DEFECT-FREE THIN FILM MEMBRANES FOR H_2 SEPARATION AND ISOLATION

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Abstract

Our long-term goal is to synthesize defect-free thin film membranes with crystalline inorganic molecular sieves (zeolites) for use in hydrogen production technologies. 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 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., zinc oxide, gallium oxide, alumino silicates, silico titanates) and result in materials with thermal stability up to 600°C. The pore sizes and shapes are defined crystallographically (<1Å 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.

Introduction

This is project is focused on the research and development of crystalline, inorganic, molecular sieve (zeolite) thin film membranes for light gas molecule separations. In particular, we are interested in separating and isolating H_2 from CH_4, CO, CO_2 and N_2 gases. 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. The crystalline frameworks have "tunable" pores that are capable of size exclusion separations. We envision impact of positive results from this program in the near term with hydrocarbon fuels, and long term with biomass fuels.

During this reporting period, we focused our research on the synthesis of various classes of microporous phosphate-based, alumino silicate and silico titanate phases, both as bulk and thin film materials. Within this arena, we have begun to explore the gallium/phosphate phase space; five new phases have been synthesized. Furthermore, we have focused our efforts on the membranes synthesis and diffusion studies of different silicate-based zeolite membranes. These membranes have been successfully synthesized as defect-free membranes with separation abilities of key gas molecules. We continue our collaboration with New Mexico State University in the area of molecular dynamics modeling, transition state theory and simulations of light gas molecules diffusing through our membrane materials.

Discussion

This year, we have focused on the synthesis of novel Ga/F/P based microporous materials. In this area, we have worked on synthesizing phases with specific pore sizes for light gas molecule sieving and separation. Furthermore, we have attempted to synthesize the new phases as thin film membranes.

First, $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}0.5H_2O$, a new microporous 3D framework material was synthesized as a bulk crystalline powder, fully characterized and in press (Bonhomme, 2001). Its three dimensional framework (Figure 1) is composed of novel distorted "bowl-shaped" octameric double four-ring units, which are built up by corner-sharing PO_4 and GaO_4 tetrahedra and GaO_4F trigonal bipyramids. The structure consists of a pseudo-hexagonal array of cylindrical twelve-member pores running parallel to the *c* axis hosting the protonated 4-dimethylaminopyridine (4-DMAP) molecules. These pores are interconnected along the *b* axis through double eight-ring windows. The framework remains stable up to 300°C under oxygen. However, attempts to remove the organic molecule from the pores has been unsuccessful to date (both by calcination and solvent extraction, ie., HCl/EtOH wash). Pore sizes are in the range for light gas separations.

Second, a new 3D open-framework fluorogallophosphate, $Ga_5(PO_4)_5F_4 \cdot 2[N_2C_4H_{12}]$, was synthesized solvothermally using either 1,4-diazabicyclo[2.2.2]octane (DABCO) or piperazine as a templating agent (Bonhomme, 2001). The 3D framework is built-up by corner linked PO_4 tetrahedra, GaO_4F trigonal bipyramids and GaO_4F_2 octahedra (see figure 2). The building block of the structure is an hexameric unit of composition $[Ga(PO_4)]_5F_4$. The organic template molecules reside in cavities formed by the intersection of 8 member channels running along [100] and irregular pores parallel to [001]. The crystalline framework remains stable up to 350°C under oxygen. Pore sizes are in the range for light gas separations.

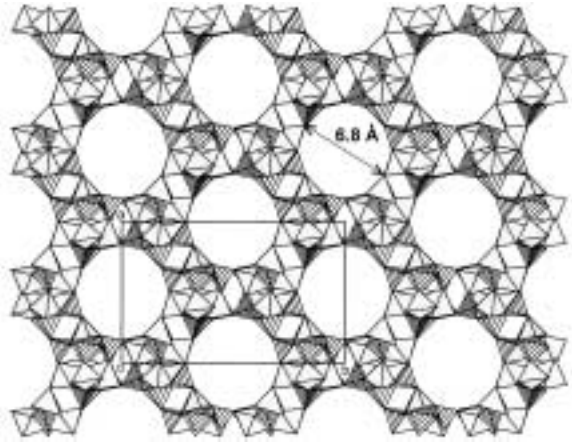


Figure 1: 3D framework of $Ga_4(PO_4)_4F{\cdot}N_2C_7H_{11}{\cdot}0.5H_2O$; pore residing H_2O and 4-DMAP molecules not shown, for clarity.

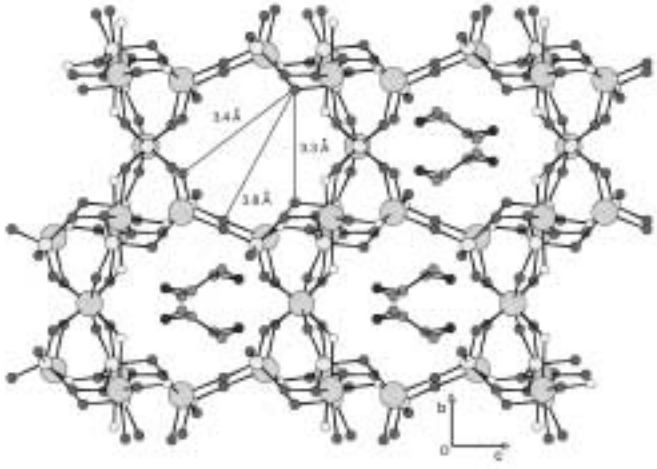


Figure 2: $Ga_5(PO_4)_5F_4 \cdot 2[N_2C_4H_{12}]$, view down 8-ring channels that contain the occluded piperazine molecules.

Initial Ga/P and F-based microporous thin film materials' growth studies have been tried on Ga_2O_3 substrates. To date, it appears that the Ga_2O_3 substrates are resistant to film growth, yet the phases do grow as unsupported bulk. Therefore the Ga_2O_3 substrate is not interfering with the syntheses. Attempts to physically attach the bulk phases to the substrate are ongoing. Initial alumina studies on Al_2O_3 did show selectivity of $N_2/He > 20$. Experiments are continuing.

This year we have also focused on silicate-based thin film membranes that are able to separate the light gases of choice. One area of interest is in the alumino silicates. We have been focusing on making defect-free Al/Si films for three reasons: (1) they are easily grown on alumina substates and allow us to perfect the methodology for making the larger-pored, commercially available zeolites, (2) literature reports show that various metal doped zeolites show light gas

separation ability, and (3) the methodology for Al/Si films will be similar for Ti/Si films (more difficult phases due to high pH requirements).

We have started working with commercially available and well-studies ZSM-5 porous zeolites. These zeolites are valuable for hydrocarbon separations. Because we can make these defect-free with our seeding methods, we will extend our experience to other zeolites.

For the ZSM-5 films, the as-synthesized membranes have zero permeation, due to Na cations and occluded H_2O molecules. Then, the film is heat-treated and has selectivity for certain light gases. In Figure 3, the SEM shows that crystals grow deep into the substrate pores, and only small and on surface not continuous layers.

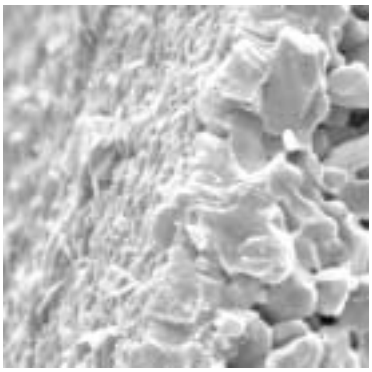


Figure 3: Cross section of alpha alumina disk/pellets with a 1 micron thick defect-free thin film of Zeolite ZSM-5 (right side is substrate with larger pores, center and left side is the film).

We are now able to synthesize defect-free thin film membranes that show no SF_6 or CO_2 permeance. Because crystals are grown on both sides of the support, the flux through the membrane is still low. However initial studies do show preferential movement of smaller, nonpoloar gas molecules (ie. H_2) as compared to the larger, nonpolar (ie. CO_2) ones. One example of flux studies on pure gases, through a Na-ZSM-5 dehydrated membrane (at RT, flux sccm; permeance $\approx 10^{-6}$ mole/m^2 Pa sec), with crystals on both sides of membrane: $H_2/N_2 \geq 61$, $He/N_2 \geq 7$, $H_2/CH_4 = 7$, $H_2/CO_2 \geq 80$, $H_2/O_2 \geq 11$.

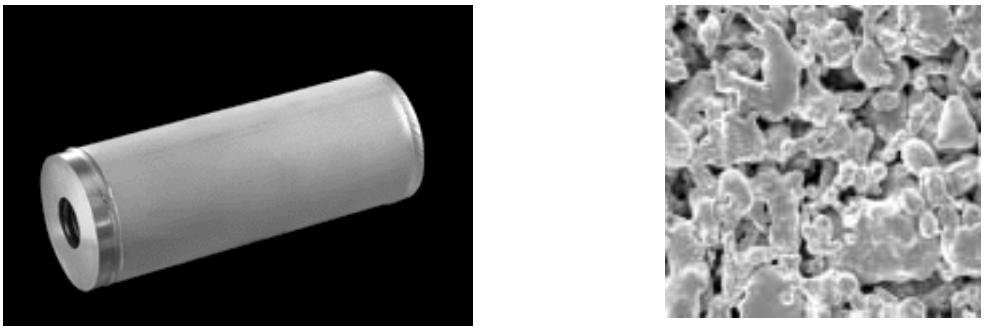
This compares well to literature values of pure gas volume detection methods for ZSM-5 films (Lai, 2000; Nobel, 1999; Nobel, 2000) which show a low permeance $\approx 10^{-7}$ mole/m^2 Pa sec, and selectivity of $H_2/N_2 \geq 3.91$, $He/N_2 \geq 3.22$, $N_2/CO_2 = 0.625$, $H_2/N_2 = 100$ (only at elevated temperature of 150°C and low permeance of 10^{-10}).

However there are crystals grown on both sides of the disk. One side is cleared of crystals by mechanical means. When one side is cleared, flux is increased 3 fold. The synthesis method involves mechanical application of colloid-based seeding of about 0.1micron size powdered crystals. Multiple layers of differing thicknesses and concentrations are applied to fill in defect

sites. Permeation values on this membrane and membranes with one crystal side removed are still being collected.

We have also begun research into various silico titanates phases for thin film membranes. Work to date has shown that due to high pH and long reaction times and temperatures, the alumina substrate dissolves. Work continues into reaction modifications for thin film growth.

Industry is interested in working with membranes on sturdy supports; supports need to be compatible with plant conditions. In an effort to keep in line with industry values, we have begun research into thin film growth on stainless steal supports. We have had discussions with Pall Corporation (a separations membrane manufacturing company, East Hills, NY), as a possible future commercialization partner of defect-free membranes for gas and chemical separations. On a fact-finding visit to their facilities (2/9/01), we were supplied with a sample of porous stainless steel (316, 316L) metal substrate, shown in Figure 4. Initial attempts to synthesize a crystalline film only produced an amorphous gel. We are now attempting seeding techniques to promote film growth.



a. b. __ ≈ 10 microns

Figure 4: (a) porous metal filter cartridges are made with Pall PSS s-series (b) SEM, top view, of Pall PSS s-series support only.

Though commercialization of these materials is still in the future, some early investigations show that membrane technology continues to grow in importance on the world market. Some economic estimates of membrane commercialization show that worldwide sales of synthetic membranes is greater than $2B, with an annual growth of 12-15% expected. Furthermore, 75% of the market belongs to the U.S., Japan, and Western Europe. For gas separation membranes in particular, economic estimates from 1996 predict that by 2000, the membrane gas separation business would grow to about $500M (Puri, 1996).

Conclusion

This program is focused on the synthesis, modeling, validation and testing of defect-free thin film membranes for the separation and isolation of H_2 gas. These robust thin films are made of chemically and mechanically stable crystalline inorganic molecular sieves (zeolites). Successes

from this program will have direct effects on national concerns such as hydrocarbon fuels and biomass energy. The membranes are molecular sieve/zeolite crystalline phases that are capable of molecular sieving small gas molecules, thereby allowing for H_2 purification.

This year we have accomplished our milestones and have made in-roads into developing industrial partnerships necessary for future commercialization of our membranes. We continue our collaboration with NMSU for modeling and simulation with focus on silicates and silicotitanates. We have synthesized one of the phases as a thin film membrane, tested for permeation and separations, and have shown excellent separation values for various light gases of interest. Work continues on improving our silicate-based defect-free thin film membranes.

Future Work

Future work plans for next year include the continuation of our work on synthesis, modeling and thin film growth of novel microporous phases for light gas separations, including novel alumino silicates and silico titanate phases. Furthermore, we plan to explore the thin film growth of alumino silicates zeolites doped with other elements for maximized adsorption and selectivity of H_2 over other light gases of interest. The permeation work will focus on the study of pure and mixed gas systems, both at room temperature and 80°C. We will continue to attempt thin film syntheses on stainless steel and alumina supports. Again we plan to tie this research with the modeling and simulation efforts of this past year, with collaborators at New Mexico State University (Dr. Martha Mitchell, Dept. of Chemical Engineering). Our focus will be on the silico titanates and how they compare to known silicate-based zeolites. We will continue to build interactions and collaborations with outside industries for potential future collaborations and commercialization partnerships.

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