Defect-free Thin Film Membranes for H_2 Separation and Isolation

PDP 17

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DOE / H_2, Fuel Cells & Infrastructure Technologies
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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94-AL85000

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Objectives

Goal: Synthesis of robust microporous zeolite membranes to improve on the H_2 separation technologies of polymers and precious metals

Relevance to Hydrogen:

Need to produce H_2 reliably, at low cost

Use of reforming to produce H_2

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

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

Objectives

Synthesis

Defect-free Inorganic crystalline thin-film membranes
1 sided vs. 2 sided membranes (thickness variables)
Synthesis efforts with Al/Si & Si phases
Film growth on variety of supports (oxides, SS316, composite)
Testing on-line at various temperatures

Permeation

Testing new membranes, RT and elevated Temps, and varying pressure:
pure: H_2, N_2, CO, CO_2, O_2, He, H_2O, CH_4, H_2S & SF_6;
mixed: 50/50 CH_4/H_2 , CO_2/H_2 ; simulated reformate stream

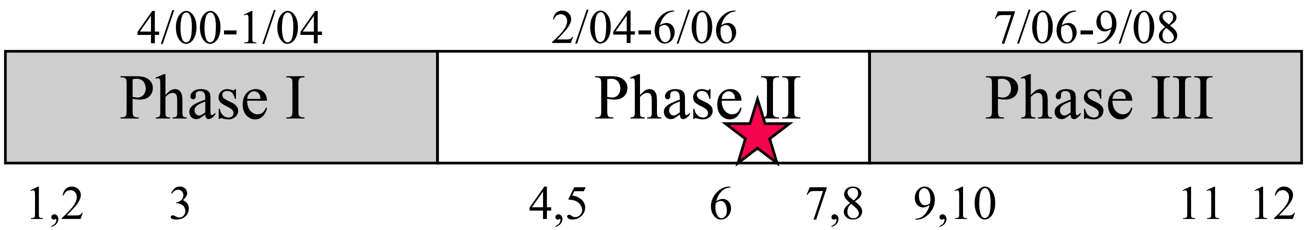
Modeling/Simulation

Light gases through ZSM-5 at elevated real-world operating temperatures
Validation through permeation testing

Business Partners/Collaborations

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

Overview: Project Timeline



- Phase I: Membrane synthesis and characterization
  1. Membrane composition
  2. Permeation unit construction
  3. Pure Gas testing
- Phase II: Membrane Optimization
  4. Various substrates for membranes
  5. Mixed gas testing
  6. Variable temperature testing
  7. Variable pressure testing
  8. Variable zeolite framework testing
- Phase III: Applied to commercialization
  9. Optimize membrane support
  10. Industrial Gas Streams (Industry involvement; Lab & pilot-scale)
  11. Scale up
  12. Commercialization Processes

★ current status

Overview: Budget

Funding Interrupted January 2005

Total FY05 funding: ≈ $125K*

DOE: $200K/year original ⟶ *NEW: $125K/FY05

$180K to Sandia	$105K Sandia
$15K subcontracted to NMSU (modeling)	$ 15K NMSU
$ 5K subcontracted to NMTech (membrane)	$ 5K NMT

In-kind funding (approximate: labor, samples, testing, travel) FY05:

- $ 1K Intelligent Energy, Inc.
- $ 1K Pall Corporation
- $ 0.5K G.E. Dolbear & Associates, Inc (NDA signed 10/04)

Total FY04:

- DOE: $200K
- In-kind: ≈ $11K (Mesofuels, Pall)

Overview: Partners

Industrial Partners:

- Intelligent Energy, Inc., Anand Chellappa: Reforming Gas Steam Composition
- Pall Corporation, Jim Acquaviva: Membrane Supports, Visits to both facilities
- G.E. Dolbear & Associates, Inc.: Non-disclosure Agreement placed, discussions on testing our membranes at elevated temps

Academic Partners:

- New Mexico State University, Martha Mitchell, Dept. of Chemical Engineering: modeling and simulation
- New Mexico Tech University, Junhang Dong, Dept. of Chemical Engineering: novel thin film membranes and permeation mixed gas testing

National Participation:

- Welk: DOE/H_2 Separations Workshop, Washington, DC, 9/8-9/04
- Nenoff: BES H_2 Separations Review Panel: Rockville, MD, 3/31/05-4/1/05
- Nenoff: Co-Editor (w/ R.Spontek), *MRS Bulletin* "Hydrogen Purification: An Important Step Towards a Hydrogen-based Economy", for May 2006 publication.

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Overview: Technical Barriers and Targets

DOE Technical Barriers for Separation Membranes (for H_2 Production):

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- G. Efficiency of Gasification, Pyrolysis, & Reforming Technology
- AB. Hydrogen Separation and Purification

DOE Technical Targets for Separation Membranes for 2010 (Pd membranes):

- Flux Rate = 200 scfh/ft^2
- Cost = <$100/$ft^2$
- Durability = 100K hours
- Operating Temp = 300-600 °C
- Parasitic Power* = 2.8 kWh/1000 scfh

* recompress H_2 gas to 200psi

Approach

Development of Defect-free thin film zeolite membranes for Hydrogen Production:

1) Synthesize membranes with Silicate-based frameworks
   use supports that are industrially relevant

2) Model/Simulate/Validate permeation of light gases through the frameworks

3) Analyze flux and permeation of gases (pure, binary, mixed gas streams)
   at ambient and varying temperatures/pressures

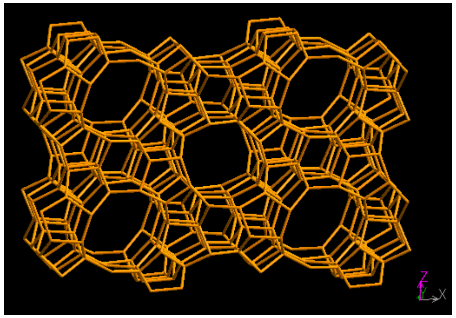
4) Optimize membranes' flux, permeation and durability; optimize permeation
   and separation values by choice of membranes, temp, pressure and
   stream component concentration

5) Foster industrial contacts for membrane stream and pilot-scale testing,
   and future commercialization partnerships

Technical Accomplishments/Progress

- Permeation Unit: testing **mixed gases (RT & higher),** H_2O/steam, H_2S; GC additions
- Defect-free Silicalite membranes synthesized & permeation tested
  - 1 sided vs. 2 sided tested
  - pressurized stream vs. steady state
  - **50/50, mixed gases** (including steam and H_2S)

MFI: silicalite



- As temperatures increase (RT-300°C),
  - 1-sided membranes increase in H_2 selectivity
  - 2-sided membranes decrease in H_2 selectivity
- **H_2O should be removed** from stream prior to membrane; aids C-permeation, hinders H_2
- Simulation of industrial simulant (no H_2O) separation at 500°C shows selectivity for H_2
- **H_2S & H_2O inclusion:** no destruction to membrane in permeation testing up to 300°C
- Utilizing ceramic membrane supports: Inoceramic Alumina disks/tubes
  - Oxide-coated SS316 (TiO_2; SiO_2/Al_2O_3; ZrO_2 coatings)
  - Pall Corp. ZrO_2 coated SS316 tubes

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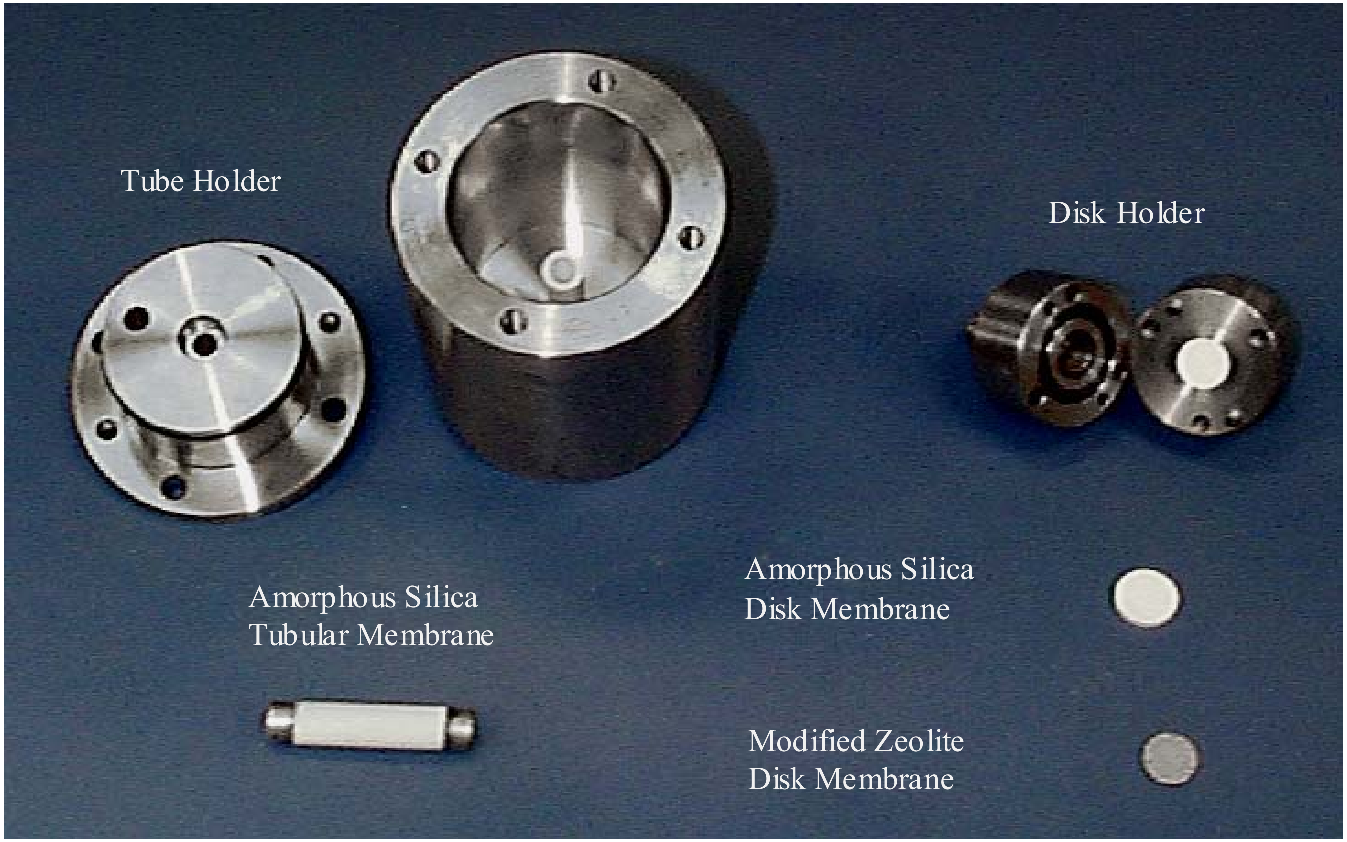
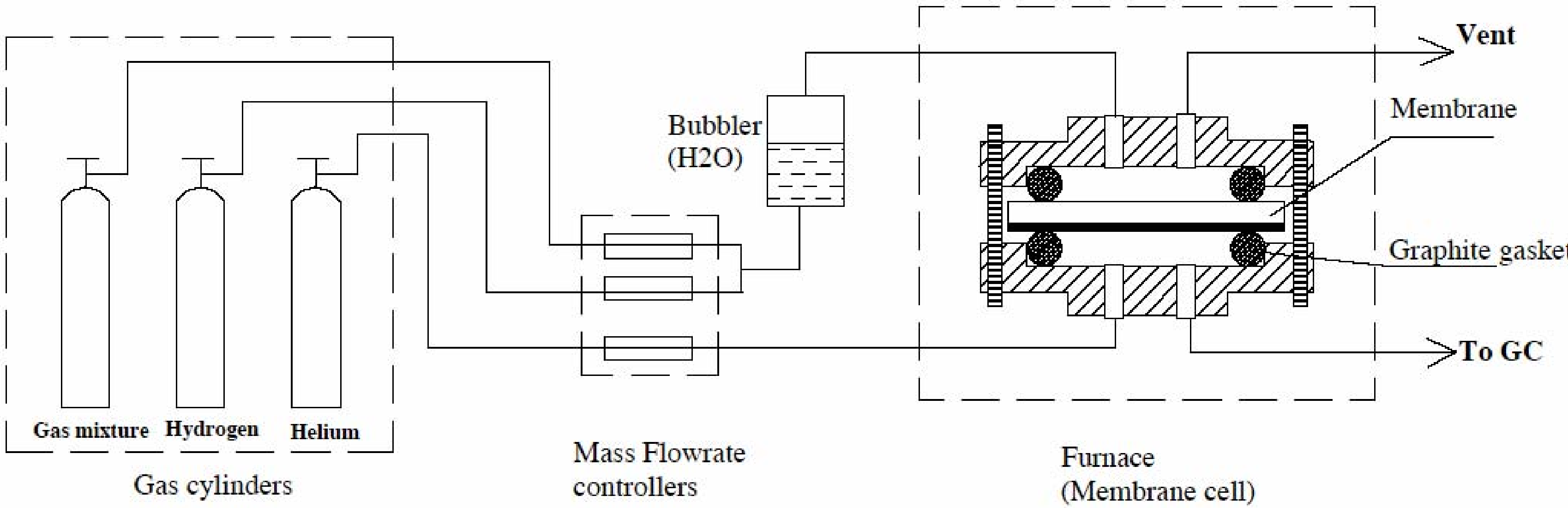
Technical Accomplishments/Progress (con't)

Membrane Supports and Permeation Test Cells:



Technical Accomplishments/Progress (con't)

Updated Mixed Gas & Steam Permeation Testing at SNL and NMT



NMTech: permeation testing using the Wicke-Kallenbach method

Sweep flow = 15 ml/min, Atmospheric Pressure (87kPa)

SNL: permeation testing under pressure of 16psi

Temperature = RT ≈ 500°C

$S_i = (y_i/(1-y_i))/(x_i/1-x_i))$, where x_i and y_i is mol fractions of permanent gases

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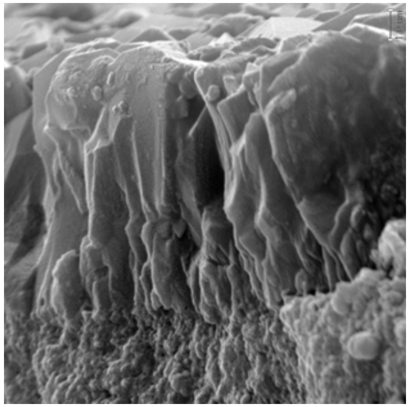
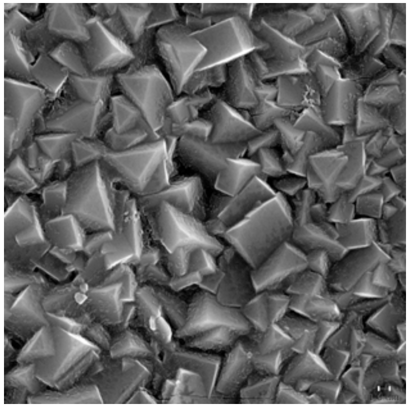
Technical Accomplishments/Progress (con't)

Traditional MFI Membranes



1.0 Micron



1.0 Micron

Silicalite ≈ 10^{-6} - 10^{-7} mole/(m^2 Pa sec)

RT, Pure Gases

$H_2/N_2 = 1.4$

$H_2/CH_4 = 0.625$

$He/N_2 = 1.1$

$CH_4/N_2 = 2.28$

$H_2/CO_2 \geq 0.34$

$H_2/O_2 = 1.7$

$CH_4/CO_2 = 0.54$

$H_2/CO = 1.43$

Silicalite-1 Gel Composition:

2600 H_2O: 53 Na: 92 TPA^+ : 100 Si

40g H_2O, 0.25 g NaOH, 25 g LUDOX SM-30,

3 g TPAOH, 1.5 g TPABr

pH~10.5

- Age for 24 hrs. while stirring
- Place support and gel in autoclave overnight (24 hrs.) at 170-180°C
- Test membrane for defects using permeation unit
- Calcine defect-free membranes; ramp to 400°C at a rate of 0.5°C/min., hold for 12 hours, and cool to RT at a rate of 0.5°C/min.

Result: Two- sided defect-free ~7 micron thick Zeolite Membranes

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Technical Accomplishments/Progress (con't)

SNL Silicalite Membrane

2 sided membranes

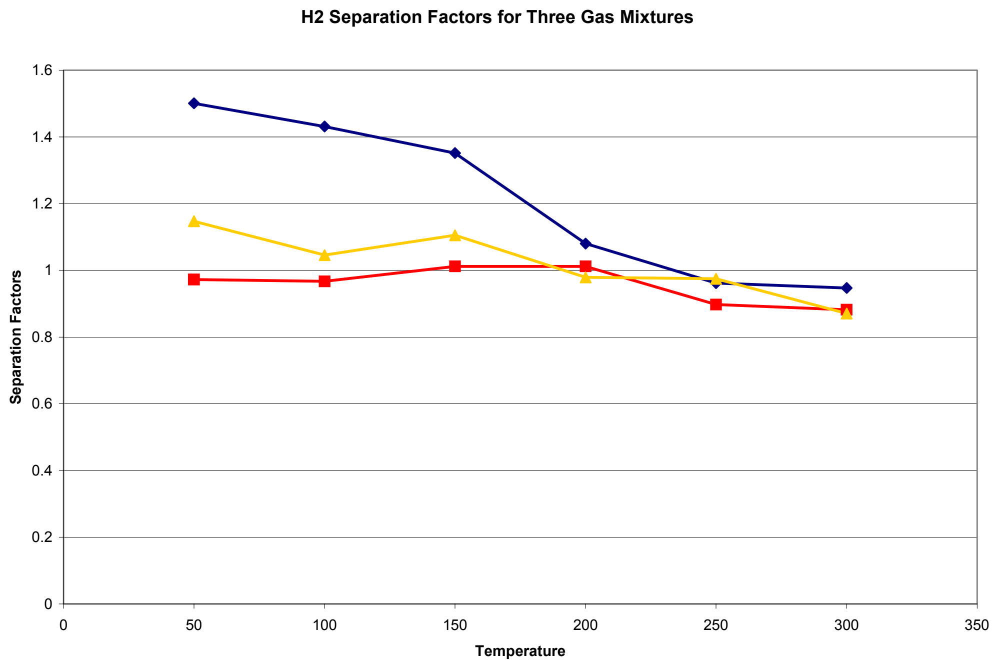
ΔP = 15 PSIG

Precalcined DF Membrane

Temperature Ramped to 300°C

Three gas mixtures were tested at decreasing 50°C intervals:

- 50/50 H_2/CO_2
- 50/50 H_2/CH_4
- Reformate Simulant: 76% H_2, 13.6% CO_2, 6.8% CO 3.4 % CH_4 (Intelligent Energy)



Silicalite, Selectivity Factors at Variable Temperatures:

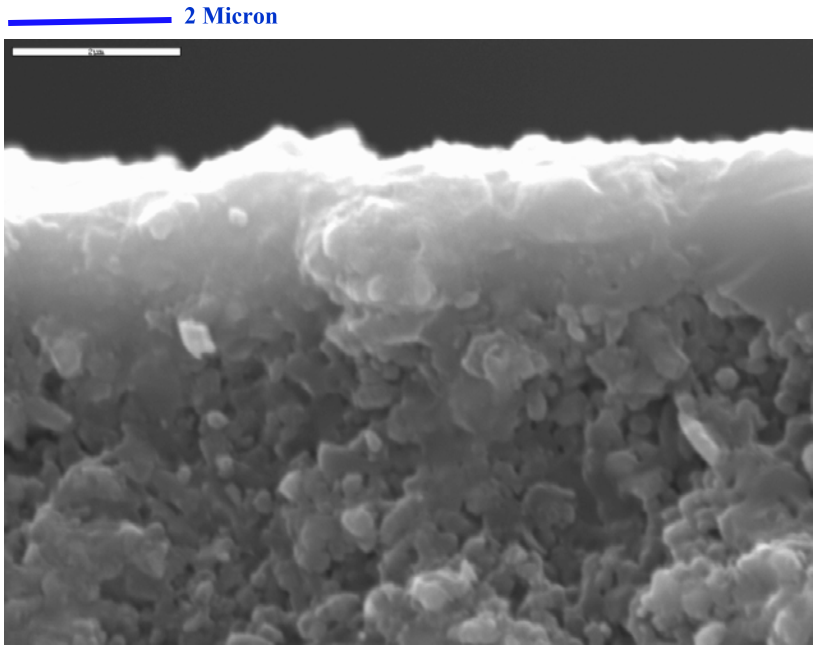
	RT	50°C	100°C	150°C	200°C	250°C	300°C
H_2/CO_2 (50/50)	0.21	1.15	1.05	1.11	0.98	0.97	0.87
H_2/CH_4 (50/50)	0.48	0.97	0.97	1.01	1.01	0.90	0.88
Reformate, H/All	0.47	1.50	1.43	1.35	1.08	0.96	0.95
200ppmH_2S/N_2		0*					

**20ppm H_2S detection limit*

Technical Accomplishments/Progress (con't)

New MFI Membrane Synthesis: Ultra Thin Film Zeolite Membranes

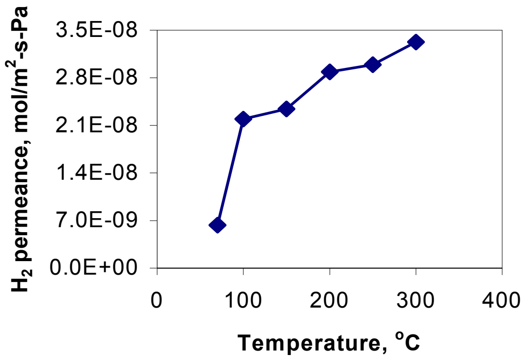
Hydrothermal synthesis methods on alumina disks and tube supports
General Synthesis formula (Silicalite):
SiO_2:TPAOH:NaOH:H_2O
Supports polished and suspended in the solutions in an autoclave
180°C, 4 hours
Thermal treatment repeated 2x
Recovered, washed, dried in air
Calcined 450°C (slow ramp)

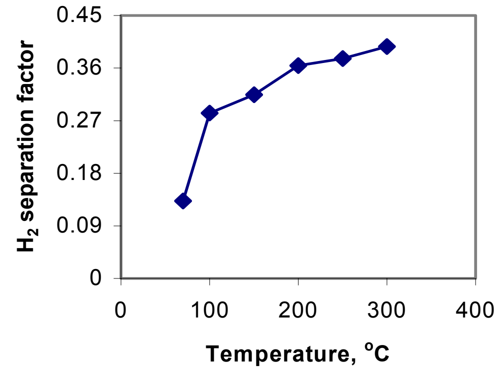


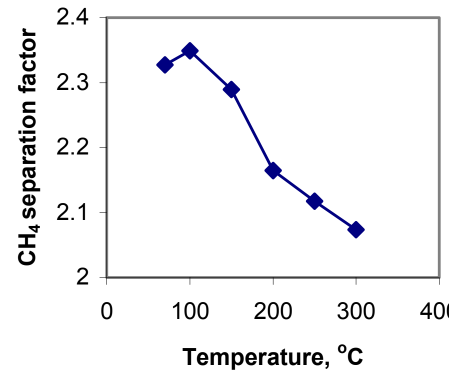
Result: One sided defect-free ~1.5 micron thick Zeolite Membranes

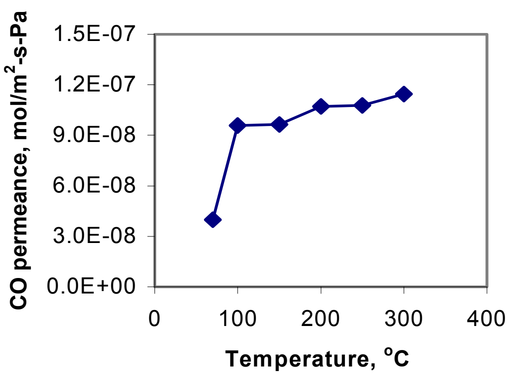
Separation Factors:
H_2/SF_6 (@ RT) = 175
p/o-xylene (@300°C) = 8.5
p-x flux = $1x10^{-5}$ mol/m^2-s

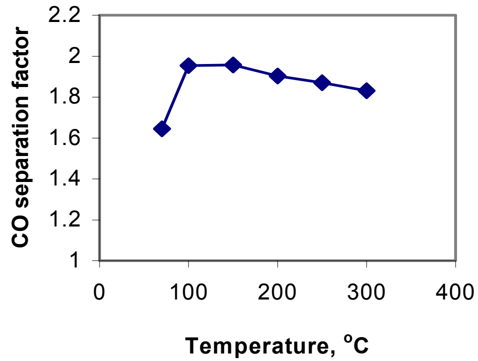
Technical Accomplishments/Progress (con't)

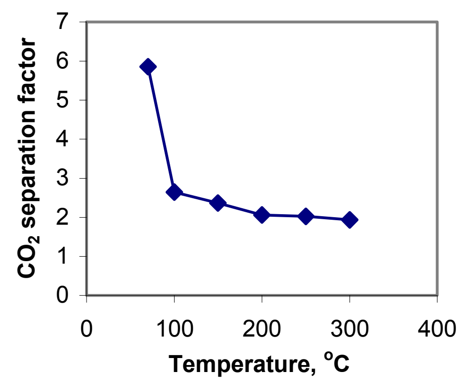










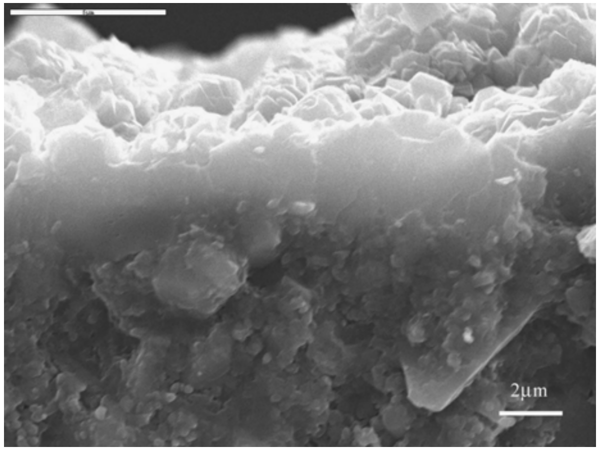


Industrial Stream Tested: 50% H_2, 6% CO, 0.02% H_2S, 4% CH_4, 10% CO_2 and 30% H_2O in mol fraction

Single sided thin films: H_2 separation factor increases with temperature (300°C), hindered by H_2O, but still increasing; lack of H_2O will greatly increase H_2 selectivity*

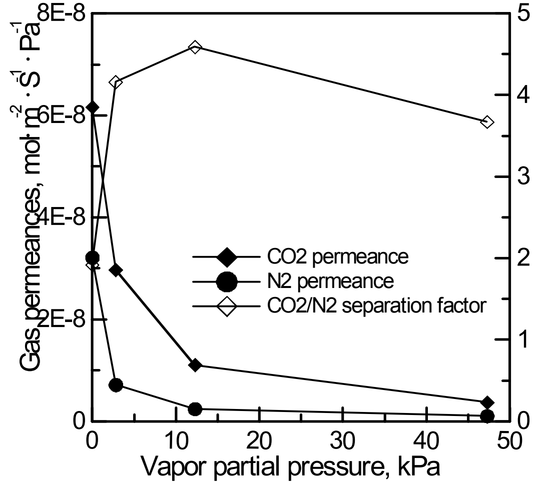
*Dong, etal., AIChE J., 46(10), 1957, 2000.

Technical Accomplishments/Progress (con't)



FAU membrane

Effect of H_2O Partial Pressure on CO_2/N_2 sep at 200°C



Based on preliminary light gas separations with FAU membrane (1-sided): H_2O has a strong affinity to the CO_2, by increasing the permeance.*

Theory: by eliminating the H_2O from the stream, $CO/CO_2/CH_4$ selectivities will continue to decrease with temperature, and **H_2 will selectivity from reforming stream will continue to increase with temp** as predicted by modeling/simulation

*Gu, Dong, Nenoff; Ind. Eng. Chem. Res., 2005, 44, 937.

Technical Accomplishments/Progress (con't)

Molecular Dynamic Simulations :
Comparing Simulations with Experiments for Validation

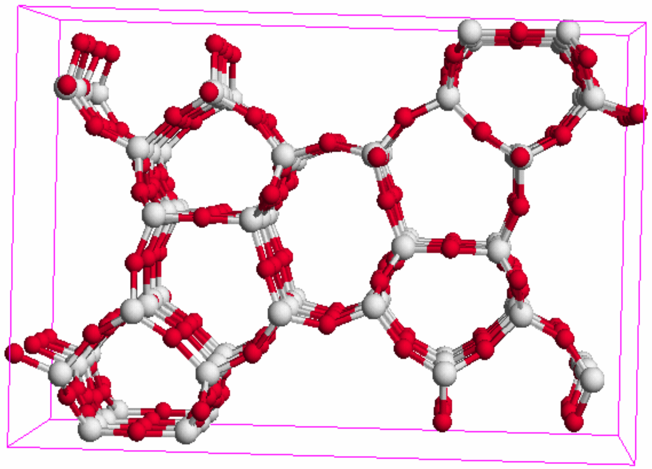
Force Field used:

$$U(r^N) = \sum_{bonds} \frac{1}{2} K_b [b - b_0]^2 + \sum_{angles} \frac{1}{2} K_\theta (\theta - \theta_0)^2 + 4\varepsilon[(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6]$$

T=500°C; no H_2O in simulation mixture
Rigid framework
Total time of simulation 500 ps
Periodic boundary conditions in all three directions
Cutoff distance
- –9 angstroms for pure and binary mixtures
- –11 angstroms for quaternary mixtures

Unit cell used
- –4 for pure and binary mixtures
- –8 for quaternary mixture

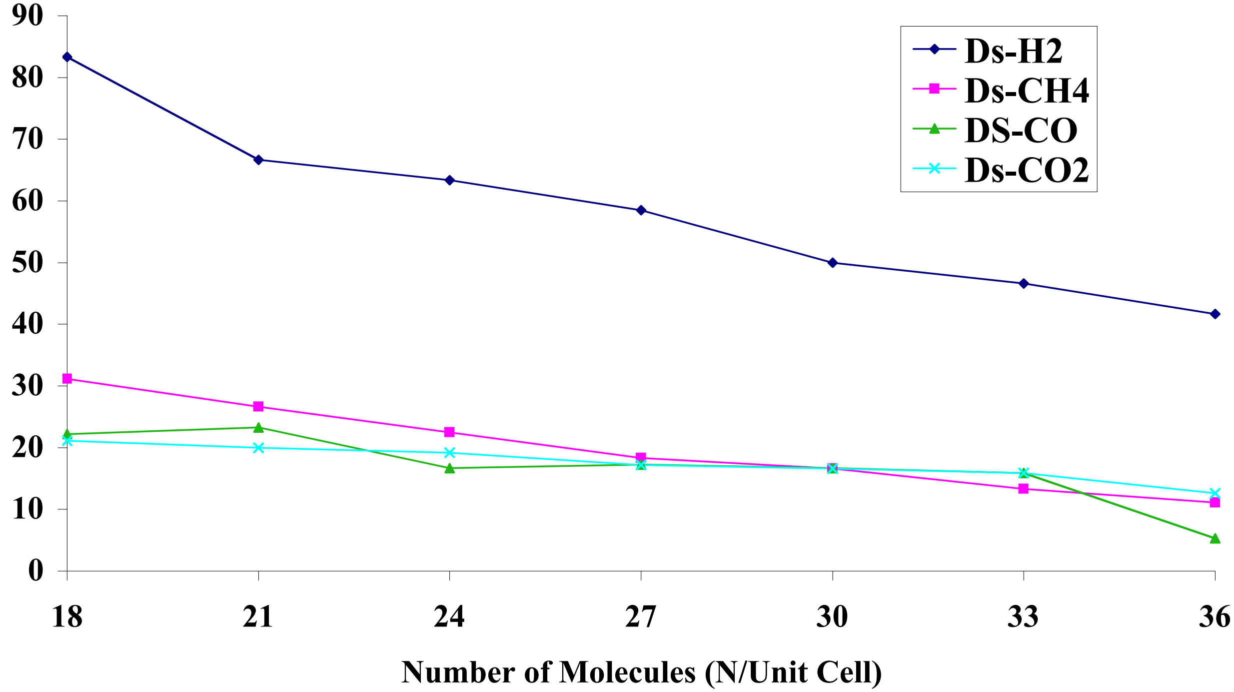
MFI: silicalite



Technical Accomplishments/Progress (Simulations con't)

Displacement of H_2 in Silicalite vs. competing gases

Quaternary/simulant: 76% H_2, 13.6% CO_2, 6.8% CO, 3.4 % CH_4 (No H_2O)



Simulation predicts H_2 purification at Temperature (500°C) but maximum at low loadings

Responses to Previous Year Reviewer's Comments

Reviewers Comments are all helpful in guiding our project!

1) Need to step up testing:

- we have focused on testing our membranes under varying conditions including RT-300°C, with pure, binary and industrial simulant mixtures
- we have tested under two different conditions of pressurized streams and Wicke-Kallenbach method

2) Focus on Real World Operations:

- focus on one industrial simulant gas mixture, 50-300°C
- we have compared MFI single vs. double sided membranes
- H_2O/steam operation capability added: water affects separation values but membrane is stable at least up to 300°C
- H_2S operation capability added: membranes remain stable at least to 300°C

Responses to Previous Year Reviewer's Comments (con't)

3) Fundamental Aspects of Zeolite Membrane should be emphasized - to advance the know-how of film growth

Our synthetic research is advancing the basic understanding in :

- novel methods to synthesizing very thin zeolite films (≈1.5microns)
- a new direction in synthesizing "defect-free" for MFI frameworks through oligomer modification
- new directions in different pore frameworks (ie., FAU)
- negative affect of H_2O on H_2 selectivity due to affinity for C molecules

Future Work

- **Remainder of FY05:**

  Midyear funding cuts terminate work in 6/05 for the remainder of FY05
  ($100K pull back in Jan 05; limited remaining funds)

  Temperature: continue to increase on Intelligent Energy, Inc. simulated stream

  Investigate effect of pressure plus temperature on selectivity

  Investigate effect of H_2O removal from stream prior to membrane

- **FY06:** *Restored Funds to complete FY05 milestones and continue with FY06; higher selectivity using zeolites:*

  Investigate <u>pervaporation</u> with zeolite membranes for H_2 selectivity

  Investigate <u>Catalytic Membranes</u> for H_2 Production from reforming stream

  Investigate effect of membrane modification on separation values

  Investigate membrane lifetimes versus H_2S

  Investigate H_2S scrubbing with membrane catalytic coatings

  Work with Pall Corporation to design and scale membranes & catalytic reactors

Supplemental Slides

Publications & Presentations

Presentations:

Welk M. E., Nenoff, T.M. "Defect-free Zeolite Membranes for H_2 Purification", ACS Fall Meeting, Philadelphia, PA, 8/25/04.

Welk M. E. (plenary), Nenoff, T.M. "Microporous Zeolite Membranes", DOE/H_2 Separations Workshop, Washington DC, 9/8/04.

Nenoff, T. M.; Welk, M. E. "Membranes for light gas separations", Univ. CA, Santa Barbara, Dept. of Chemistry Seminar, 10/22/04.

Nenoff, T. M.; Welk, M. E. "Membranes for light gas separations", New Mexico State University, Dept. of Chemical Engineering Seminar, 10/29/04.

Nenoff, T. M. "Inorganic Thin Films for H_2 Separation and Purification", presentation to representatives of DaimlerChrysler Corporation, Sandia National Labs, Livermore, CA, 1/13/05.

Upadhyayula, V.K.K; Mitchell, M.C.; Gallo, M;. Nenoff, T.M. "Evaluating Materials for High Temp H_2 Separation Using GCMC and MD Simulations", AIChE National Sp Meeting, Atlanta, GA, 4/12/05.

Publications:

Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of methane and hydrogen in titanosilicates", *J. Phys. Chem*., **2004**, *121*(4), 1910-1916.

Welk, M. E.; Nenoff, T. M.; Bonhomme, F. "Defect-free thin film zeolite membranes for H_2 Purification and CO_2 Separation", Proceedings 14th International Zeolite Conference, Cape Town, South Africa, **2004**, 690-694.

Welk, M. E., Nenoff, T. M. "Mixed Gas Permeation Studies Through Defect Free ZSM-5 and Silicalite Zeolite Membranes.", *J. Membrane Science*, **2005**, in prep.

Gu, X.; Dong, J; Nenoff, T. M. "Reforming stream gas separations through MFI Zeolite Membranes", *J. Membrane Science.*, **2005**, in prep.

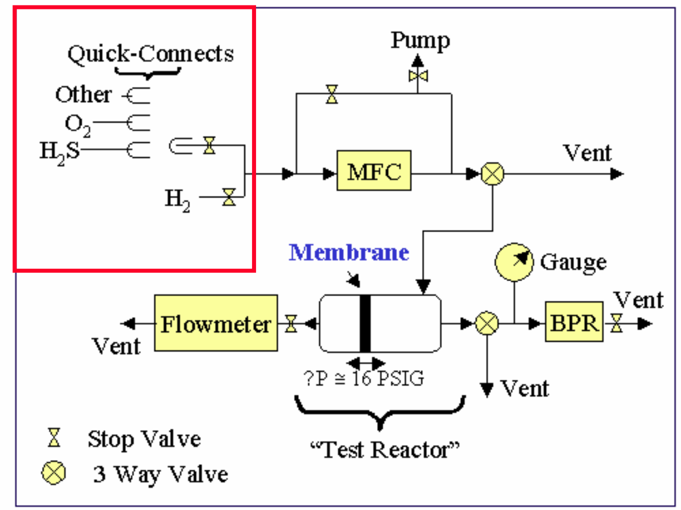
Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

The operation and testing of pure and mixed gases through the membranes in the permeation unit, at temperatures between RT and 500°C, and at 16psi.

Hydrogen Safety

- H_2 separate from O_2 & other gases by plumbing
- Entire permeation unit is located inside a fume hood
- H_2S and CO sensors set according to OSHA limits (tested yearly)



- Thorough analysis of gas, equipment specs, process & pressure testing to ensure safety AND to pass Sandia's corporate ES&H regulations (SOPs, PHS, PSDP)

- All operators in compliance with required corporate training policies