

# Defect-free Thin Film Membranes for H<sub>2</sub> Separation and Isolation

PDP 17

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DOE / H<sub>2</sub>, Fuel Cells & Infrastructure Technologies  
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# Objectives

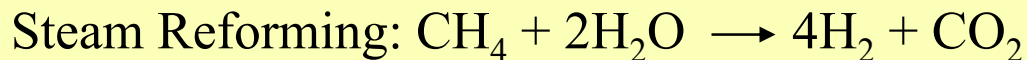
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**Goal:** Synthesis of robust microporous zeolite membranes to improve on the H<sub>2</sub> separation technologies of polymers and precious metals

## Relevance to Hydrogen:

Need to produce H<sub>2</sub> reliably, at low cost

Use of reforming to produce H<sub>2</sub>





# Objectives

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## 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 reformat stream

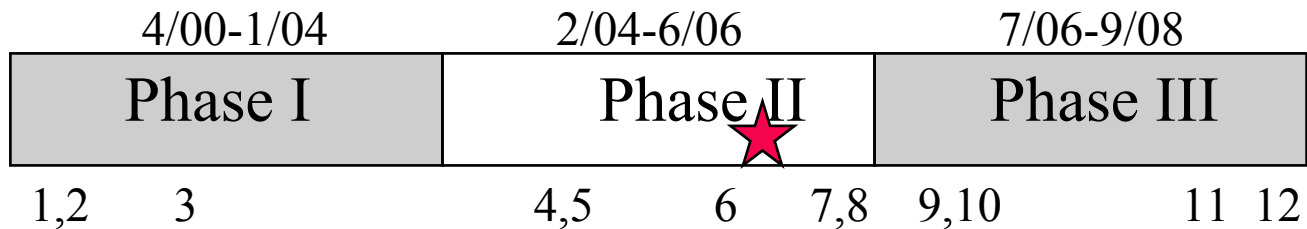
## Modeling/Simulation

- 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

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## Funding Interrupted January 2005

Total FY05 funding:  $\approx$  \$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:  $\approx$  \$11K (Mesofuels, Pall)



# Overview: Partners

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## 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<sub>2</sub> Separations Workshop, Washington, DC, 9/8-9/04
- Nenoff: BES H<sub>2</sub> 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.



# Overview: Technical Barriers and Targets

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## DOE Technical Barriers for Separation Membranes (for H<sub>2</sub> 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<sup>2</sup>
- Cost = <\$100/ft<sup>2</sup>
- Durability = 100K hours
- Operating Temp = 300-600 °C
- Parasitic Power\* = 2.8 kWh/1000 scfh

\* recompress H<sub>2</sub> gas to 200psi



# Approach

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

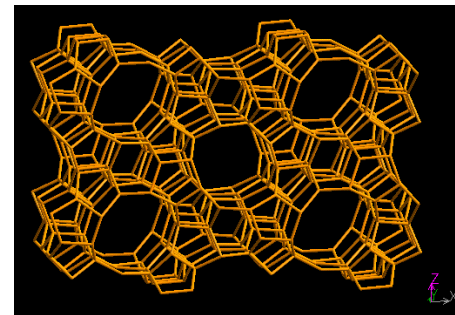
- 1) Synthesize membranes with Silicate-based frameworks use supports that are industrially relevant
- 2) Model/Simulate/Validate permeation of light gases through the frameworks
- 3) Analyze flux and permeation of gases (pure, binary, mixed gas streams) at ambient and varying temperatures/pressures
- 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<sub>2</sub>O/steam, H<sub>2</sub>S; 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<sub>2</sub>S)
- As temperatures increase (RT-300°C),
  - 1-sided membranes increase in H<sub>2</sub> selectivity
  - 2-sided membranes decrease in H<sub>2</sub> selectivity
- **H<sub>2</sub>O should be removed** from stream prior to membrane; aids C-permeation, hinders H<sub>2</sub>
- Simulation of industrial simulant (no H<sub>2</sub>O) separation at 500°C shows selectivity for H<sub>2</sub>
- **H<sub>2</sub>S & H<sub>2</sub>O inclusion:** no destruction to membrane in permeation testing up to 300°C
- Utilizing ceramic membrane supports: Inoceramic Alumina disks/tubes
  - Oxide-coated SS316 (TiO<sub>2</sub>; SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>; ZrO<sub>2</sub> coatings)
  - Pall Corp. ZrO<sub>2</sub> coated SS316 tubes

MFI: silicalite



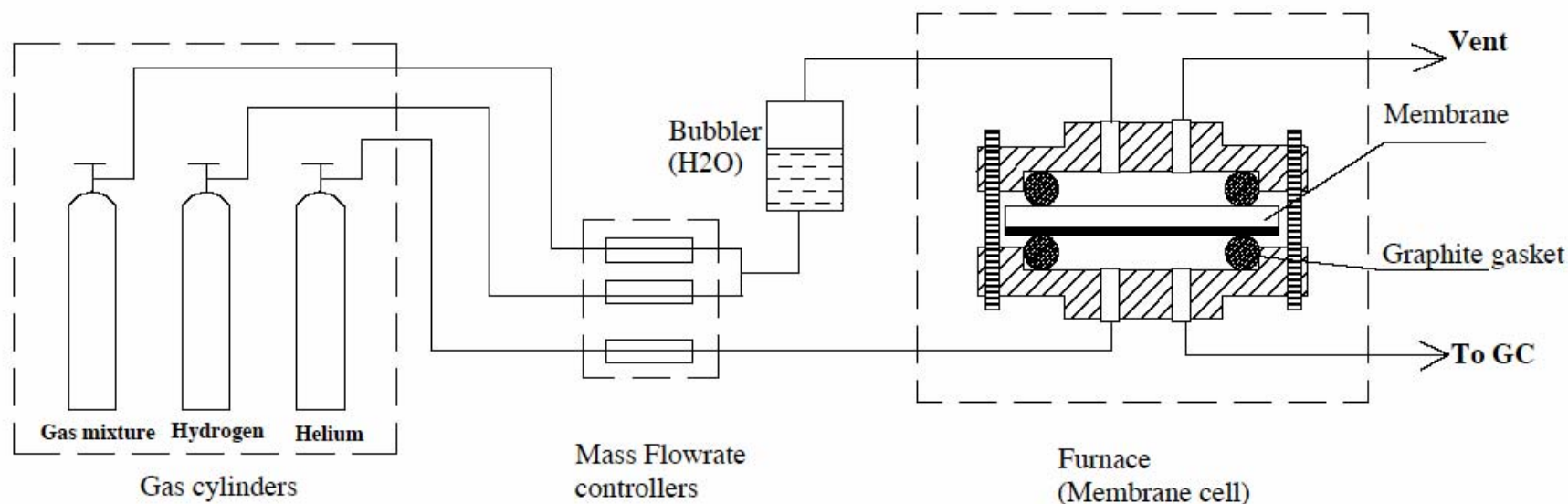
# Technical Accomplishments/Progress (con't)

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)

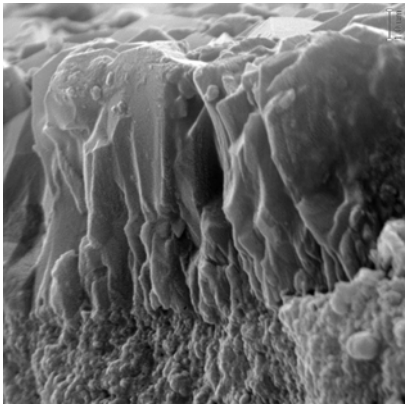
SNL: permeation testing under pressure of 16psi

Temperature = RT  $\approx$  500°C

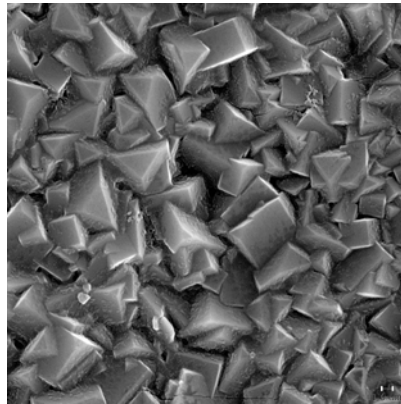
$$S_i = (y_i/(1-y_i))/(x_i/1-x_i), \text{ where } x_i \text{ and } y_i \text{ is mol fractions of permanent gases}$$

# Technical Accomplishments/Progress (con't)

## Traditional MFI Membranes



1.0 Micron



1.0 Micron

**Silicalite**  $\approx 10^{-6} - 10^{-7}$  mole/(m<sup>2</sup> Pa sec)

RT, Pure Gases

H<sub>2</sub>/N<sub>2</sub> = 1.4

H<sub>2</sub>/CH<sub>4</sub> = 0.625

He/N<sub>2</sub> = 1.1

CH<sub>4</sub>/N<sub>2</sub> = 2.28

H<sub>2</sub>/CO<sub>2</sub>  $\geq$  0.34

H<sub>2</sub>/O<sub>2</sub> = 1.7

CH<sub>4</sub>/CO<sub>2</sub> = 0.54

H<sub>2</sub>/CO = 1.43

**Silicalite-1 Gel Composition:**  
**2600 H<sub>2</sub>O: 53 Na: 92 TPA<sup>+</sup> : 100 Si**  
40g H<sub>2</sub>O, 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**

# Technical Accomplishments/Progress (con't)

## SNL Silicalite Membrane

*2 sided membranes*

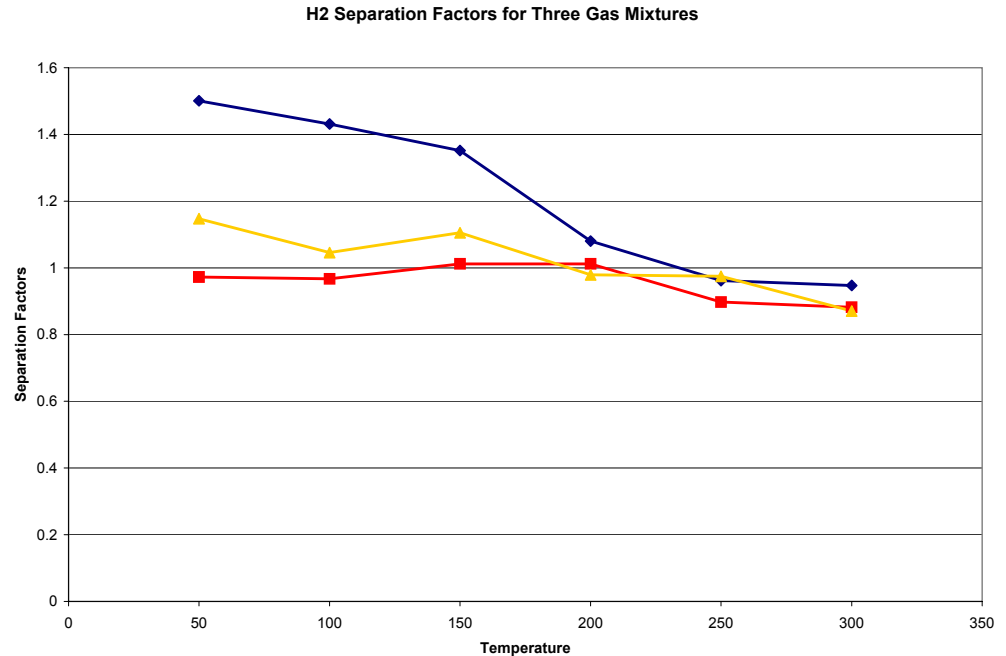
$\Delta P = 15$  PSIG

Precalcined DF Membrane

Temperature Ramped to 300°C

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

- ◆ 50/50 H<sub>2</sub>/CO<sub>2</sub>
- ◆ 50/50 H<sub>2</sub>/CH<sub>4</sub>
- ◆ Reformate Simulant:  
76% H<sub>2</sub>, 13.6% CO<sub>2</sub>, 6.8% CO  
3.4 % CH<sub>4</sub> (Intelligent Energy)



## Silicalite, Selectivity Factors at Variable Temperatures:

	RT	50°C	100°C	150°C	200°C	250°C	300°C
H <sub>2</sub> /CO <sub>2</sub> (50/50)	0.21	1.15	1.05	1.11	0.98	0.97	0.87
H <sub>2</sub> /CH <sub>4</sub> (50/50)	0.48	0.97	0.97	1.01	1.01	0.90	0.88
Reformate, H/All 200ppmH <sub>2</sub> S/N <sub>2</sub>	0.47	1.50	1.43	1.35	1.08	0.96	0.95
		0*					

\*20ppm H<sub>2</sub>S 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):



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)

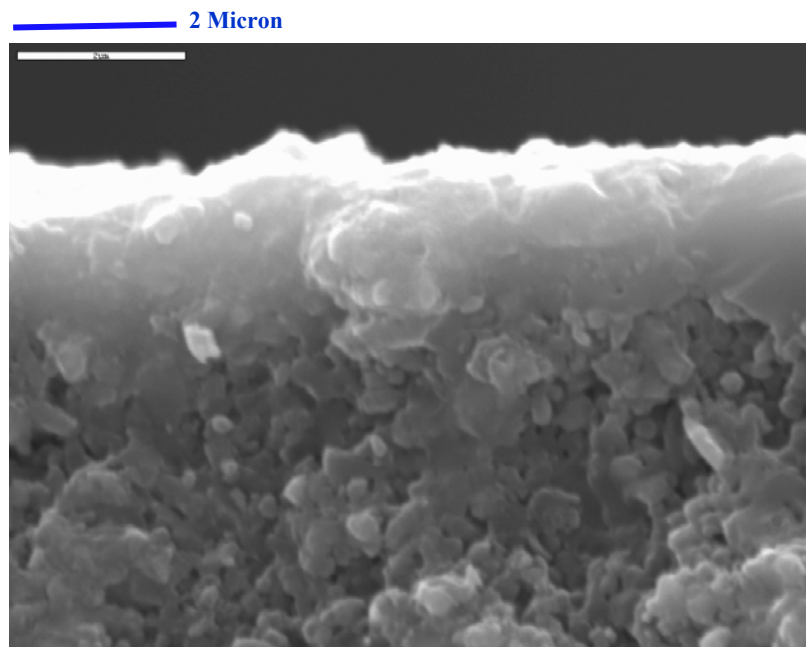
**Result: One sided defect-free ~1.5 micron  
thick Zeolite Membranes**

Separation Factors:

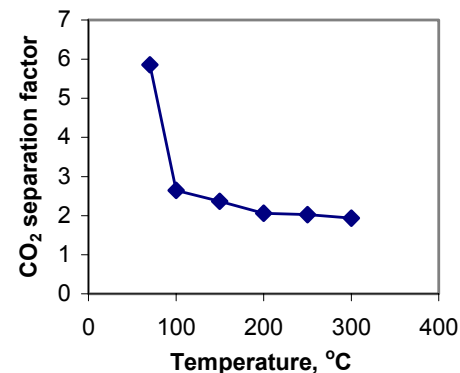
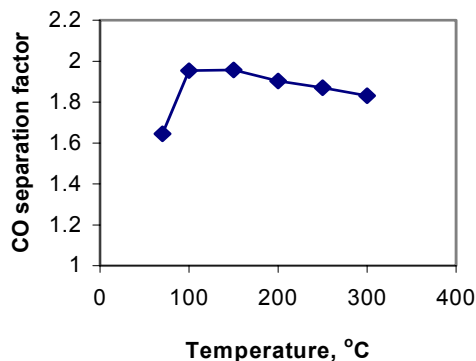
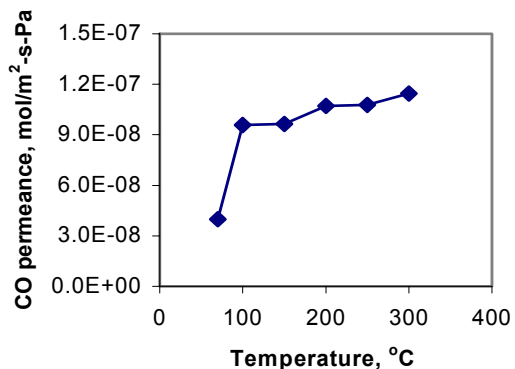
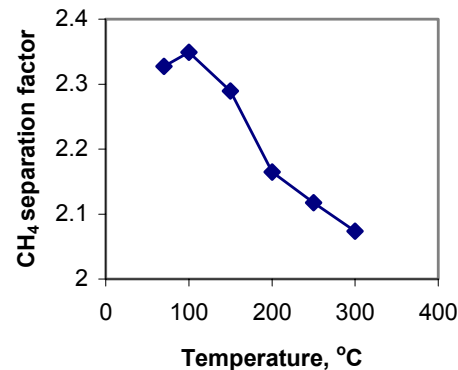
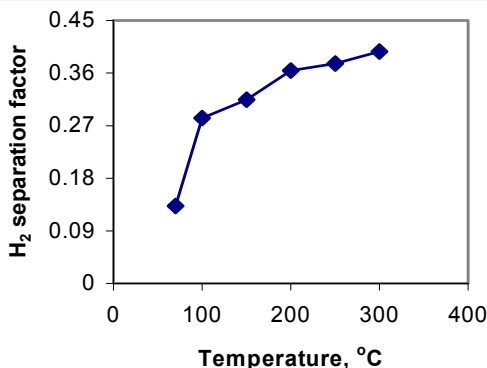
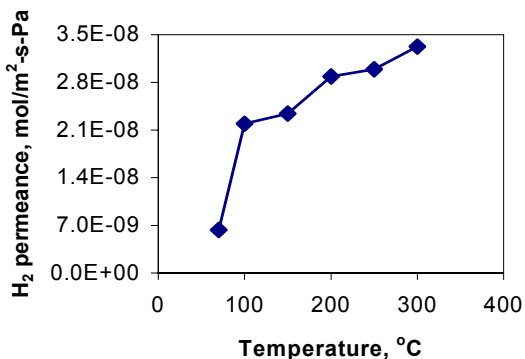
$\text{H}_2/\text{SF}_6$  (@ RT) = 175

p/o-xylene (@300°C) = 8.5

p-x flux =  $1 \times 10^{-5}$  mol/m<sup>2</sup>-s

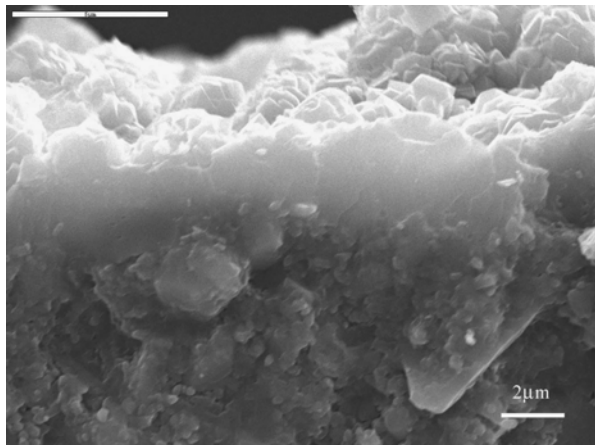


# Technical Accomplishments/Progress (con't)



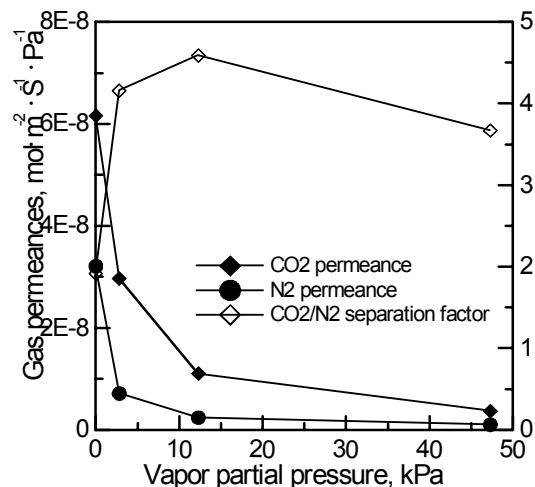
Industrial Stream Tested: 50% H<sub>2</sub>, 6% CO, 0.02% H<sub>2</sub>S, 4% CH<sub>4</sub>, 10% CO<sub>2</sub> and 30% H<sub>2</sub>O in mol fraction  
Single sided thin films: H<sub>2</sub> separation factor increases with temperature (300°C), hindered by H<sub>2</sub>O, but still increasing; lack of H<sub>2</sub>O will greatly increase H<sub>2</sub> selectivity\*

# Technical Accomplishments/Progress (con't)



FAU membrane

Effect of H<sub>2</sub>O Partial Pressure on CO<sub>2</sub>/N<sub>2</sub> sep at 200°C



Based on preliminary light gas separations with FAU membrane (1-sided): H<sub>2</sub>O has a strong affinity to the CO<sub>2</sub>, by increasing the permeance.\*

**Theory:** by eliminating the H<sub>2</sub>O from the stream, CO/CO<sub>2</sub>/CH<sub>4</sub> selectivities will continue to decrease with temperature, and **H<sub>2</sub> 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:

$$U(\mathbf{r}^N) = \sum_{\text{bonds}} \frac{1}{2} \mathbf{K}_b [\mathbf{b} - \mathbf{b}_0]^2 + \sum_{\text{angles}} \frac{1}{2} \mathbf{K}_\theta (\theta - \theta_0)^2 + 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

T=500°C; no H<sub>2</sub>O 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

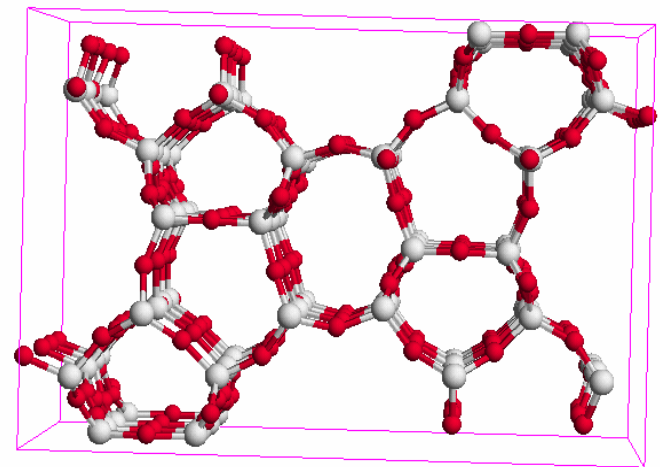
–11 angstroms for quaternary mixtures

Unit cell used

–4 for pure and binary mixtures

–8 for quaternary mixture

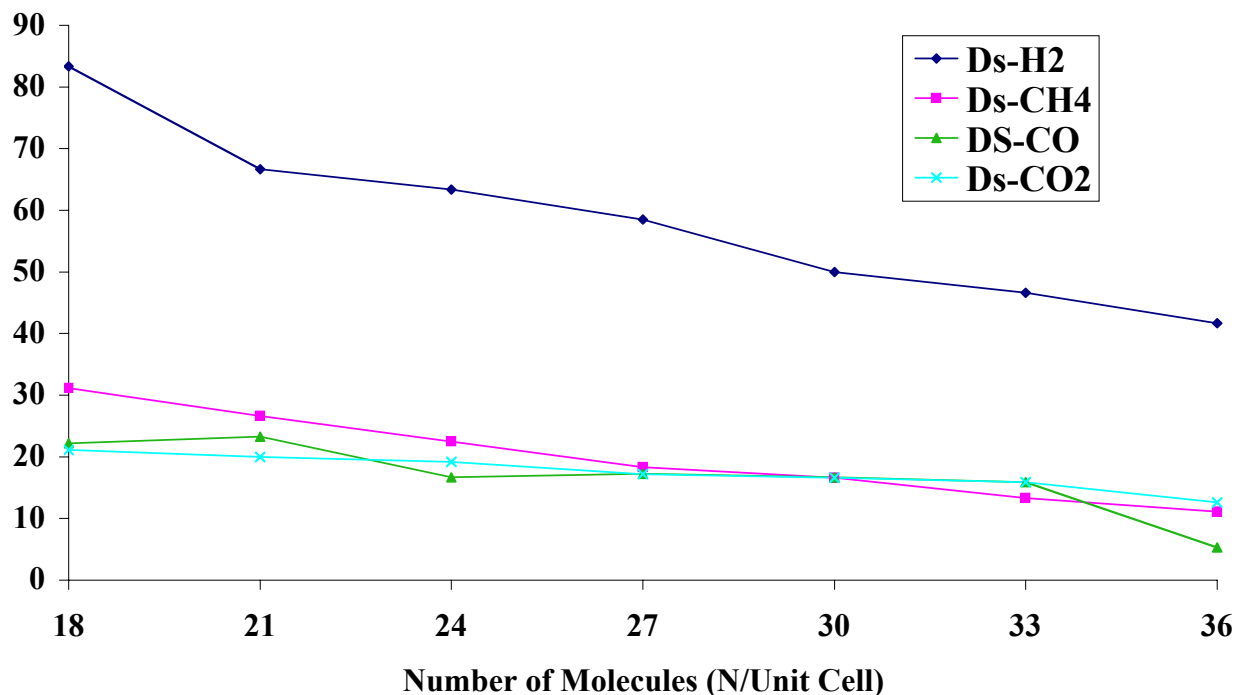
MFI: silicalite



# Technical Accomplishments/Progress (Simulations con't)

## Displacement of H<sub>2</sub> in Silicalite vs. competing gases

Quaternary/simulant: 76% H<sub>2</sub>, 13.6% CO<sub>2</sub>, 6.8% CO, 3.4 % CH<sub>4</sub> (No H<sub>2</sub>O)



Simulation predicts H<sub>2</sub> purification at Temperature (500°C) but maximum at low loadings



# Responses to Previous Year Reviewer's Comments

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**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<sub>2</sub>O/steam operation capability added: water affects separation values but membrane is stable at least up to 300°C
- H<sub>2</sub>S operation capability added: membranes remain stable at least to 300°C



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

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## 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 ( $\approx 1.5$ microns)
- 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

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- **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<sub>2</sub>O removal from stream prior to membrane**

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

Investigate pervaporation with zeolite membranes for H<sub>2</sub> selectivity  
Investigate Catalytic Membranes for H<sub>2</sub> Production from reforming stream  
Investigate effect of membrane modification on separation values  
Investigate membrane lifetimes versus H<sub>2</sub>S  
Investigate H<sub>2</sub>S scrubbing with membrane catalytic coatings  
Work with Pall Corporation to design and scale membranes &  
catalytic reactors



# Supplemental Slides

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# Publications & Presentations

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## Presentations:

- Welk M. E., Nenoff, T.M. “Defect-free Zeolite Membranes for H<sub>2</sub> Purification”, ACS Fall Meeting, Philadelphia, PA, 8/25/04.
- Welk M. E. (plenary), Nenoff, T.M. “Microporous Zeolite Membranes”, DOE/H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> Purification and CO<sub>2</sub> Separation”, Proceedings 14<sup>th</sup> 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

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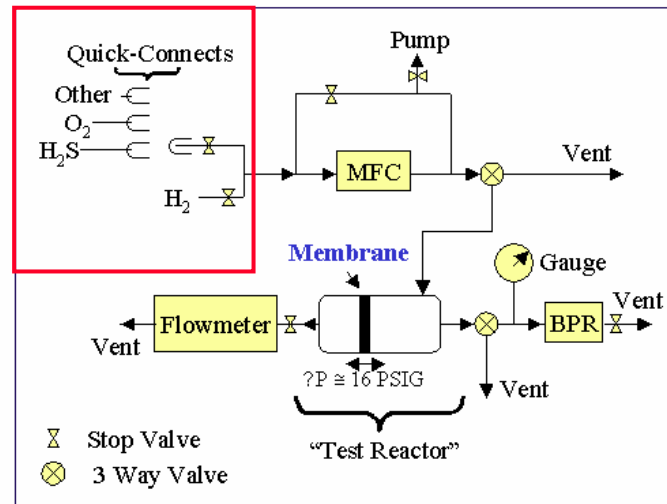
*The most significant hydrogen hazard associated with this project is:*

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<sub>2</sub> separate from O<sub>2</sub> & other gases by plumbing
- Entire permeation unit is located inside a fume hood
- H<sub>2</sub>S 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