H₂ SEPARATION THROUGH ZEOLITE THIN FILM MEMBRANES

Margaret E. Welk, Tina M. Nenoff

Sandia National Laboratories, PO Box 5800, MS 0734, Albuquerque, NM 87185-0734
mewelk@sandia.gov

Introduction

The synthesis and testing of inorganic zeolite membranes has been intensely studied because of their potential applications in the domains of gas separation, pervaporation, reverse osmosis and in the development of chemical sensors and catalytic membranes. Specifically, development of new technologies, such as zeolite membranes, for H₂ separation and purification has a high priority for the future of H₂ as a fuel source. H₂ is commonly produced by the reforming of hydrocarbons, creating CO₂, CO, CH₄ and H₂O as by-products. A successful membrane for the separation of H₂ from other reformate gases must have both high flux and high selectivity for H₂ in the presence of these other gas species. Inorganic membranes, which have good thermal stability and chemical inertness, are highly attractive. Distinctively, zeolite membranes combine pore size and shape tunability with the inherent mechanical, thermal, and chemical stability necessary for long term separations. The effective pore size distribution, and hence the separation performance, of a defect free zeolite membrane is intrinsically governed by the choice of the zeolitic phase.

Numerous pure gas permeation studies have been performed on MFI-type zeolite membranes that allow ideal selectivities to be calculated. Typical literature selectivity values of H₂ from CO₂, CH₄ and CO range from 2 to 8, below the values necessary for successful industry integration. It is well recognized that gas mixtures flowing through separation membranes will behave differently than pure gases owing to adsorption effects and other phenomena. We report here the study of the permeance and selectivity of both ZSM-5 and silicalite-1 zeolite membranes under the flow of three gas mixtures, two chosen as benchmarks (50/50 mol% H₂/CH₄ and 50/50 mol% H₂/CO₂) and one chosen to emulate an industrial methane reformate stream. The H₂ selectivities for both membranes outstrip the calculated ideal selectivity values from pure data by eight times or more.

Experimental

Gases. Reagent grade pure gases were purchased from Matheson Trigas. H₂, CO₂, O₂, CH₄, N₂, CO were used to test the permeability of the membranes. SF₆ was used to assess membrane quality, He was used to clean and purge the unit, shown in Figure 1. Three reagent grade gas mixtures pre-mixed by Matheson Trigas were also tested: 50/50 mol% H₂/CH₄, 50/50 mol% H₂/CO₂, and a four gas component mixture that approximates a methane steam reformate stream, excluding the water vapor (will be referred to as the reformate mixture): 76.2% H₂, 13.6% CO₂, 6.8%CO, and 3.4% CH₄.

Membrane Synthesis. A thorough description of the silicalite membrane growth has been published elsewhere. The support cleaning, seed synthesis, and seedling methodology for the ZSM-5 membranes are identical to the steps for silicalite also can be found in the same reference. A description of the ZSM-5 gel and hydrothermal synthesis of the ZSM-5 membranes is presented here.

In the gel used for the hydrothermal synthesis, the silicon source for the membrane synthesis was colloidal silica Ludox SM-30; the source of aluminum was Al₂(SO₄)₃·18H₂O and NaOH is the alkalinity source. Ludox SM-30 was filtered prior to use to remove any SiO₂ flakes; all other reagents were used as received. 2.14 g of NaOH, and 0.832 g of Al₂(SO₄)₃·18H₂O were added to 68.4 g of H₂O, and stirred until dissolved. 20 g of Ludox SM-30 was added drop-wise to the mixture while stirring. Each gel was then aged for 24 hours while being stirred at room temperature. Gels that were not aged under agitation did not result in selective membranes. The aged gels in this work were homogeneous and no precipitate had formed prior to the reactions.

The alpha-alumina substrates supplied by Inoceramic GmbH have a 1.8 μm average pore size, a diameter of 13 mm and a thickness of 1 mm. Their high density ensures good mechanical properties and robustness. MFI zeolite seeds were rubbed onto both sides of the cleaned substrates; the seed synthesis and application has been described elsewhere. The seeded substrates were held vertically in the Teflon lined Parr reactor using Teflon holders to prevent sedimentation on top of the membrane. The homogenous gel was then poured in the reactor until the membrane was fully immersed. The hydrothermal syntheses were carried out in Parr reactors with a 23 ml Teflon liner at 170°C for 12 hours under autogenous pressure.

After the hydrothermal synthesis, the two-sided membrane was removed from autoclave, washed with DI water and dried in air at 50°C for few hours. A permeation test on the as-synthesized, uncalcined membrane allows the rapid assessment of its quality before the time-consuming calcination step. At this stage, a good quality membrane should be impermeable for SF₆. The SF₆ kinetic diameter of 5.5 Å is similar to the pore dimensions of the calcined ZSM-5 zeolite (diameter range 5.1 – 5.6 Å). Substantial SF₆ diffusion through the uncalcined membrane indicates the presence of detrimental membrane defects larger than the zeolite pores which will be opened during calcination. Any existing large defects (partial coverage of the substrate and micro-cracks) may be repaired by a second hydrothermal synthesis step, using a shorter reaction time and more diluted starting gel.

Once the quality of the membrane was established, the water was removed from the membrane pores by calcination in air. A calcination temperature of 600°C led to cracks in the membrane and drastic reduction in permeation performance unless a slow temperature ramp rate was used. The stress at the interface between the zeolitic layer and the alumina substrate due to thermal expansion mismatch has to be minimized by using slow heating rates below 1°C/min. A typical successful temperature profile for the calcination is a heating and cooling rate of 0.5°C/min with a maximum temperature of 600°C maintained for 6 hours. This ensures the removal of water from the pores without creating detrimental defects within the membranes.

Characterization Techniques. The zeolite membranes were characterized by X-ray diffraction (Siemens D500 diffractometer, Cu Ka radiation, Bragg-Brentano geometry) and by Scanning Electron Microscopy (JEOL–6300V equipped with a Link Gem Oxford 6699 EDAX attachment).

Permeation Measurements. The membrane permeations were measured at room temperature using pure and mixed gases and a constant trans-membrane pressure of 16 PSI controlled by a backpressure regulator (see Figure 1). The membrane was sealed in a Swagelok fitting using Viton O-rings. The gas flow through the membrane was measured using an acoustic displacement flowmeter (ADM 2000 from J&K) and a digital bubble flowmeter (HP-9301). Between permeation measurements with different pure (SF₆, H₂, CO₂, O₂, CH₄, N₂, CO) and mixed (50/50 H₂/CO₂, 50/50 H₂/CH₄, the reformate mixture) gases, the whole system was purged, flushed with He and evacuated several times. For the pure gases, the ideal gas selectivity was calculated as the ratio of the permeances in the steady regime.

Residual Gas Analyzer. For the mixed gas studies, an RGA (Stanford Research Systems QMS 200 Residual Gas Analyzer) in Pressure vs. Time graphing mode was attached to the permeate side of the membrane. The RGA tracks the partial pressure of each gas species over time using an internal mass spectrometer. Data points are taken once per second. Before each run, both sides of the membrane were evacuated and flushed with He three times. The permeate side of the membrane was then filled with He to atmospheric pressure, and the retentate side was evacuated just prior to the initiation of mixed gas flow. A constant trans-membrane pressure of 16 PSI was controlled by the back pressure regulator. Selectivities were calculated as the ratio of the partial pressures of the gas species of interest.

Results and Discussion

The mixed gas permeance and selectivity results have been presented elsewhere.25 Table 1 below includes the selectivity data, where selectivity = (y_1/y_2)_permeate/(y_1/y_2)_inlet. Please see reference 25 for graphs and additional details.

Table 1. H2 Selectivity Through ZSM-5 and Silicalite Membranes Using Gas Mixtures

<table>
<thead>
<tr>
<th></th>
<th>Reformate Mix</th>
<th>50/50 H2/CO2</th>
<th>50/50 H2/CH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 H2</td>
<td>58.8</td>
<td>60.1</td>
<td>39.4</td>
</tr>
<tr>
<td>Selectivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicalite-1 H2 Selectivity</td>
<td>21.5</td>
<td>22.9</td>
<td>16.9</td>
</tr>
</tbody>
</table>

According to the pure gas data, the ZSM-5 membrane was calculated to have an ideal selectivity for H2 from the other reformate gases around 4 to 10, depending on the gas species.25 In both 50/50 gas mixtures, the actual selectivities jumped almost 8-fold to 39.4 and 60.1. The selectivity for H2 in the reformate mixture jumped to 58.8, a value more than six times that of the pure gas approximation.

Both ZSM-5 and Silicalite-1 are MFI type zeolites. Although they have identical structures, the pore chemistry differs owing to the presence of even a small amount of aluminum replacement of the silicon atoms in the ZSM-5 compound. The pore chemistry directly impacts adsorption and therefore, the permeation characteristics of the membranes, particularly the pure gas permeation results. Silicalite-1 membranes have a higher permeance for pure CO2 than for pure H2 because of the adsorption of CO2 to the all-silica pore surfaces, while the ZSM-5 membranes show a strong preference for H2 even though the percentage of aluminum substituting for silicon is very small ~ 0.25%. With gas mixtures, the silicalite membranes are selective for H2, having lower H2/CO2 selectivities as compared with the ZSM-5 membranes for the 50/50 H2/CO2, the 50/50 H2/CH4 and the reformate gas mixtures.

Conclusions

The testing of the permeation of mixed gases through both ZSM-5 and Silicalite-1 zeolite membranes has revealed the extraordinary selectivities of these membranes for H2. The ZSM-5 membrane had the following H2 selectivities for the 50/50 H2/CH4 mixture, the 50/50 H2/CO2 mixture and the reformate mixture respectively: 39.4, 60.1, and 58.8, respectively. The silicalite membrane had lower H2 selectivities for the same gas mixtures, 16.95, 22.9 and 21.73. The high permeances and extremely high selectivities of these membranes make them viable choices for H2 gas separation applications.

Further studies on these MFI-type membranes continue, and include elevated temperatures, increased lifetime studies, pressure variations, and additional gas mixtures. We will also investigate different microporous materials as well as b-axis oriented MFI type zeolite membranes. The effects of different support materials on membrane performance are also under investigation.

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References