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Zeolite Membranes for Gas Separations

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Zeolite Membranes for Gas Separations

CONTRACT INFORMATION

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Other Funding Sources	Center for Separations using Thin Films Chevron Research and Technology Company
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METC Project Manager	Venkat K. Venkataraman
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OBJECTIVES

To form zeolite films on inorganic supports, and test them for CO_2/H_2, CO/H_2, and H_2O/H_2 separations. The separation conditions will be studied up to 773 K and 3 MPa pressure.

BACKGROUND INFORMATION

Gasification of coal and other organic fuel sources produces H_2 as well as CO, CO_2, and H_2O. The use of these gasification products as a source of H_2 for fuel cells requires gas separations at high temperatures and high pressures. The separation process must also be able to work in the presence of H_2S, COS and mercaptans. Zeolite membranes can meet these requirements.

Zeolites are crystalline inorganic materials with well-defined pore openings that are on the order of molecular dimensions. Zeolite particles are presently used as selective sorbents for various gas separations based on their sorptive and molecular sieving properties. They can tolerate very high temperatures and sulfur compunds due to their inorganic structure. A very recent developement is to fabricate a dense zeolite layer on a tubular support which can be used as a membrane. This configuration allows one to operate the separation step continuously. Also, a membrane structure allows one to vary the temperature, pressure and feed composition without interruption.

PROJECT DESCRIPTION

We proposed to demonstrate the effectiveness of a catalytic membrane reactor (a ceramic membrane combined with a catalyst) to selectively produce methanol by partial oxidation of methane. Methanol is used as a chemical feed stock, gasoline additive, and turbine fuel. Methane partial oxidation using a catalytic membrane reactor has been determined as one of the promising approaches for methanol synthesis from methane. Methanol synthesis and separation in one step would also make methane more valuable for producing chemicals and fuels. Another valuable fuel product is H_2. Its separation from gasification products would be very valuable as a chemical feedstock and a clean fuel for fuel cells.

RESULTS

Silicalite-alumina composite membranes prepared in our laboratory by an in-situ zeolite synthesis method were used in the gas permeation experiments. The preparation procedure is discussed elsewhere [1]. Silicalite-1 is a pure-silica zeolite with a cage size of 0.58 nm, and it was deposited on a tubular, asymmetric, γ-alumina support. The γ-alumina layer had a pore size of 5 nm. Both single-gas permeation and gas-mixture separation experiments were conducted.

As a first step in evaluating the membrane for gas separations, single gas permeation experiments with N_2, CH_4, and CO_2 were carried out, and permeation flux versus temperature data were obtained at 1.3 bar from 300-600 K. These data are plotted in Fig. 1. The data show that the permeance of each gas went through a minimum. The temperatures at which the minimum occurs are 400 K, 450 K, and 450 K for N_2, CH_4, and CO_2 respectively. Researchers at Kyushu university [2] also observed a minimum permeance of N_2 through silicalite-1 at 400 K, but they did not report minimums for the other gases. Transport of all gases was activated at higher temperatures, and the activation energies were 4.1, 3.8, and 6.3 kJ/mol for N_2, CH_4, and CO_2 respectively. Permeances at 600 K for CH_4 and CO_2 were lower than those at 300 K, and the N_2 permeances at 300 K and 600 K were the same. Therefore, to exceed the productivity at room temperature, temperatures higher than 600 K are required.

Separation experiments for N_2/CH_4 mixtures were also conducted. The feed mixtures contained 10 - 30 mol% N_2 in CH_4, because these are typical N_2 concentrations in natural gas. The separation selectivities were about 1.5, and CH_4 permeated faster than N_2 through the membrane.

Single-gas permeation of H_2, and separation of H_2/SF_6 mixture were also carried out with the silicalite-1 membrane. Flux of H_2 with the silicalite-alumina composite membrane was 8 times lower than the flux with the alumina membrane. Separation selectivity for H_2/SF_6 was 11.9, and the selectivity increased slightly as the temperature increased from 361 to 583 K.

Composite membranes of silicalite and Ni-SAPO-34 on the γ-alumina supports were also prepared. Initially, reproducible data for gas permeances could not be obtained. The stability of SAPO-34 membranes has been reported to be affected by H_2O vapor. When the feed gases were passed through $CaSO_4$, a desiccant made by Drierite, stable and reproducible permeances were obtained. Ratio of CO_2 to N_2 single-gas permeance was 4.3. When the gases were not dried, ratios as high as 9.5 were observed. Permeation experiments for CO_2 and H_2 were performed, but no significant single-gas selectivity was obtained. Compared to the reported promising selectivities for CO_2/N_2, this lack of selectivity was not expected.

FUTUER WORK

For better understanding of the single gas permeation, high pressure permeation experiments for N_2, CH_4 and CO_2 with the silicalite-1 membranes are planned. Pressure in these experiments will be up to 10 bar, and the temperature will be 300-600 K. Also, we plan to continue the preparation of Ni-SAPO-34 and silicalite-1 membranes using different gel compositions as well as other supports such as SAPO membranes, stainless steel, and silica. We will then perform permeation and separation experiments for these membranes for the following gas mixtures: CO_2/H_2, CO/H_2, and H_2O/H_2.

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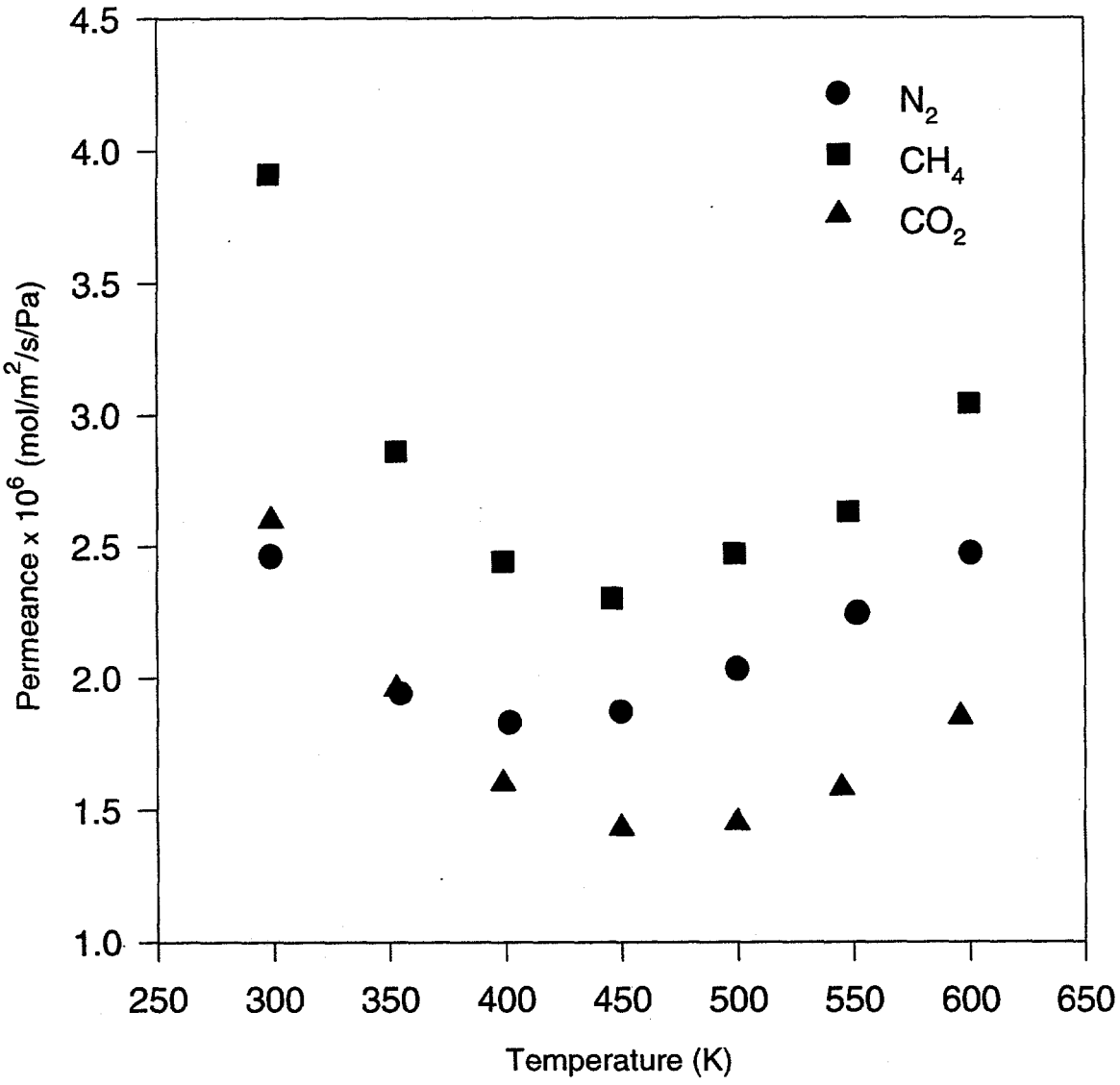

Figure 1. Single Gas Permeances Versus Temperature For A Silicalite-1 Membrane