Project Title: CO_2 Separations Using Zeolite Membranes
Type of Report: Final Report
Performance Period: July 1, 1998 to June 30, 2001
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Date Issued: **June 30, 2001**
DOE Award No. DE-FG2698-FT40123

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Summary:

Zeolite and other inorganic molecular sieve membranes have shown potential for separations based on molecular size and shape because of their small pore sized, typically less than 1 nm, and their narrow pore size distribution. The high thermal and chemical stability of these inorganic crystals make them ideal materials for use in high temperature applications such as catalytic membrane reactors. Most of the progress with zeolite membranes has been with MFI zeolites prepared on porous disks and tubes. The MFI zeolite is a medium pore size structure having nearly circular pores with diameters between .53 and .56 nm. Separation experiments through MFI membranes indicate that competitive adsorption separates light gas mixtures. Light gas selectivities are typically small, however, owing to small differences in adsorption strengths and their small sizes relative to the MFI pore opening. Furthermore, competitive adsorption does not work well at high temperature where zeolite membranes are stable and have potential application.

Separation by differences in size has a greater potential to work at high temperature than competitive adsorption, but pores smaller than those in MFI zeolites are required. Therefore, some studies focused on the synthesis of a small, 8-membered-pore structures such as zeolite A (0.41-nm pore diameter) and SAPO-34, a chabazite (about .4-nm pore diameter with about 1.4 nm cages) analog. The small pore size of the zeolite A and SAPO-34 structures made the separation of smaller molecules by differences in size possible.

Zeolite MFI and SAPO-34 membranes were prepared on the inside surface of porous alumina tubes by hydrothermal synthesis, and single gas and binary mixture permeances were measured to characterize the membrane's performance. A mathematical diffusion model was developed to determine the relative quantities of zeolite and non-zeolite pores in different membranes by modeling the permeation date of CO_2. This model expresses the total flux through the membrane as the sum of surface diffusion through zeolite pores and viscous flow and Knudsen diffusion through non-zeolite pores. As predicted by the model, the permeance of CO_2 decrease with increasing pressure at constant pressure drop for membranes with few non-zeolite pores, but the permeance increased through viscous flow pores and was constant through pores allowing Knudsen diffusion. Membranes having more non-zeolite pores had lower CO_2/CH_4 selectivities.

The SAPO-34 membranes were characterized for light gas separation applications, and the separation mechanisms were identified. Single gas permeances of CO_2, N_2, and CH_4 decreased with increasing kinetic diameter. For the best membrane at 300K, the He and H_2 permeances were less than that of CO_2, because He, H_2 and CO_2 were small compared to the SAPO-34 pore, and differences in the heat of adsorption determined the permeance order. The small component permeated the fastest in CO_2/CH_4, CO_2/N_2, N_2/CH_4, H_2/CH_4, and H_2/N_2 mixtures between 300 and 470 K. For H_2/CO_2 mixtures, which were separated by competitive adsorption at room temperature, the larger component permeated faster below 400K. The room temperature CO_2/CH_4 selectivity was 36 and decreased with temperature. The H_2/CH_4 mixture selectivity was 8 and constant with temperature up to 480 K. Calcination, slow temperature cycles, and exposure to water vapor had no permanent effect on membrane performance, but temperature changes of approximately 30 K/min decreased the membrane's effectiveness.

The effects of humidity on gas permeation were studied with SAPO-34 membranes of different qualities. Membranes with high CO_2/CH_4 selectivities (greater than 20) were stable in water vapor under controlled conditions, but degradation was seen for some membranes. The

degradation opened non-SAPO-34 pores that were larger than SAPO-34 pores as shown by the I-C_4H_{10} permeance, CO_2/CH_4 selectivity, and CO_2 flux pressure dependence. In SAPO-34 pores, water apparently adsorbed and increased the gas permeances. Thus, the effect of water on gas permeation is a useful indicator of the membrane quality.

PUBLICATIONS:

Poshusta, J.C., R.D. Noble, J.L. Falconer, *Characterization of SAPO-34 Membranes by Water Adsorption*, **Journal of Membrane Science, 186(1),** 25-40 (2001).

Poshusta, J.C., T.A. Vu, E.A. Pape, J.L. Falconer, R.D. Noble, *Separation of light gas mixtures using SAPO-34 Membranes*, **AIChE Journal,** 46 (2000) 779-789.

Poshusta, J.C., J.L. Falconer, R.D. Noble, *Temperature and Pressure Effects on CO2 and CH4 Permeation through MFI Zeolite Membranes*, **Journal of Membrane Science**, 160 (1999) 115-125.

Poshusta, J.C., T.A. Vu, J.L. Falconer, R.D. Noble, *Synthesis and Permeation Properties of the SAPO-34 Tubular Membranes*, **Industrial and Engineering Chemistry Research**, 37 (1998) 3924-3929.

Posthusta, J.C., J.L. Falconer, R.D. Noble, *Temperature and Pressure Effects in CO2/CH4 Permeation in Zeolite Membranes*, **Proceedings of the Fifth International Conference on Inorganic Membranes**, Nagoya, Japan (1998), 132-134.

Poshusta, J.C., T.A. Vu, J.L. Falconer, R.D. Noble, *Synthesis and Gas Permeation Properties of Tubular Zeolite Membranes*, **Proceedings of the International Workshop on Zeolitic Membranes and Films**, Gifu, Japan (1998) 9-12.

PRESENTATIONS:

Poshusta, J.C. (speaker), R.D. Noble, J.L. Falconer, Characterization of SAPO-34 Membranes by the Effects of Humidity on Gas Permeation, Proceedings of the 12th Annual Meeting of the North American Membrane Society, May 24-27, 2000.

Poshusta, J.C. (speaker), T.A. Vu, J.L. Falconer, R.D. Noble, Effects of Temperature, Pressure, and Humidity on Light Gas Permeation through SAPO-34 Membranes, AIChE Annual Meeting, Dallas, Oct. 31-Nov. 5, 1999.

Poshusta, J.C. (speaker), E.A. Pape, T.A. Vu, J.L. Falconer, and R.D. Noble, Separation of Light Gas Mixtures through SAPO-34 Membranes, poster presentation at the International Conference on Membranes, Toronto, Canada, June 12-18, 1999.

Poshusta, J.C. (speaker), E.A. Paper, V.A. Tuan, J.L. Falconer, and R.D. Noble, Temperature and Pressure Dependence of Light Gas Mixtures through SAPO-34 Membranes, Materials Research Society, San Francisco, April 5-9, 1999.

Poshusta, J.C. (speaker), J.L. Falconer, R.D. Noble, Modeling of Single Gas Permeance in Zeolite Membranes, Proceedings of the 9th Annual Meeting of the North American Membrane Society, May 31-June 4, 1997.