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## **DEFECT-FREE THIN FILM MEMBRANES FOR H<sub>2</sub> 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) and result in materials with thermal stability over 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 a new project, begun in December 1999, and 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<sub>2</sub> from CH<sub>4</sub>, CO and N<sub>2</sub> 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 to the synthesis of microporous phosphate-based phases, both as bulk and thin film materials. Within this

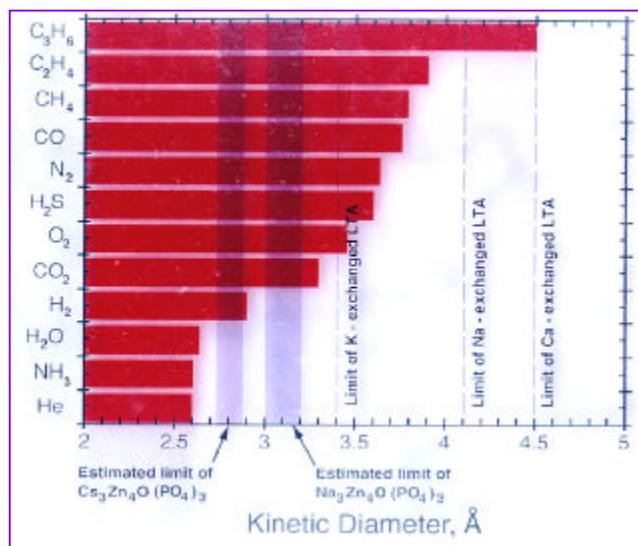
arena, we have begun to explore the gallium/phosphate phase space; five new phases have been synthesized. We have also updated our unique permeation unit to accommodate novel membrane disks for pure and mixed gas studies. Also, we have exciting new results and computational validation (collaboration with New Mexico State University) by molecular dynamics modeling, transition state theory and simulations of light gas molecules diffusing through commercially available molecular sieves and our novel materials.

## Discussion

This year, we are building the proper equipment modifications to our *unique* permeation equipment for testing in this project. Furthermore, we are focusing on ZnPO phases that have internal porosity accessible to certain light gases and are easily synthesized as thin film membranes.

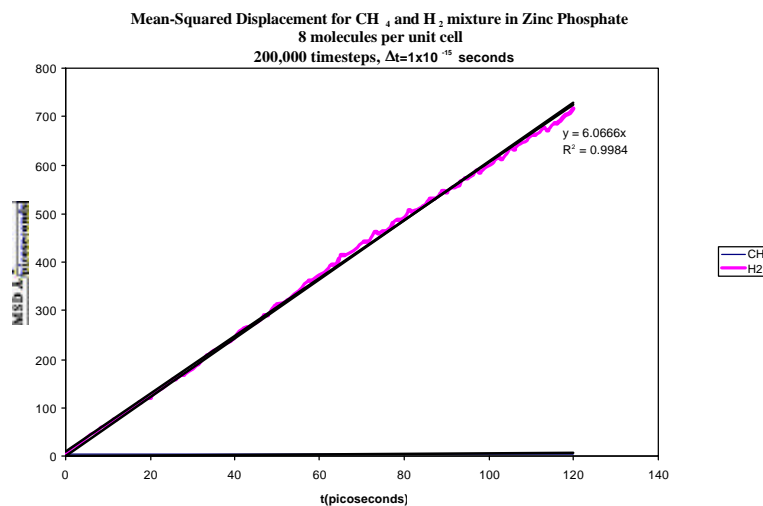
Known, commercially available zeolites that have pore sizes in the range of light gas molecules are Zeolite LTA. Changing the cation in the pores effectively changes the kinetic diameter of the opening of the pore. K/LTA has an effective pore diameter of 3.4Å. (See figure 1) However, to get into the range of H<sub>2</sub> separation and isolation, smaller pored zeolites are necessary.

**Figure 1: Zeolite kinetic diameters versus molecule kinetic diameters (Å)**



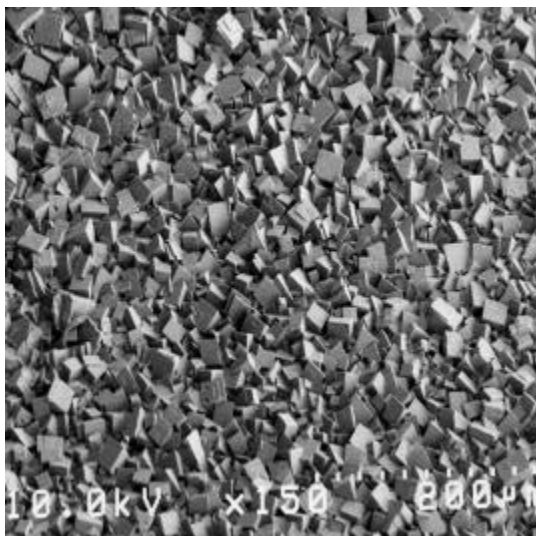
We have combined bulk and thin film synthesis with modeling and simulation to make small pored zeolite films specifically for H<sub>2</sub> separations. Na<sub>3</sub>Zn<sub>4</sub>O(PO<sub>4</sub>)<sub>3</sub> and CsZn<sub>2</sub>OPO<sub>4</sub> were synthesized, characterized and studied.<sup>1</sup> Through permeation modeling and simulations, we determined that Na<sub>3</sub>Zn<sub>4</sub>O(PO<sub>4</sub>)<sub>3</sub> should accommodate H<sub>2</sub>, but not CO<sub>2</sub>; while CsZn<sub>2</sub>OPO<sub>4</sub> should allow H<sub>2</sub>, but still be impermeable to H<sub>2</sub>O and NH<sub>3</sub>. An example of the calculated output is in figure 2, which shows the mean-squared displacement vs. time for a mixture of four H<sub>2</sub> and four CH<sub>4</sub> per unit cell (this also mimics the pure gas studies). The hydrogen moves through the system but the methane is essentially stationary.<sup>2</sup>

**Figure 2: Mean-Square displacement (movement) H<sub>2</sub> molecules through Zn/P cages (pink line overlaying black calculated slope) versus CH<sub>4</sub> molecules (horizontal black line).**



We have been able to synthesize and characterize the cesium phase as a thin film membrane. (See figures 3 and 4) To date, we have been able to synthesize the sodium phase as a bulk crystalline powder, but not as a defect-free thin film..

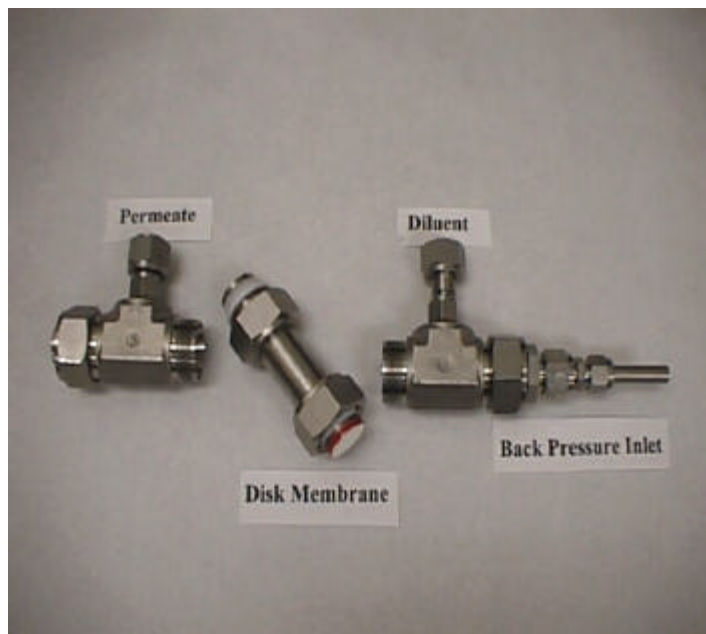
**Figure 3: Scanning Electron Micrograph (SEM) of CsZn<sub>2</sub>OPO<sub>4</sub>**



Permeation data has shown that at room temperature studies, single gas testing, there is good crystal coverage on the membranes. These films show significant permeabilities only to H<sub>2</sub> and He. *This is consistent with molecular sieving.* While the films can be made leak-free, they are still fairly thick (ca. 20 µm), and thus do not yield high gas flow rates yet. This is shown in the low flux ratios of H<sub>2</sub>/SF<sub>6</sub> = 6.05 and H<sub>2</sub>/N<sub>2</sub> = 5.42. Close inspection by SEM shows that a crystalline layer of zeolite has been

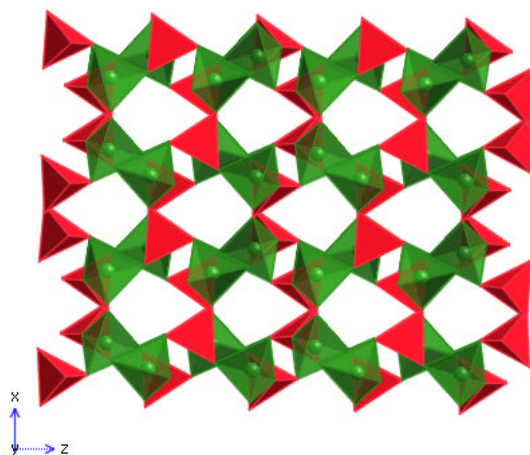
synthesized but that a densified layer is forming between the crystals and the substrate, inhibiting molecular sieving. We continue to work on the elimination of this problem.

*Figure 4: Thin Film Membrane sealed into permeation holder for testing*



Because of initial successes, we are also focusing on the synthesis of bulk and thin films of novel microporous phases (such as gallophosphate based molecular sieves) and known aluminosilicate zeolites. We have been able to synthesize five new bulk crystalline phases with characterization studies underway. One of the phases is a microporous GaPO<sub>4</sub> phase, with pores of 3.9 x 3.2Å.<sup>3,4</sup> Attempts are underway to synthesize this and the other phases as thin film membranes.

Preliminary economic calculations as to the importance of membranes in current industry were also performed this year. The first commercialization of a membrane gas separation was in 1979, and currently there are 10,000 commercial membrane systems in various gas separations applications. Industry experts (including Air Products) estimated in 1996 that the gas separation business was valued at \$85M in the US and was growing at a rate of approximately 8%/year. They estimated that by 2000, the membrane gas separation business would grow to about \$500M.<sup>5</sup>

*Figure 5: Novel GaPO<sub>4</sub> phase*

### Conclusion

This new program (started in December 1999) is focused on the synthesis, modeling, validation and testing of defect-free thin film membranes for the separation and isolation of H<sub>2</sub> 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<sub>2</sub> purification.

This year we have accomplished our milestones. We have updated our unique permeation testing unit to fit thin film disk membranes. We have formed a collaboration with NMSU for modeling and simulation; initial studies indicate Zincphosphate crystalline phases capable of the sieving. We have synthesized one of the phases as a thin film membrane, tested for permeation and separations, and are making further improvements on the material. We have also expanded the synthesis research to gallium phosphate (Ga/P) phases; we have synthesized 5 new bulk phases, 2 of which contain microporous phases. Work continues on synthesizing the Ga/P as thin films.

### 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 gallophosphates and silicotitanate phases. Furthermore, we plan to explore the thin film growth of aluminosilicates zeolites doped with other elements for maximized adsorption and selectivity of H<sub>2</sub> 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. 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, NMSU).

We will also begin to build interactions and collaborations with outside industries for potential future collaborations and commercialization partnerships.

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