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DOE/H_2, Fuel Cells and Infrastructure
Annual Review Meeting, May 19-22, 2003

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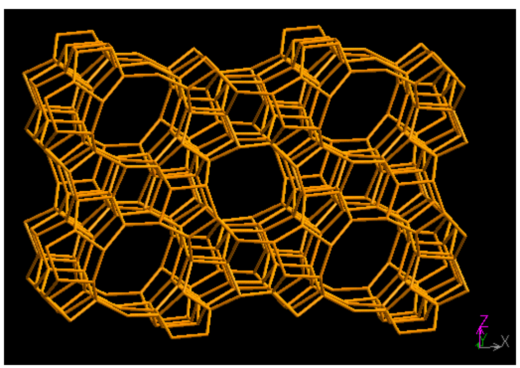
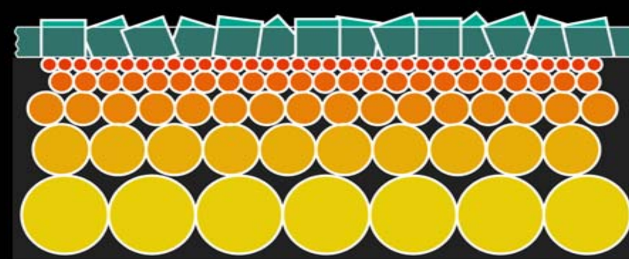
for the United States Department of Energy under Contract DE-AC04-94-AL85000

H_2 Separation Membranes: Introduction

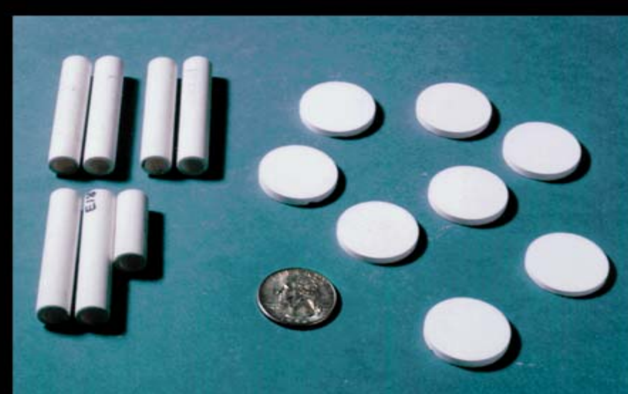
Goal: Synthesis of robust microporous zeolite membranes to improve on H_2 separation technology of polymers of Pd alloys;
Leverage technology to syngas separations, gas purification, biomass, gas enrichment, dehydration



Pore Structure ZSM-5



Schematic: Nonselective porous membrane support w/ selective molecular sieve top layer



Actual membrane supports

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H_2 Separation Membranes: Relevance

Relevance to Hydrogen:

Need to produce H_2 reliably, at low cost

Use of reforming to produce H_2

- Technical Barriers:
    - Defect-free
    - Manufacturability
- Technical Targets:
    - high permeation
    - high selectivity
    - low cost
    - high durability

Steam Reforming: $CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2$

Dry Reforming (MCFC): $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$

H_2 Separation Membranes: Objectives

Objectives:

Synthesis

Defect-free Inorganic crystalline thin-film membranes:
synthesis efforts with Al/Si & Si/Ti phases (organic vs. alkali templating)
film growth on variety of supports (oxides, SS316, composite)

Permeation

Testing new membranes:

H_2, CO, CO_2, O_2, He, H_2O, CH_4 & SF_6;
mixed 50/50 CH_4/H_2 and 50/50 CO_2/H_2

Modeling and Simulation

Light gases through 1D ZSM-22 and compare to ZSM-5
Validation through permeation testing

Business Partners/Collaborations

Basic research "directed" toward commercialization
Industry (manufacturers, end-users), University

H_2 Separation Membranes: Approach (plan/milestones)

Project Method is "R&D":

Basic & Applied Research, Testing, Validation plus Business Development,
Current Milestones due dates

Task 1: Thin Film and Bulk Growth:

Growth of Al/Si zeolite thin films and/or doped with other elements
Synthesis of defect-free silicotitanate (Si/Ti) thin film membranes.
Characterization of all new phases (X-ray diffraction, thermal analyses, surface area, and elemental analysis).
Membrane growth on various substrates (scale-up viability assessment).

Task 2: Modeling and Simulation:

Model separation values for pure light gases interacting with 1D channel pores compare to 3D pores (ZSM-22 vs. ZSM-5).
Model separation values for mixtures of light gases interacting with 1D channel pores compare to 3D pores (ZSM-22 vs. ZSM-5).

H_2 Separation Membranes: Approach (plan/milestones)

Task 3: Permeation Studies

Maintain unit to including repair of Residual Gas Analyzer
to study selectivity to mixed gases.

Permeation studies of pure gases through membranes.

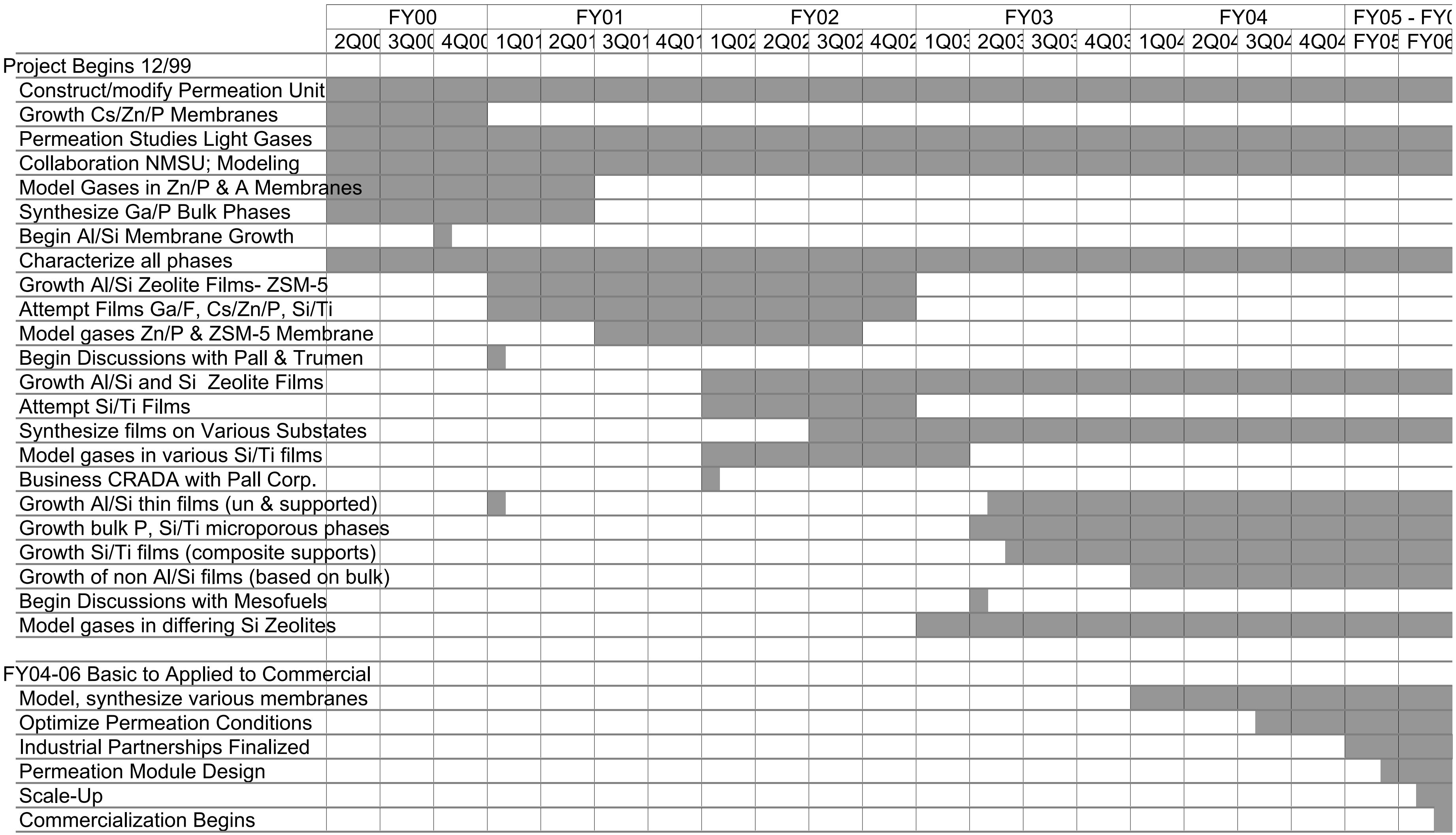
Permeation studies of mixture gases through membranes.

Task 4: Business Development:

Initiate an agreement for product development with an industrial partners.
ie., NDA, licensing or scale-up development work;
Mesofuels; Pall; Trumem.

Pursue new collaborative funding opportunities with industrial partners

H_2 Separation Membranes: Timeline



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H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

- Permeation Unit: testing **CO and mixed gases**, RGA in repair; awaiting H_2S approval

- First evidence of **Zeolite W** (MER) membrane synthesis! 3D channel pores
  From attempted ZSM-22 growth. Secondary growth for defect-free underway

- Defect free Si/Ti membranes synthesized and permeation tested
  New Phase! Durable, Selective, Still under investigation
  To be tested versus simulation data

- All **Si ZSM-5 Silicalite** : Long lifetime and confirmed reproducible permeation
  results; growth on composite and oxide substrates;
  $CO_2 > CH_4 > H_2 > He > (N_2, CO) > O_2$

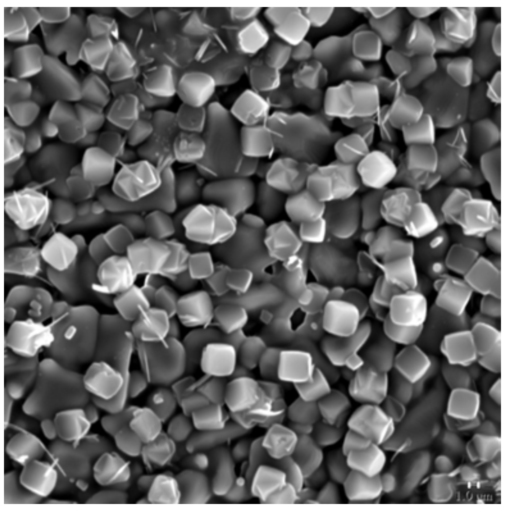
- Utilizing ceramic membrane supports: Inoceramic Alumina disks/tubes
  Trumem oxide-coated SS316 (TiO_2; SiO_2/Al_2O_3; ZrO_2 coatings)
  Pall is sending ZrO_2 coated SS316 tubes

- Modeling/Simulation: Preferential **H_2 separation** through ZSM-5 vs. ZSM-22

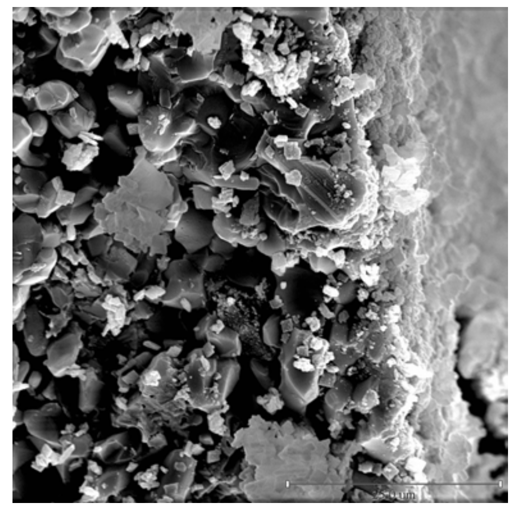
H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

A. Thin Film and Bulk (for future films) Growth:

1. New Silicotitanate Phase grown as thin film!
   Bulk shown to exhibit H_2 separation
   Durable, Unknown Phase, Selective (still being investigated)
   Calcination procedure being determined



Blocky silicotitanate crystals on an alumina support.



Cross section of silicotitanate crystal membrane on an alumina support.

2. **Silicalite** membranes : Lifetime studies (1+ years) show good durability; high reproducibility in procedure yielding consistent permeabilities

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H_2 Separation Membranes: (1/02 - 4/03) Accomplishments/Progress

B. Modeling and Simulation:

1. Studies on Silicalite vs. ZSM-22 continuing
2. Early indication 1D pores of ZSM-22 easily blocked by gases, no good for gas separation

C. Permeation Studies for Validation - Testing pure and mixed gases

1. CO testing (ES&H approved);
2. RGA for mixed gases: in repair;
3. H_2S testing to be developed,
   working with ES&H for approval.

D. Business Development

1. Initiated interaction with Mesofuels Inc.; "Portable reforming unit"
   Non Disclosure Agreement (NDA) in progress
2. Attended HyTeP as SNL representative;
3. Invited by Sen. Jeff Bingaman (D-NM) for H_2 and Fuel Cell
   Economic Development discussions (SNL rep, industry attendees)

H_2 Separation Membranes: Interactions and Collaborations

Presentations:

M. E. Welk, T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation", Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver, BC, Canada, June 2003.

T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation", Spring National ACS meeting, New Orleans, LA, March 2003. *Invited Lecture*.

T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 Separation and Isolation", National Hydrogen Association Meeting, Washington DC, March 2003.

T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H_2 Separation and Isolation", 14th World Hydrogen Energy Conference, Montreal, Canada, June 10, 2002.

Publications:

Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of methane and hydrogen in titanosilicates", *J. Phys. Chem*., **2003**, submitted.

Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO_2 Selectivity and Lifetimes of Silicalite Membranes". *Micro. & Meso. Materials*, **2003,** in press.

Bonhomme, F.; Thoma, S. T.; Nenoff, T. M. "Two ammonium templated gallophosphates: Synthesis and structure determination from powder diffraction data of 2D and 3D-GAPON". *Micro. & Meso. Materials*, **2002**, *53*, 87.

Nenoff, T. M.; Bonhomme, F. "Defect-free thin film membranes for Hydrogen separation and isolation". 14th World Hydrogen Energy Conference Proceedings, Montreal, Canada, 2002.

Symposium:

"Modeling and Simulation in Surface and Colloid Science"; Tina M. Nenoff, Martha Mitchell, Marcus Martin, *Co-Organizers* ACS National Fall Meeting, NYC, NY Sept 7-13, 2003

H_2 Separation Membranes: Interactions and Collaborations

Cooperative Efforts:

- NDA in progress with Mesofuels Inc, Alb. NM

- Collaboration with NMSU extended to new Al/Si and Si/Ti phases

- CRADA #1596 with Pall Corporation for study of microporous materials on separation membranes; examining routes for collaboration (ie., Proposals, etc.); membrane supports, possible module design

- Cooperation with Trumem International, LLC, for oxide-coated membrane supports

- Attended HyTeP as SNL speaker/representative in Santa Fe, NM, 4/23/03

- Invited by Senator Jeff Bingaman (D-NM) for H_2 and Fuel Cell Economic Development discussions (included national lab & industry attendees), Albuquerque, NM, 4/25/03

H_2 Separation Membranes: Plans, Future Milestones (5/03-9/04)

- Synthesis and characterization:

Ion exchanged or metal doped Al/Si films
Si/Ti film growth continued
Novel bulk microporous phases, future thin films
Membrane growth on various substrates, for scale-up viability
assessment (ie., SS316 vs. oxide vs. composite)
Attempt use of ALD (Atomic Layer Deposition):
metal oxide layer on top of zeolite layer to catalyze H_2S

- Permeation:

Pure and mixed gases, RT and 80°C; seek ES&H approval for H_2S

- Modeling:

Simulation of gas permeation thru different Al/Si type zeolite membranes
ie., ZSM-5 vs. Zeolite W

- Business Development:

Build partnerships with end-users & membrane Co.
(ie.,Mesofuels; Pall; Trumem)

H_2 Separation Membranes: Responses to Panel's Questions

1. Strength/Robustness of Membranes:

   Stable in air and water.
   Durable in temperature cycling (Si/Ti >500C),
   continuous treatment and gas exposure,
   over time (1+ year Silicalite).
   mechanically durable to handling, transport and heat cycles.

2. Water and H_2S Stability of Membranes:

   Steam: Membranes are not water soluble.
   (a) a cold trap or other dehydrator could be used either up- or downstream of the membrane to remove steam.
   H_2S:
   (a) use of a Metal Oxide to remove upstream of membrane,
   (b) development of a "catalytic" membrane;
   layer of metal oxide on top of the zeolite membrane

H_2 Separation Membranes: Responses to Panel's Questions

3. Cost **Estimate** of Zeolite Membranes vs. Pd Membranes:

(a) Pd in limited and politically-sensitive supply for "H_2 Economy"

Currently supplied from Russia and South Africa

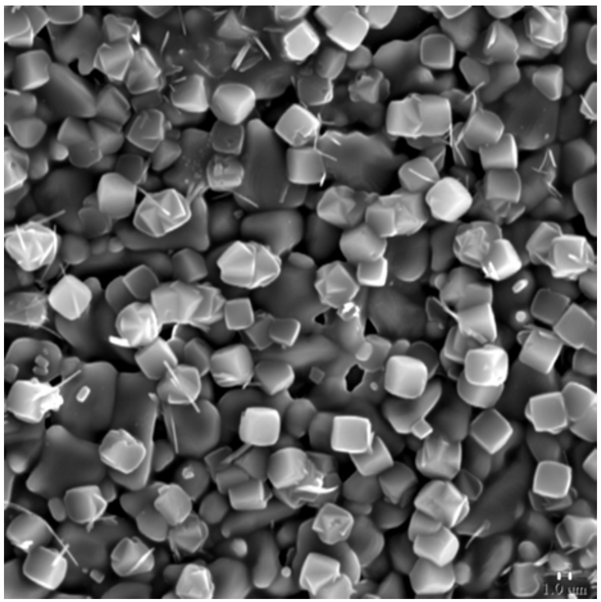
(b) Industry approximation of Pd film ≈ \$100/ft^2 or installed \$250/ft^2

(c) Zeolite films estimated $\leq$ \$200/ft^2 installed

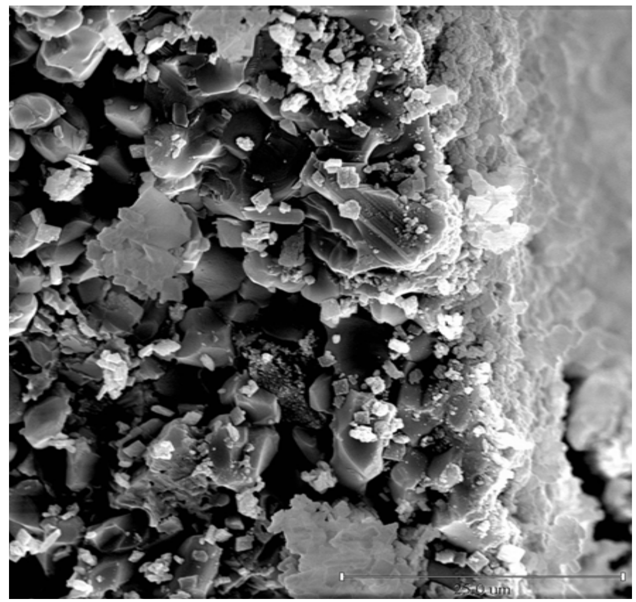
Assuming zeolite membranes will become nearly as commercially viable as Pd membranes, cost will drop!!

H_2 Separation Membranes: Current Year Highlights: Si/Ti Membranes

Unidentified/New Silicotitanate phase grown as film



Blocky silicotitanate crystals on an alumina support.



Cross section of silicotitanate crystal membrane on an alumina support.

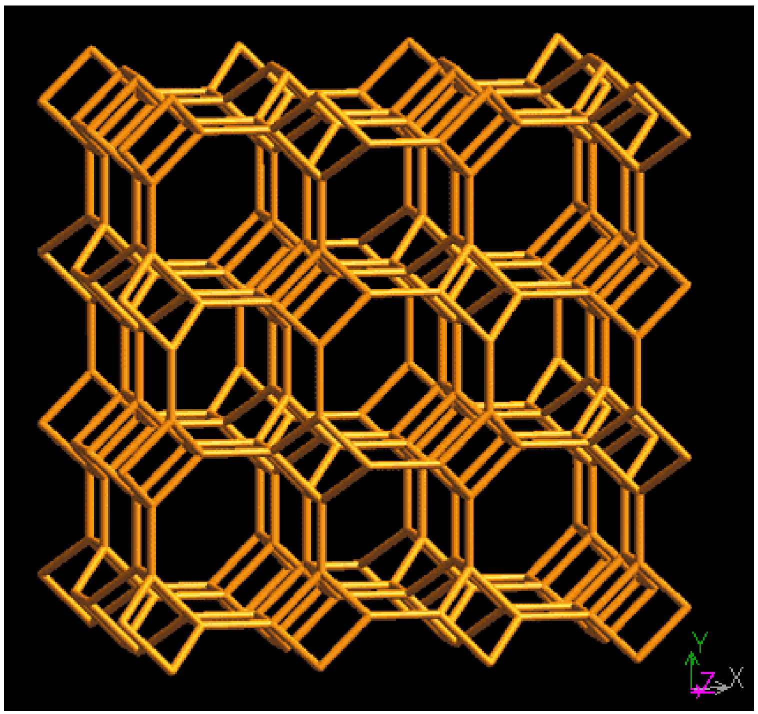
Preliminary permeation values @ RT, SNL Si/Ti $\approx 10^{-8}$ mole/(m^2 Pa sec)

H_2/N_2 = 2.3
H_2/CH_4 = 1.9
He/N_2 = 2.0
CH_4/N_2 = 1.2
H_2/CO_2 = 3.0
H_2/O_2 = 3.2
CH_4/CO_2 = 1.5

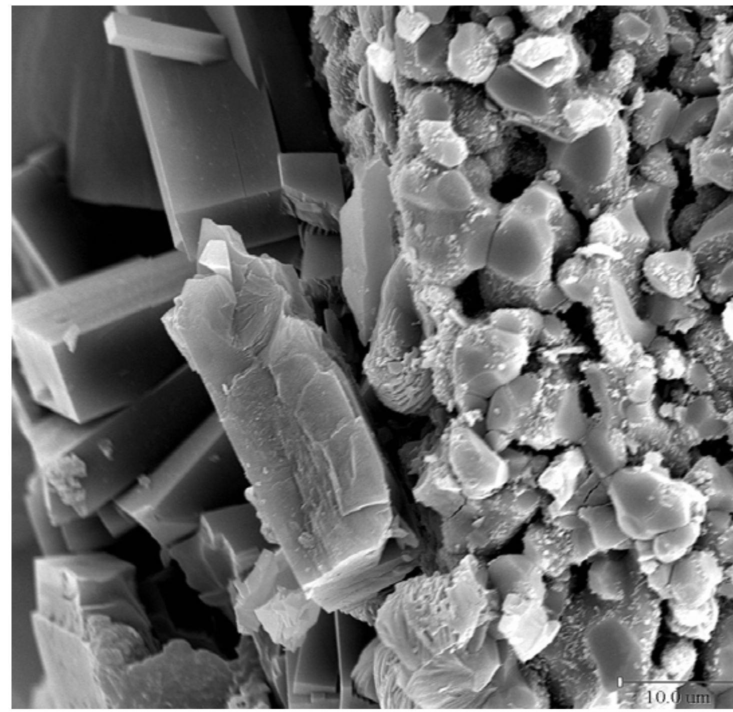
Work in Progress though Selectivity Evident! Calcination procedure not perfected yet. Template pore blockage still interfering with gas permeation.

H_2 Separation Membranes: Current Year Highlights: Si/Al Membranes

Zeolite W: 8 rings, 3D Pores

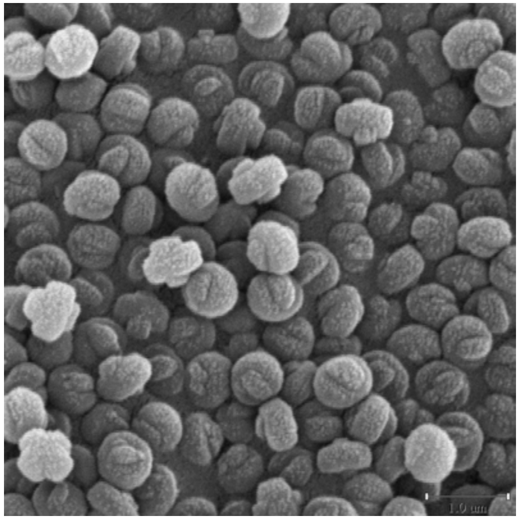


Cross Section of Zeolite W Film
On Alumina Support

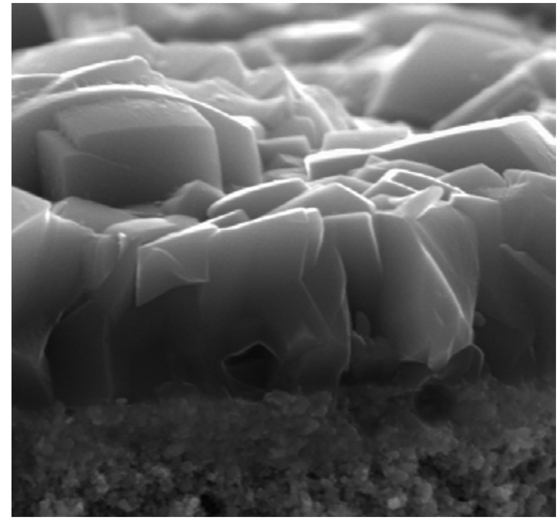


First reference of Zeolite W as a thin film membrane
Continued research needed to fill defects and study permeation

H_2 Separation Membranes: Current Year Highlights : Silicalite Films



Seed Crystals Uniform in size, 1µm



10 µm thick Silicalite Membrane on composite support

Permeation and Regenerability

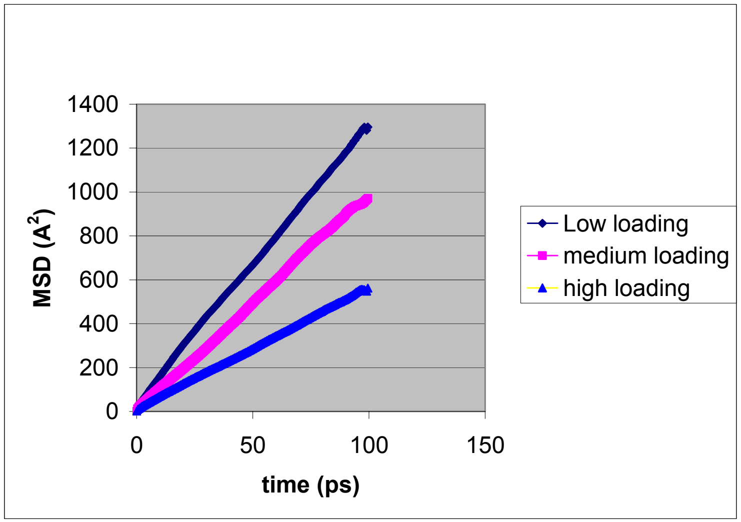
Single Gas Permeance (10^{-7} mole/m^2 s Pa)

Trans-membrane pressure= 16 PSI

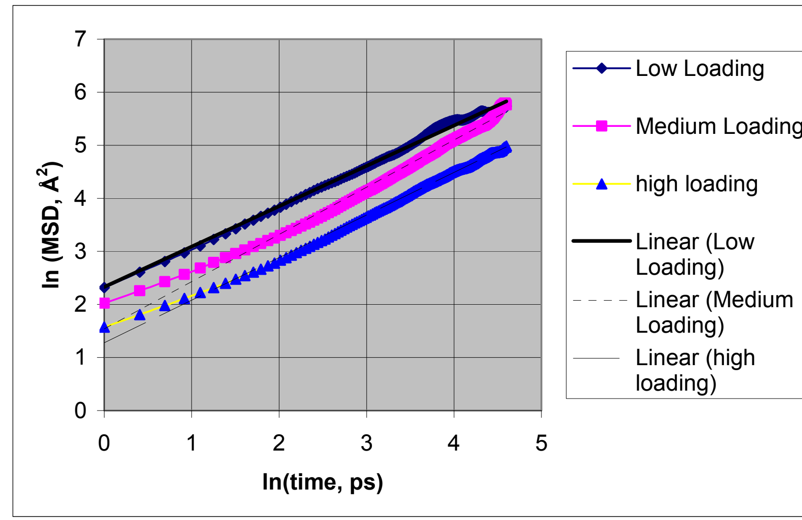
as / (Kinetic ∅ (Å)) Membrane	He (2.6)	SF_6 (5.5)	H_2 (2.8)	CO_2 (3.3)	O_2 (3.5)	CH_4 (3.8)	N_2 (3.6)	CO (3.7)
18A	1.8	< 0.05	2.4	2.9	1.4	-	-	1.6
21A	1.2	< 0.04	1.6	3.0	1.3	1.7	1.1	-
22A	1.5	< 0.02	2.0	5.9	1.2	3.2	1.4	1.4
22B	1.5	< 0.03	2.9	4.9	-	-	-	-
22B "regenerated"	1.1	-	1.4	2.9	-	-	-	-
28A	0.8	< 0.03	1.9	5.1	1.3	2.6	1.6	1.6

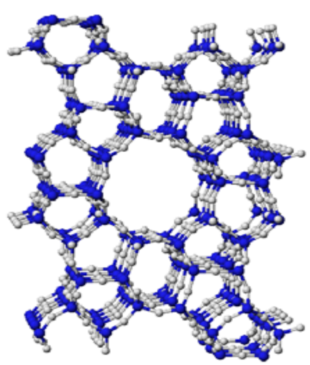
Current Simulation Studies at NMSU

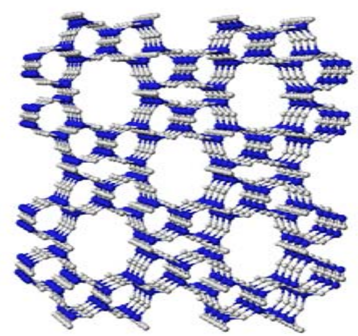
Mean-squared displacement of H_2 in Silicalite



Mean-squared displacement of H_2 in ZSM-22







Simulation of Diffusion of H_2 in Silicalite vs. ZSM-22
H_2 moves much more quickly through Silicalite due to its multidimensional channels;
Gas molecules cannot "pass" each other, causing blockage in ZSM-22