IV.C Separations

IV.C.1 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 as water management membranes in proton exchange membranes (PEMs)
- Replace existing expensive and fragile Pt catalysts
- Test the separation of light gases (pure and mixtures) through the membranes
- Demonstrate effective light gas separations and commercialization potential of zeolite membranes

Technical Barriers

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

- A. Fuel Processor Capital Costs
- C. Operation and Maintenance (O&M)
- D. Feedstock Issues
- F. Control and Safety
- O. Selectivity

Approach

- Synthesize and optimize defect-free thin film zeolite membranes
- Model/simulate permeation of light gases through various frameworks/pores for optimized performance
- Analyze flux and permeation of pure, binary and industrially-relevant mixed 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

Accomplishments

- Synthesized both single sided ultra thin defect-free zeolite membranes and double sided zeolite membranes with different selectivities for various gas molecules; selectivity based upon a combination of molecular sieving through the pores and adsorption of the various composition frameworks.
- Compared permeation through all silica and aluminosilicate zeolite membranes, both on alumina supports and on composite oxide-coated stainless steel supports.

- Modified our unique in-house permeation unit to include a gas chromatograph for mixed gas permeation testing, including traditional reforming streams with or without the steam component. The unit can test both disk and tube membranes, multiple pure or mixed gases, in a temperature range of 25-500°C. Compared steady-state flows to pressurized permeation systems.

Future Directions

- Complete FY 2005 milestones delayed by funding cutbacks, including: reforming stream without steam in a steady state pressure permeation unit (to match modeling/simulation studies), and high temperature (up to 500°C) mixed gas studies on double sided membranes.
- Synthesize and characterize thin films and bulk novel microporous phases including of aluminosilicate (Al/Si) zeolite thin films doped and/or ion exchanged with other elements and unsupported aluminosilicate zeolite membranes.
- Use atomic layer deposition of catalytic metals on top of zeolite membrane.
- Develop catalytic membrane reactors (catalyst loaded zeolite membranes) for one step H_2 production from reforming streams.
- Synthesis of membranes on oxide-coated porous stainless steel (commercially viable) supports.
- Model and simulate the movement of gas molecules through the various molecular sieve thin films. Then compare the calculated data with actual permeation data for validation of models and prediction capabilities.
- Study the permeation and flux of pure, binary and industrially-relevant mixed gases (H_2, CO, CO_2, CH_4, H_2S, N_2, H_2O and SF_6), through membranes studied from room temperature to 500°C.
- 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) as a replacement for 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 stable (chemically and mechanically stable) inorganic matrix to the membrane [1-3]. The crystalline frameworks have "tunable" pores that are capable of size exclusion separations. The frameworks are made of inorganic oxides (e.g., silicates, aluminosilicates, and phosphates) that bring different charge and electrostatic attraction forces to the separation media. The resultant materials have high separation abilities plus inherent thermal stability over 600°C and chemical stability. Furthermore, the crystallographically defined (<1Å deviation) pore sizes and shapes allow for size exclusion of very similarly sized molecules. In contrast, organic polymer membranes are successful based on diffusion separations, not size exclusion. We envision the impact of positive results from this project in the near term with hydrocarbon fuels, and long term with biomass fuels.

Approach

The approach for this project in FY 2005 is the development of one-sided ultra thin film defect-free zeolite membranes for the selective separation of light gases under steady state reaction conditions. The development of these membranes includes membranes synthesis, modeling/simulation of gas movement through the membranes, and permeation studies of the separation and isolation of H_2. 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. These were used to

compare against the traditional two-sided 7 micron thick zeolite membranes that were run under mild pressure (about 16 psig).

Previous work at Sandia has successfully shown the ability to grow defect-free aluminosilicate and phosphate-based molecular sieve membranes. The continued focus 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), the upgrade of our permeation unit for high temperature and steady-state permeation experiments, and the establishment of industrial partners for eventual commercialization.

We are studying and comparing silicate and aluminosilicate frameworks to better determine the relationship between adsorption, sieving and then permeation. To study the effect and compatibility of support types, we are studying and comparing unsupported film growth with film growth on ceramic supports. We have extended our studies to include ceramic coated stainless steel supports which allow for phase match with the ceramic and have the durability of stainless steel. With all materials synthesized, we perform characterization in-house to better understand structure-permeability relationships. These include X-ray diffraction, thermal analyses, elemental analyses 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. We have upgraded our permeation capabilities to include a new unit that can be run from room temperature to elevated temperatures (500°C), and in both steady-state and pressurized modes. The new unit has a gas chromatograph/mass spectrometer (GC/MS) characterization systems, enabling us to monitor and quantify the concentrations of mixed gases present in the permeate stream. We also 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, H_2O, SF_6, and binary and industrially-relevant mixtures of these gases.

Although we are still working to understand them, these results indicate that we can tune the membrane materials to have selectivity for various light gases. This is even more valuable as it is with crystalline inorganic zeolite membranes that are chemically, thermally and mechanically robust and stable. In comparison to Pd alloy films, the zeolite membranes perform well. According to the literature [4], Pd on alumina had relative ratios of light gas separations of $H_2/N_2 = 110$ at elevated temperature of 350°C. 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 requires stainless steel to make membranes an economically viable technology. Early economic analysis has also shown that for an installed Pd membrane complete with permeation module, the cost is estimated up to $200/ft^2. In comparison, zeolite membranes, plus modules, are currently estimated at $200/ft^2 (importantly, this is the value before mass commercialization price reductions) [5].

Results

FY 2005 funding was cutback considerably in January 2005; approximately to half its initial allocation. Partial FY 2005 funding was restored after approximately 3 weeks of project shutdown; the partial funding allowed for reduced project activity until the funds were exhausted in May 2005. During this interruption, we were able to maintain our contractors' work; we have also managed to reestablish much of our original in-house work for the year, though milestones have been scaled back. With regards to contractors, we have synthesized thin film silicalite membranes with New Mexico Tech University (NMTech) through a novel method and performed mixed gas studies at a variety of temperatures under steady state conditions; at New Mexico State University (NMSU), we have continued with light gas permeation studies through various zeolite membranes at varying temperatures. At Sandia, we have received and installed the new gas chromatograph and have begun testing with it with mixed gas studies at elevated temperatures.

In the area of thin film membranes we have successfully synthesized micron thick silicalite (all silica ZSM-5) and aluminosilicate ZSM-5 zeolite membranes on both pure alumina and composite oxide-coated stainless steel disks. Our permeation testing of the material shows that these membranes can be synthesized with minor intracrystalline

defects or defect-free. Defect-free is determined by permeation selectivity owing 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). We currently run our experiments at room temperature. However, we have done preliminary permeation studies at 80 and 120°C on both silicalite and aluminosilicate ZSM-5 membranes.

Ultra Thin Zeolite Membranes at Steady State Permeation

Membrane Preparation

In an effort to expand our membrane synthesis/ fabrication portfolio, we have been working with NMTech on alternative MFI zeolite membrane synthesis and testing techniques. The resultant membranes are one sided and thin (about 1.5 microns thick, see Figure 1). The permeation testing unit allowed for steady-state permeation testing and enabled us to do mixed gases up to 300°C on disk membranes. As expected, at higher temperatures, H_2 had enhanced purification values. We anticipate even better results with future studies up to 500°C.

Due to the small size of this collaboration, we were only able to do one set of experiments which are presented in the following. We used the complex industrial simulant mixture (component ratio provided by Intelligent Energy, LTD).
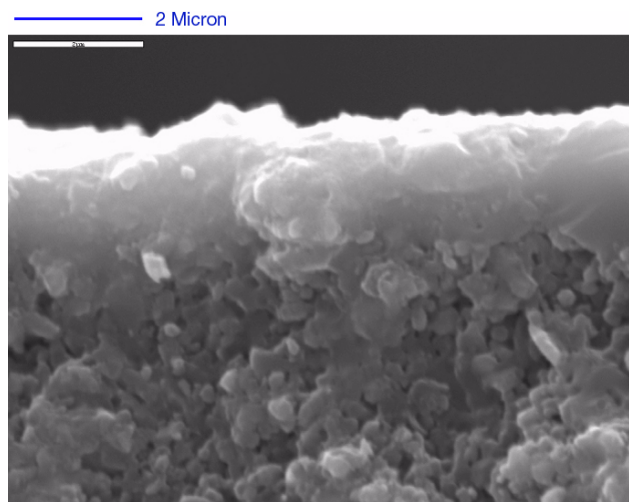
Figure 1. Cross Section View by SEM of an Ultra Thin One-Sided 1.5 Micron Thick Silicalite Zeolite Membrane on an Alumina Porous Support

Disk-shaped silicalite-1 MFI membrane was synthesized by the in-situ hydrothermal method. The substrate was porous α-alumina disk with a mean pore size of 100 nm, the edge of which was enameled before being used for membrane synthesis. The detailed preparation procedure has been reported in previous work [6].

Gas Permeation

Zeolite membranes were sealed with graphite gaskets. The effective membrane area for permeation is 2.54 cm^2. A feed gas stream was formed by mixing 10 ml/min H_2 with a 4 ml/min gas mixture (CO 29.97%, H_2S 0.1%, CH_4 19.98% and CO_2 49.95% in mol fraction) and then passing through a water bubbler at 66 °C, which evolved a final composition of 50% H_2, 6% CO, 0.02% H_2S, 4% CH_4, 10% CO_2 and 30% H_2O in mol fraction (named as Gas Mixture I). At the permeate side, a gas stream of 15 ml/min He was used to sweep permeates. Separation measurement was performed at the temperature ranging from 70 to 300°C and atmospheric pressure of 0.87 atm (NMTech). The gas effluent compositions were identified using a temperature controlled detector in a gas chromatography (HP 5890 II) equipped with Hayesep® DB column.
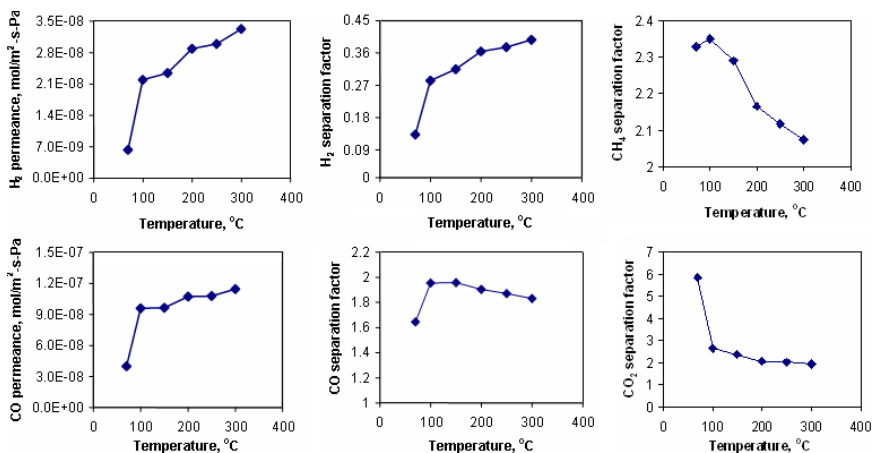
The separation factors for the multi-component mixture were calculated by an equation $S_i = (y_i/(1-y_i))/(x_i/(1-x_i))$ [6], where x_i and y_i is mol fractions of permanent gases, which include H_2, CH_4, CO and CO_2 in the effluents of feed and permeate side. H_2O and H_2S were not considered for calculation because H_2O was not a permanent gas and the concentration of H_2S was too low in the mixture.

Results and Discussion

Figure 2 shows the separation results of Gas Mixture I through the MFI membrane. As shown in this figure, H_2 permeance was much lower than other components under lower temperature, which indicated adsorption diffusion mechanism dominating gases transport through MFI zeolite membrane under present conditions. Zeolite channels were blocked by adsorbing components such as H_2O, CO_2, CH_4 and CO. As a result, the nonadsorbing hydrogen had difficulty passing through the zeolite channels. Higher CO_2 permeance at 70°C, in comparison with other components, was

attributed to its stronger adsorption. The elevated temperature reduced molecules adsorption in zeolite channels, which gave more free space for hydrogen molecules passing. Thus, H_2 permeance increased with temperature throughout 70-300°C with a separation factor varying from 0.13 to 0.4, as shown in Figure 2.

Different from H_2, the CO_2 permeance first increased with increasing temperature from 70°C to 100 °C and then slightly decreased over the temperature range of 100-150°C. When further increasing temperature (>150°C),

Figure 2. Permeation Graphics of One-Sided Silicalite Membrane with the Reformate Gas Mixture (at steady-state), with Composition of 50% H_2, 6% CO, 0.02% H_2S, 4% CH_4, 10% CO_2 and 30% H_2O in mol fraction

the CO_2 permeance increased again with temperature gradually. At low temperature, CO_2 permeance was affected by two competing factors, diffusion rate and adsorption strength, which caused a maximum of CO_2 permeance at low temperature. At high temperature, since zeolite adsorption tended to be negligible, the permeance mainly depended on diffusion rate, which increased with the increasing of temperature. It was observed that the separation factor of CO_2 decreased from 5.9 to 1.9 with the increasing of temperature from 70°C to 300°C. CO and CH_4 components, which had relatively weak adsorption compared with CO_2, had similar tendency in permeance and separation factor varying with temperature. From 70°C to 100°C, significant increase in permeance for both components was observed, which was due to the weakened adsorption of H_2O and CO_2 when increasing temperature. With the further increase of temperature, the permeance exhibited slightly increased. The separation factors for the two components increased first with temperature and then decreased during the temperature range of 70-300°C. However, the variations were relatively limited, as shown in Figure 2. It should be noted that at 300°C, the separation process still exhibited hydrogen rejection to some extent, which was different from what was reported in [6]. This could be attributed to the existence of H_2O in the feed gas. The zeolite channels adsorbing H_2O had much strong affinity to CO_2, CO and CH_4, which affected membrane

separations [7]. Therefore, removing the water will increase the H_2 selectivity. This is further supported by our own data which shows a dramatic increase in selectivity for H_2 with temperature.

We plan to continue our research collaboration in this area by studying these membranes with the same reforming stream minus the water/steam component. This data will give us a further understanding as to the role of the water molecule on H_2 selectivity through the membranes. It will also allow us to correlate our permeation data directly with the modeling data for the same stream at 500°C (see following).

Comparison to FY 2004 "Old" Membranes (2-sided, pressurized permeation)

This year we compared varying preparation methods and permeation testing conditions for the zeolite membranes in order to optimize their development. The permeation characteristics of several silicalite zeolite membranes grown on porous α - alumina supports via hydrothermal synthesis have been tested using gas mixtures. The following gas mixtures: 50/50 H_2/CO_2, 50/50 H_2/CH_4 and a simulated reformate stream mixture: 76.2% H_2, 13.6% CO_2, 6.8% CO, and 3.4% CH_4, were tested. Also tested were the pure gases present during methane reforming processes (H_2, CO_2, CH_4, CO, N_2 and O_2) that measured under a pressurized flow system of 16 psig.

The membranes were tested from room temperature (RT) to 300°C. There was slight variation in selectivity toward H_2 in all the mixtures, with the lowest (selectivity 0.5) at RT and the maximum at 50 and 100°C (selectivity 1.50). There was effectively equal preference for the gases as the temperature approached 300°C.

The lack of change in selectivity with temperature indicates that these thick membranes probably have intercrystalline defect sites that increase in size with temperature, thereby eliminating selectivity effects even with a pressurized flow. This is in negative contrast with our data for the single sided membranes (see above). We therefore have deduced that the single sided ultra thin membranes are optimal for the separation of H_2 from reforming streams.

Modeling and Simulations

We are working closely with NMSU (Dr. Martha Mitchell) in our attempt to correlate modeling/ simulation data to experimental data. We are studying the self-diffusivity (as a function of loading in zeolite cages) of the following gas mixtures: binary mixtures H_2/CO_2 and H_2/CH_4, and the 4-component (quaternary) industrial stream of $H_2/CO/CO_2/CH_4$. The molecular dynamics simulations are all performed on a silicalite membrane at 500°C [8].

The results obtained from the simulation studies indicated that silicalite membranes are effective for separating hydrogen from mixtures of hydrogen, methane, carbon monoxide and carbon dioxide. The relative rates of self diffusion of mixtures of light gas molecules in silicalite were studied in binary and quaternary mixtures. The diffusion coefficients of the gases were obtained at constant high temperature of 500C and at varying overall loading of silicalite pore. In both binary and quaternary mixtures, self diffusion in silicalite shows normal diffusion, i.e., the gas species obeys the Einstein relationship and the total diffusion coefficient of the gases decreases as a function of loading.

The MFI structure (i.e., Silicalite) has three different pore directions, each with its own pathway. In the simulations, the type of pore and shape of the pore helps in determining selectivity of gas molecule type. In both binary and quaternary mixtures, self diffusion in silicalite shows normal diffusion, i.e., the gas species obeys the Einstein relationship and the total diffusion coefficient of the gases decreases as a function of loading. The results indicate the diffusion of all gases species for both the binary and quaternary mixtures was predominant in both straight and sinusoidal channels, with the majority in the straight channels. Furthermore, the methane diffusion coefficient was higher in the quaternary mixture than in the binary mixture. This is explained by the lower concentration of the large molecule methane in the stream with respect to smaller molecules such as hydrogen; there is physically more "room" in the pores.

Summary

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 and silicates;
- Built and operated our in-house light gas permeation unit; we have amended it to enable testing of H_2S gases, mixed gases and at high temperatures. We are initiating further modification by designing and building an upgraded unit that will allow for temperatures up to 500°C, steady-state vs. pressure driven permeation, and mixed gas resolution through GC/MS analysis;
- Have shown in preliminary experiments high selectivity for H_2 from binary and industrially-relevant mixed gas streams under low operating pressures of 16 psig;

- Synthesized membranes on commercially available oxide and composite disks (this is in addition to successes we have in synthesizing zeolitic membranes to tubular supports [9]);

- Signed a non-disclosure agreement with industrial partner G. E. Dolbear & Associates, Inc., and have ongoing agreements with Pall Corporation for in-kind support supplies and interest in scale-up for commercialization.

Special Recognitions/Awards

1. Tina Nenoff with Dr. Richard Spontak (Univ. NC), have been awarded a proposal to become co-editors for an upcoming 2006 Material Research Society (MRS) Bulletin issue entitled "H2 Purification: An Important Step Toward the Hydrogen Economy."

FY 2005 Presentations

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

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

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

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

5. 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.

6. 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.

FY 2005 Publications

1. 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.

2. 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.

3. 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.

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

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9. Reed, S. G.; Stone, R. G.; Nenoff, T. M.; Trudell, D. E.; Thoma, S. G. "Gas Impermeable Glaze for Sealing a Porous Ceramic Surface" US Patent 6,716,275, April 6, 2004.