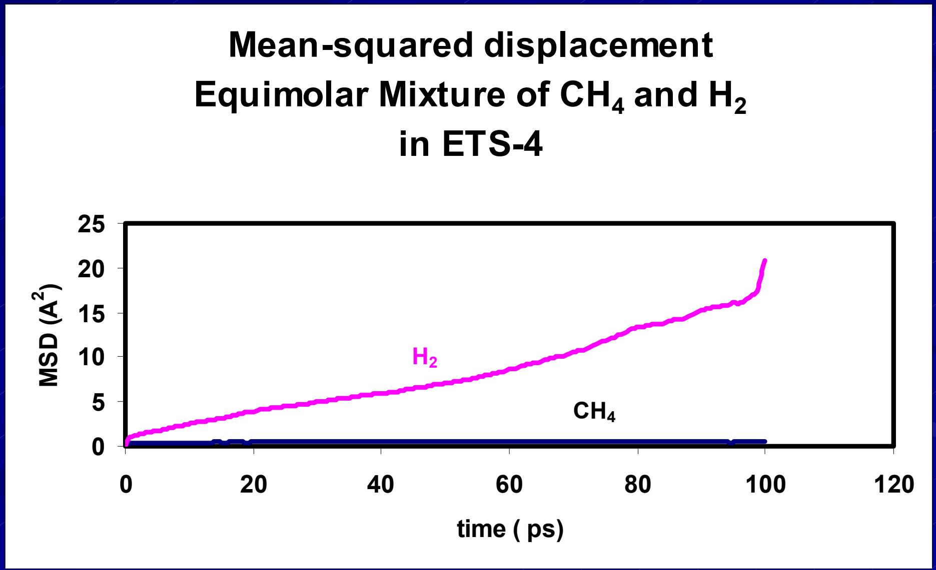


Simulation of Diffusion of H_2 vs. CH_4 in Zorite and ETS-4. H_2 moves quickly through both types of cages; CH_4 moves very slowly through Zorite and DOES NOT MOVE through ETS-4.

ETS-4





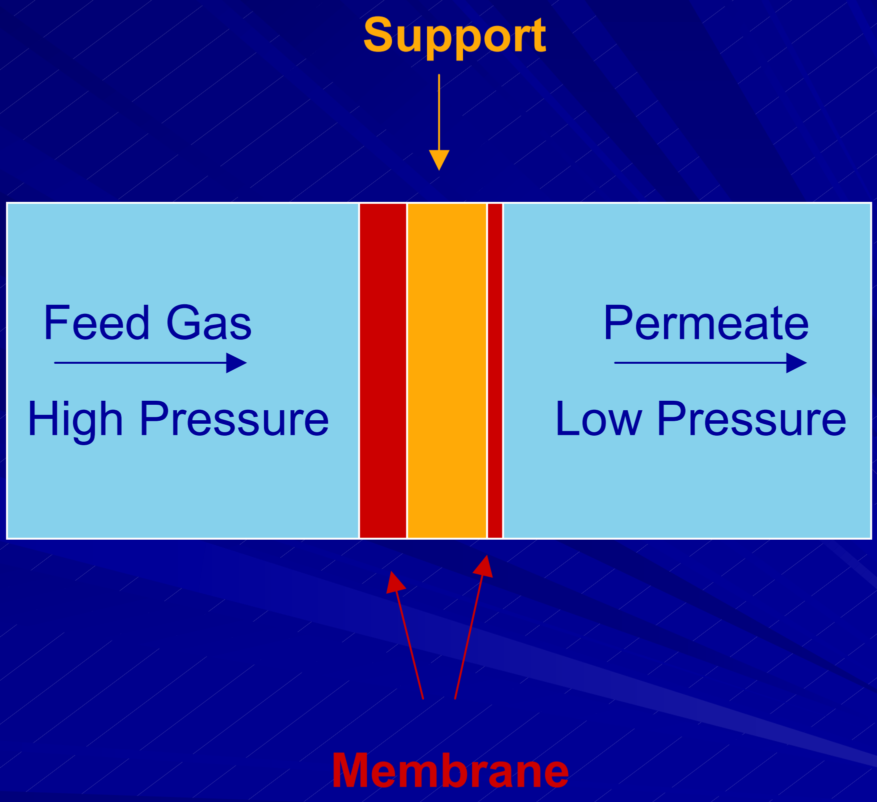


Modeling effort is a partnership between SNL and NMSU

*Mitchell, M. C.; Gallo, M.; Nenoff, T. M. *J. Chem. Phys.* **2004**, *121*, 1910.

Engineered Zeolite Hetero-structures

- Recent theoretical work has suggested that by creating a heterostructure of controlled membrane thicknesses and support thicknesses and porosity, *both Permeance and Selectivity* can be increased. *
  - By controlling the thicknesses and porosities of the membrane and support, the pressure drop experienced across the 1st membrane can positively affect the final permeate flow rate and composition.
    - This new work has yet to be tested experimentally.



*Gardner, T. Q. et. al. **2004**, In Preparation

Current Stance vs. DOE Targets

	Zeolites, Current	Metallic Membrane 2010 DOE Targets
Cost	<$200/ft^2 unoptimized	<$100/ft^2
Flux	10 scfh/ft^2 for highest selectivity at RT & low P	200 scfh/ft^2
Operating Temperature	Up to 650 °C pure gases only (1)	300-600 °C
Durability	13,000 hours (2)	100K hours
Parasitic Power		2.8 kWh/1000 scfh

Although these targets were designed for metallic membranes, zeolite membranes will meet every one easily, except flux.

(1) Lin, Y. S. *Separation and Purification Technology* **2001**, *25*, 39.
(2) Kapteijn, F. et. al. *J. Membr. Sci.* **1996**, *117*, 57.

Acknowledgments

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Martha Mitchell, NMSU: permeation modeling & simulation

Collaborative Discussions:

Chris Cornelius, SNL

Industrial Collaborations:

Trumem LLC; Intelligent Energy, Ltd.; Pall Corporation