TITLE: CO_2 SEPARATION USING ZEOLITE MEMBRANES

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ABSTRACT

Objective

The objective of this research is to synthesize and modify zeolite membranes and evaluate their performance for CO_2/N_2 separation related to flue gas effluent from coal-fired power plants. Both single component and binary feed mixtures, with and without humidification, will be used and the permeation flux and selectivity will be determined as a function of temperature and pressure. Two approaches to obtain appropriate membranes for this separation will be used. One approach will be to synthesize zeolite membranes that have selective permeation properties for CO_2. The second approach will be to chemically modify a zeolite membrane after synthesis to make it more selective for CO_2.

The Japanese government (NEDO Research and Development of High Temperature CO_2 Separation and Utilization Technology Program) has set a target permeance of 3×10^{-7} mol/(m^2 s Pa) and CO_2/N_2 selectivity of 100 for inorganic membrane technology. Current zeolite membranes synthesized by our research group can meet the permeance target and, therefore, improved selectivity without a significant decrease in permeance will be the focus of this study. The variation in zeolite structure and sorption properties will allow us to "tune" the separation to obtain high selectivity.

Results and Discussion

Two types of molecular sieve membranes, MFI (0.55 nm pore size) and SAPO-34 (0.4 nm pore size) were prepared by hydrothermal synthesis on the inside surface of porous α-alumina tubes. Analysis of completed membranes by x-ray diffraction and SEM verified the synthesis of the desired materials.

The single gas permeances of H_2, CO_2, N_2, and CH_4 were measured as a function of temperature and pressure through MFI and SAPO-34 membranes. The permeances of these gases through SAPO-34 membranes decreased with increasing kinetic diameter due to the small pore size of SAPO-34. The order of the permeances through MFI do not correlate with molecular size, however. Differences in adsorption strength contribute to the permeance order through MFI membranes.

The mixture selectivities (permeance ratios) of these gases through MFI and SAPO-34 membranes were measured as a function of temperature and pressure. The selectivity of a 50/50 mol% mixture of CO_2 and CH_4 was 5.5 at room temperature and a feed pressure of 270 kPa with a 138 kPa pressure drop. The selectivity decreased with increasing temperature. The selectivity was relatively unaffected by the presence of 1 mol% water vapor in the feed mixture.

Under the same pressure conditions, room temperature CO_2/CH_4 selectivity was 30 through SAPO-34 membranes and also decreased with temperature. Below room temperature (228 K), the CO_2/CH_4 selectivity was 80. The room temperature selectivities for 50/50 mixtures of H_2/CH_4, H_2/N_2, H_2/CO_2, N_2/CH_4, and CO_2/N_2 through SAPO-34 membranes were 16, 3.6, 0.32, 3.4, and 8, respectively. The H_2/CH_4 selectivity was relatively constant with temperature up to 473 K, and dropped slightly to 12 at 523 K. A 10/90 mol% CO_2/N_2 mixture was separated with a SAPO-34 membrane, and the selectivity was about the same as the 50/50 mixture.

These results indicated that two mechanisms of separation are important. Weakly adsorbing molecules with significant differences in size (i.e. H_2/CH_4) are separated by differences in diffusivity. Relatively small molecules with a large difference in adsorption strength (i.e. H_2/CO_2) are separated by competitive adsorption. Both mechanisms may participate in a separation, however, when there is a significant difference in both molecular size and adsorption strength. The CO_2/N_2 mixture is separated by combination of differences in diffusivity and competitive adsorption. Thus, separation might be better in zeolites with high CO_2 affinity or smaller pore zeolites where N_2 is excluded from pores.

Plans

The smaller pore size of SAPO-34 demonstrated higher selectivities than MFI membranes. Further decreasing the pore size in an effort to increase the light gas selectivities may be obtained by T-atom replacement in the SAPO-34 structure or synthesis of smaller pore zeolites. Substitution of Si in SAPO-34 with Mn or Mg, the molecular sieve $MeAlPO_4$-34, has a T-O bond length shorter than Si-O and different adsorption characteristics than SAPO-34. We will prepare $MeAlPO_4$-34 membranes whose reduced the pore size and different CO_2 affinity may separate CO_2/N_2 mixtures better than our current membranes. Another structure, SAPO-20, has 0.3 nm pores, and membranes will be made from this molecular sieve to separate CO_2/N_2 mixtures.

The new and current membranes will be modified by ion exchange and treatment of the membrane surface by CO_2 surfactants. Exchange of the cation in molecular sieve structures is known to change their adsorption and diffusion properties. The ZSM-5 membranes are initially made with H^+ or Na^+ cations, but these cations will be exchanged with other +1 and +2 metal ions to study their effects on light gas separation. Perfluouronated hydrocarbon molecules are known to have a high CO_2 affinity, and existing membranes will be coated with this CO_2 selective material in an effort to increase the CO_2 separation performance.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Presentations and posters

Poshusta, J. C., E. A. Pape, T. A. Vu, J. L. Falconer, and R. D. Noble, Separation of Light Gas Mixtures Through SAPO-34 Membranes, poster to be presented at the *International Conference on Membranes*, Toronto, Canada, June 12-18, 1999.

Poshusta, J. C., E. A. Pape, 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., T. A. Vu, J. L. Falconer, and R. D. Noble, Synthesis and Gas Permeation Properties of Tubular Zeolite Membranes, *Proceedings of the International Workshop on Zeolitic Membranes and Films*, Gifu, Japan, June 28-30, 1998.

Poshusta, J. C., J. L. Falconer, R. D. Noble, Temperature and Pressure Effects in CO_2/CH_4 Permeation in Zeolite Membranes, *Proceedings of the Fifth International Conference on Inorganic Membranes*, Nagoya, Japan, June 22-26,1998.

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