Defect-Free Thin Film Membranes for H_2 Separation and Isolation

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Objectives

- Synthesize defect-free thin film zeolite membranes for H_2 isolation and purification.
- Use these as water management membranes in proton exchange membranes (PEMs).
- Replace existing expensive and fragile Pt catalysts.
- Test the separations of light gases (pure and mixtures) through the membranes.
- Demonstrate effective light gas separations and commericalization potential of zeolite membranes.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- H. Sufficient Fuel Storage for Acceptable Vehicle Range
- K. Balance-of-Plant (BOP) Components

Approach

- 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, and Reforming Technology
- AB.Hydrogen Separation and Purification

Accomplishments

- Synthesize defect-free thin film zeolite membranes and microporous bulk phases for future membrane applications.
- Model/simulate permeation of light gases through various frameworks/pores for optimized performance.
- Analyze flux and permeation of gases through membranes on unique in-house permeation unit.

- Validate modeling/simulation with actual permeation data to optimize membranes synthesized.
- Foster industrial contacts and collaborations.

Future Directions

- Synthesize and characterize thin films and bulk novel microporous phases including aluminosilicate (Al/Si) zeolite thin films doped and/or ion exchanged with other elements, unsupported aluminosilicate zeolite membranes, and silicotitanate phases (Si/Ti).
- Attempt use of atomic layer deposition of catalytic metals on top of zeolite membrane.
- Synthesize membranes on oxide-coated porous stainless steel (commerically viable) supports
- Model separation values by molecular dynamics calculations for pure and mixed light gases interacting with differing zeolite type membranes (i.e., comparing ZSM-5 to ZSM-W).
- Perform permeation and flux studies of pure and mixed gases through membranes (H_2, CO, CO_2, CH_4, N_2, and SF_6); proceed with unit alterations for H_2S testing.
- Build a partnership with a membrane company. Initiate an agreement for product development with an industrial partner.

Introduction

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. In particular, we are interested in (1) separating and isolating H_2 from H_2O and CH_4, CO, CO_2, O_2, N_2 gases; (2) water management in PEMs; and (3) replacing expensive Pt catalysts needed for PEMs. Current hydrogen separation membranes are based on Pd alloys or on chemically and mechanically unstable organic polymer membranes. The use of molecular sieves brings a chemically and mechanically stable inorganic matrix to the membrane. The crystalline frameworks have "tunable" pores that are capable of size exclusion separations. The frameworks are made of inorganic oxides (e.g., silicates, aluminosilicates, phosphates) that bring different charge and electrostatic attraction forces to the separation media. The result is materials with high separation abilities plus inherent thermal stability over 600°C and chemical stability. Furthermore, the pore sizes and shapes are defined crystallographically (<1 Å deviation), which allows for size exclusion of very similarly sized molecules. In comparison, organic polymer membranes are successful based on diffusion separations, not size exclusion. We envision impact of positive results from this project in the near term with hydrocarbon fuels, and in the long term with biomass fuels.

Approach

The approach for this project in FY 2003 is the development of defect-free thin film zeolite membranes and new bulk microporous phases for the selective separation of light gases. The development of these membranes includes the synthesis, modeling/simulation, permeation studies, and validation for the separation and isolation of H_2. The permeation studies are of pure and mixed gases through membranes, studied at room temperature and 80°C. The modeling and simulation work helps determine improved pore size and composition for sieving. The validation is the iteration of modeling/simulation data with actual permeation values to improve upon the membranes synthesized.

Previous work at Sandia has successfully shown the ability to grow defect-free aluminosilicate and phosphate-based molecular sieve membranes. The continued focus now is on the enhancement and optimization of the type of molecular sieve for separation, the methodology of film growth, the type of supports upon which to grow membranes (and remain commercially viable). We are studying aluminosilicate frameworks and metal doped frameworks to better determine the relationship

between adsorption, sieving and then permeation. To study the effect and preferability of support types, we are studying and comparing unsupported film growth versus film growth on ceramic supports. We are also beginning our studies on newly available ceramic coated stainless steel supports (allowing for phase match on the ceramic, but enhancing durability of stainless steel). With all materials synthesized, we perform characterization in-house to better understand structure-permeability relationships. Characterization methods include X-ray diffraction, thermal analyses, elemental analysis and permeation studies. Our in-house permeation unit is capable of fitting both disk and tubular membrane supports, either of ceramic oxide or stainless steel materials. This unique unit can be run from room temperature to elevated temperatures (= 500°C), though we only plan to go to approximately 80°C. The unit also contains a residual gas analyzer, enabling us to monitor and identify ratios of the permeate mixtures. We are able to leverage end sealant technology we have patented through Sandia. The gases we plan to test for this project include H_2, He, CH_4, CO, CO_2, CH_4, O_2, N_2, H_2S and SF_6, plus mixtures of these gases.

Results

In the area of thin film membranes, we have successfully synthesized micron thick aluminosilicate zeolite membranes on alumina disks (see Figure 1). Our permeation testing (see Figure 2) of the material shows that these membranes are defect-free. Defect free is denoted by permeation selectivity due to size exclusion by molecular sieving through the zeolite pores, and not through crystalline defect sites, pin holes, or crystallite mismatches (pores of this Zeolite are 5.5 Å). Molecules used for this test are He (kinetic diameter = 2.6 Å) and SF_6 (kinetic diameter = 5.5 Å). Pure gas studies are run at room temperature. The only consistent problem has been that our membranes have grown on both sides of the disk support, even when seeding occurs on one side. As a result, our flux through the membrane/support is slightly diminished from what it would be with only one side membranes.

Once the membrane is determined to be defect-free, testing on pure gases vital to the steam reforming cycle for natural gas to hydrogen fuels can begin. In the past years we have shown that the Sandia aluminosilicate membranes have fluxes on the order of 10^{-6} mole/(m^2Pa sec) and separations of H_2/N_2 61, H_2/CO_2 80, H_2/CH_4 = 7, CH_4/CO_2 11 [3]. Also, the all-silica Zeolite membranes have superior CO_2 separation from smaller light gases (such as H_2) [3,4]. Lifetime stabilities of the membranes have been undertaken in this project. In over a year of exposure to water vapor, the all silica membranes can be recalcined (to clear the pores of the zeolites) and retested for light gas selectivities. Our studies show good consistency in permeation data plus long-term durability in the actual integrity of the membrane. Furthermore, we have shown a high reproducibility in membrane synthesis procedure yielding consistent permeabilities. (See Figure 1 and Table 1.)

We have expanded our research to include silicotitanate membrane synthesis. In attempts to synthesize ETS-4 and ETS-10 as membranes, we have successfully synthesized both ETS-10 and a completely novel silicotitanate phase. This new phase exhibits initial selectivity toward H_2 and good flux (10^{-8} mole/(m_2Pa sec)), though complete removal of pore-blocking template molecules has not yet been achieved through initial calcination procedures. Further optimization of the calcination procedure will lead to improved results. (See Figure 2.)

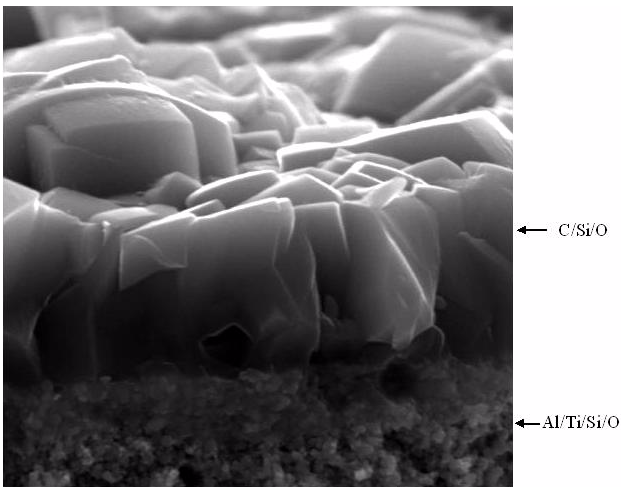

Figure 1. Cross Section View by Scanning Electron Microscope of a 10 Micron Thick Silicalite Zeolite Membrane on an Oxide Coated Stainless Steel Porous Support

We are also studying zeolite W (a 12-ring, 3D pore system) to compare it to the ZSM-5 sinusoidal pathway zeolite. We have successfully synthesized zeolite W crystals on a membrane. However, it is not yet a continuous film. Experiments continue to improve this membrane. (See Figure 3.)

Though not completely understood, these results indicate that we can tune the membrane materials to have selectivity for various light gases. This is even more valuable given that crystalline inorganic zeolite membranes are chemically, thermally and mechanically robust and stable. In comparison to Pd alloy films, the zeolite membranes perform well. According to the literature [5], Pd on alumina had relative ratios of light gas separations of $H_2/N_2 = 110$ at elevated temperature of 350C. The flux was also low (2×10^{-7} mole/m^2Pa sec). Furthermore, we have synthesized defect-free aluminosilicate zeolite thin films supported on commercially available oxide coated stainless-steel supports (SS316); industry needs stainless steel to make membranes an economically viable technology.

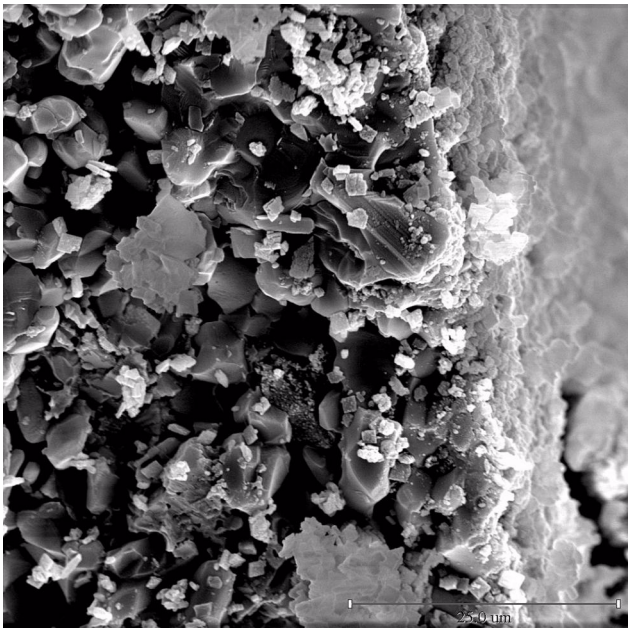

Figure 2. Cross Section of Novel Silicotitanate Crystalline Membrane on an Alumina Support

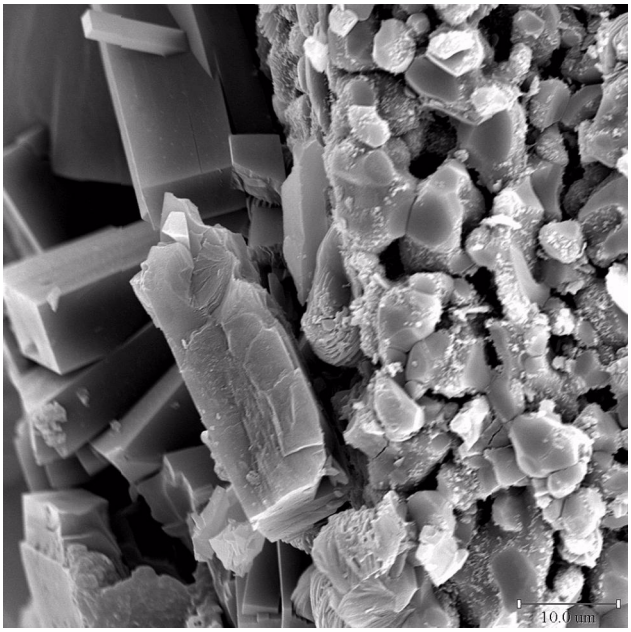

Figure 3. Cross Section of Zeolite W Crystals Grown on an Alumina Support

Table 1. Permeation values for pure gases at room temperature on various silicalite membranes; "regenerated" is calcined after one year exposure to water vapor. Flux = 10-7 mole/m2 s Pa); Trans-membrane pressure = 16 psi.

Gas / (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

Conclusions

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. They contain an inherent chemical, thermal and mechanical stability not found in conventional membrane materials. Our goal is to utilize those zeolitic qualities in membranes for the separation of light gases, and to eventually partner with industry to commercialize the membranes. To date, we have successfully:

- Demonstrated (through synthesis, characterization and permeation testing) both the ability to synthesize defect-free zeolitic membranes and use them as size selective gas separation membranes; these include aluminosilicates, silicates, silicotitanates, and phosphate-based phases.
- Built and operated our in-house light gas permeation unit; we have amended it to enable testing of CO gases, mixed gases, and at high temperatures. We are initiating further modification for H_2S permeation studies.
- Synthesized membranes on commercially available oxide and composite disks (this is in addition to successes we have had in synthesizing zeolitic membranes to tubular supports [6]).
- Synthesized a number of novel bulk and membrane silicotitanate and aluminosilicate phases, including the Si/Ti membrane that exhibits selectivity for H_2.

References

1. Tavolaro, A.; Julbe, A.; Guizard, C.; Basile, A.; Cot, L.; Drioli, E. "Synthesis and characterization of a mordenite membrane on an ?-Al2O3 tubular support." J. Mater. Chem. 2000, 10, 1131.

2. Lai, R.; Gavalas, G. R. "ZSM-5 membrane synthesis with organic-free mixtures." Microporous and Mesoporous Materials, 2000, 38, 239.

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

4. Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO2 selectivity and lifetimes of high silica ZSM-5 membranes". Micro. & Meso. Materials, 2003, in press.

5. Chou, K. S.; Wang, S. M. "Studies on the preparation of Pd/alumina/porous stainless steel membranes for hydrogen separation." J. Chinese Inst. Chem. Eng., 2000, 31, 499.

6. Thoma, S. G.; Nenoff, T. M. "A New Method for Synthesizing Defect-Free Thin Film Membranes: Composite Zeolite/Sol-gel Membranes" SD-6222, US Patent Submission, 2000.

FY 2003 Presentations

M. E. Welk, T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 and CO2 Separation and Isolation", Hydrogen and Fuel Cells 2003 Conference and Trade Show, Vancouver, BC, Canada, June 2003.

2. T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 and CO2 Separation and Isolation", Spring National ACS meeting, New Orleans, LA, March 2003. Invited Lecture.

3. T. M. Nenoff, M. E. Welk, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 Separation and Isolation", National Hydrogen Association Meeting, Washington, DC, March 2003.

4. T. M. Nenoff, F. Bonhomme, "Defect-Free Thin Film Membranes for H2 Separation and Isolation", 14th World Hydrogen Energy Conference, Montreal, Canada, June 10, 2002.

FY 2003 Publications

1. Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular dynamics simulations of binary mixtures of

methane and hydrogen in titanosilicates." J. Phys. Chem., 2003, submitted.

2. Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO2 selectivity and lifetimes of high silica ZSM-5 membranes." Micro. & Meso. Materials, 2003, in press.

3. 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.

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

Special Recognitions & Awards/Patents Issued

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

2. Invited by Senator Jeff Bingaman (D-NM) for H2 and Fuel Cell Economic Development discussions (included national lab & industry attendees), Albuquerque, NM, 4/25/03