Novel Membrane Technology for Green Ethylene Production

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ABSTRACT

This paper describes the use of a dense hydrogen transport membrane (HTM) in producing ethylene via dehydrogenation of ethane. The HTM drives the conversion of ethane by selectively removing hydrogen that is produced by the dehydrogenation reaction. Preliminary experiments show ethylene yields above the thermodynamic equilibrium limit at high ethane conversion. Moreover, this approach eliminates production of greenhouse gases in the reactor section and yields a much simpler product slate than is obtained from current pyrolysis technology. With a simpler product slate, the cost of "back end" purification could be reduced significantly. We present here preliminary results from ethane dehydrogenation experiments, and describe the development of HTMs suitable for ethylene production.

1   INTRODUCTION

Ethylene, the largest volume commodity chemical manufactured today, is currently produced by pyrolysis of ethane in the presence of steam. Thermodynamically limited in terms of its equilibrium conversion, this process requires substantial energy input. Pyrolysis of ethane also produces significant amounts of greenhouse gases (CO and CO_2) in the reactor section, because carbon directly contacts steam. In a new approach for producing ethylene [1], a dense hydrogen transport membrane (HTM) selectively removes hydrogen during the dehydrogenation of ethane, thereby shifting the equilibrium toward ethylene production. This process is shown schematically in Fig. 1.

Preliminary laboratory experiments showed that this approach gives ethylene yields significantly above the thermodynamic equilibrium limit, even at high ethane conversion. Because the HTM prevents carbon-containing species from contacting air or steam, the production of greenhouse gases is avoided in the reactor section, and a much simpler product slate is produced. The simpler product stream should significantly lower the cost of "back end" purification, which accounts for ≈70% of the capital cost and ≈50% of the energy consumption for a conventional ethylene production unit. Besides significantly reducing energy costs, the new approach should savings in feedstock costs and capital costs.
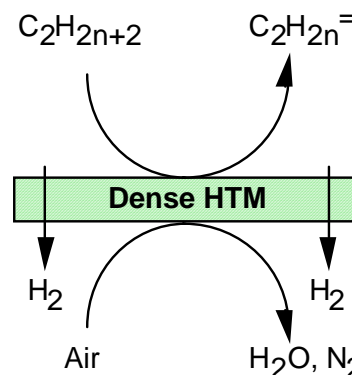

Fig. 1: Schematic of process for producing ethylene via dehydrogenation of ethane.

2   EXPERIMENTAL

A disk-type dense ceramic/metal composite HTM was used to produce ethylene by dehydrogenation of ethane at 850°C [2, 3]. Containing 50-60 vol.% Pd (balance Y_2O_3-stabilized ZrO_2), the membrane for the dehydrogenation experiment was prepared from a mechanical mixture of Pd (Technic) and TZ-3Y (TOSOH) powders that was uniaxially pressed at ≈70 MPa in a stainless steel die. After it was sintered at 1400-1450°C for 5 h in air, the membrane had a thickness of ≈0.25 mm and a diameter of ≈20 mm. In the dehydrogenation experiment, ethane at ambient pressure was passed over one side of the HTM, while air flowed over the other side. The hydrogen produced by dehydrogenation was removed and transported through the HTM to the air-side of the membrane. The air provided the necessary driving force for transport of hydrogen through the HTM. The reaction between transported hydrogen and oxygen in air can provide some of the heat needed for the dehydrogenation reaction.

Because the ethylene production rate depends directly on the rate at which hydrogen is removed from the dehydrogenation zone, the HTM must deliver a high hydrogen flux in order for the new process to be effective. The hydrogen flux of HTMs was measured using feed gases with known hydrogen concentrations. HTMs were made as either a self-supporting sintered disk, like that used in the dehydrogenation experiment, or a thin film membrane supported by a porous ceramic substrate.

Thin film membranes were prepared by mixing palladium and partially stabilized ZrO_2 powders (TZ-3Y) in a solution of α-terpineol and isopropyl alcohol with polyvinyl butyral as a binder and dibutyl phthalate as a plasticizer. The paste was prepared to give 50 vol.% Pd in the final thin film. The concentration of isopropyl alcohol was varied to control the viscosity of the paste. To prepare porous substrates for HTM thin films, alumina hydrate powder was mixed with carbon powder (0-30 wt.%) as a pore-former, and then the powder mixture was cold isostatically pressed (≈70 MPa) in the shape of either a disk or a tube. The pressed specimen was then pre-sintered at 800-900°C in air for 5 h. Paste containing the membrane components was painted onto the surface of the pre-sintered porous substrate and then was sintered for 5 h in air at 1400-1450°C.

To measure the hydrogen flux through an HTM sample, the sample (either a disk or a tube) was affixed to an Al_2O_3 tube using the assembly shown in Fig. 2. A seal formed during heating at 950°C, when spring-loaded rods squeezed a gold ring between the membrane and the Al_2O_3 tube. One side of the sample was purged with feed gas composed of 4-100% H_2/balance He, while sweep gas of 100 ppm H_2/balance N_2 purged the other side. All gases were at ambient pressure.

Gas flow rates (150 ml/min) were controlled with MKS mass flow controllers. A Hewlett-Packard 6890 gas chromatograph was used to measure the concentrations of He and H_2 in the sweep gas. The He concentration in the sweep gas was used to correct the hydrogen concentration in the sweep gas for leakage through the seal. The calculated hydrogen leakage rate was typically <10% of the total H_2 flux through the membrane.
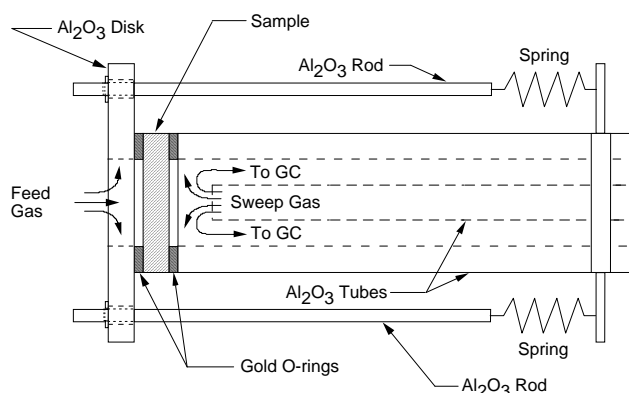

Fig. 2   Fixture for measuring hydrogen flux through HTM.

3   RESULTS

Figure 3 shows the results from an ethane dehydrogenation experiment done at 790-890°C using a self-supporting HTM disk (thickness ≈0.25 mm). This experiment was conducted at BP, Naperville, IL. In this experiment, the hydrogen produced by dehydrogenation of ethane was removed and transported to the air side of the

HTM, where it reacted with oxygen to form steam. The reaction between hydrogen and oxygen on the air side provides some of the energy needed for the dehydrogenation reaction, and establishes a low partial pressure of hydrogen, which provides the driving force for hydrogen transport through the HTM. At 850°C and 1 atm pressure, equilibrium conversion of ethane limits the ethylene yield to 64%, whereas our experiment gave an ethylene yield of 69% with a selectivity of 88% under the same conditions. Coking was not a problem in runs extending over several weeks. These results are encouraging even though the HTM probably did not give a high hydrogen flux due to its relatively large thickness (0.25 mm).
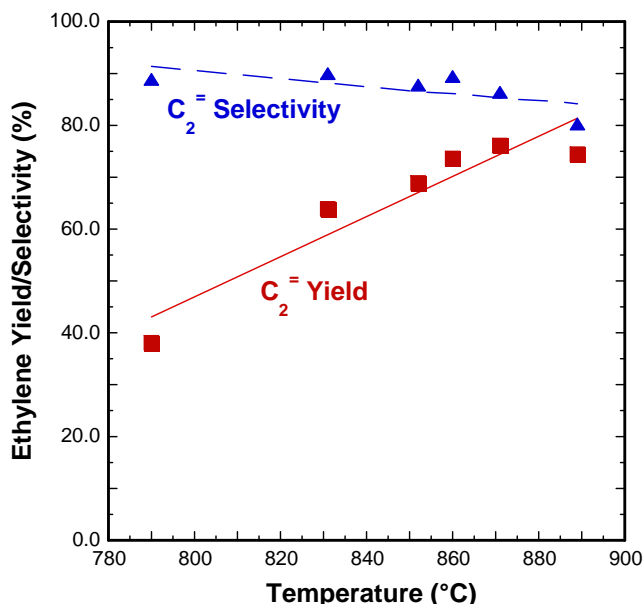

Fig. 3   Results from dehydrogenation of ethane at 850°C with 0.25-mm-thick HTM.

Increasing the hydrogen flux through the HTM would enhance the ethylene yield at lower temperatures at a reasonable residence time. Furthermore, reducing the operating temperature would suppress unwanted side reactions, eliminate NO_x formation on the air side of the HTM, and prolong the membrane's life. Figure 4 shows the hydrogen flux at 900°C versus the inverse of membrane thickness for HTMs like that used in the dehydrogenation experiment. The feed gas during these measurements was 80% H_2/balance He, and the sweep gas was N_2. The hydrogen flux varies linearly with the inverse of membrane thickness, indicating that the membrane's bulk properties control its flux in this thickness range. The HTM for the dehydrogenation experiment and the thickest membrane tested for Fig. 4 had a similar thickness (0.21-0.25 mm); therefore, their hydrogen transport properties are expected be similar. Since the dehydrogenation experiment was conducted, the hydrogen flux through HTMs has been increased significantly by reducing their thickness.
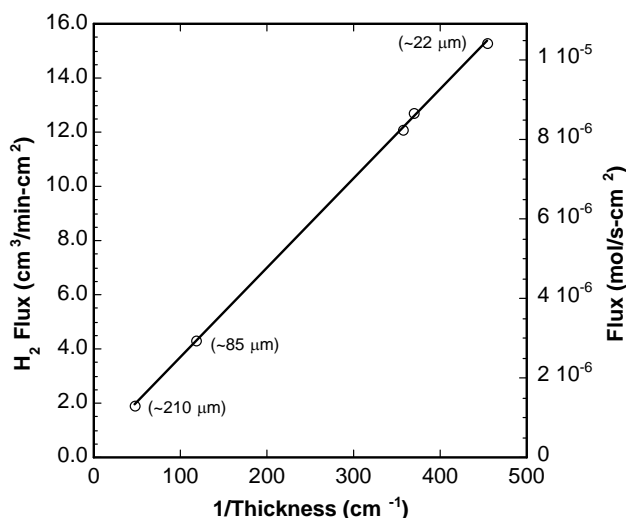
Fig. 4 Hydrogen flux at 900°C vs. inverse thickness of HTM. Feed was 80% H_2/balance He; sweep was N_2.

The data in Fig. 4 were obtained with self-supporting membranes that were prepared by polishing sintered disks. This fabrication technique is, of course, impractical for producing membranes with large surface areas, and samples made this way are very fragile. To make thinner membranes with better mechanical integrity by a scaleable method, we developed the paste-painting technique for fabricating dense thin film membranes on porous supports. A cross-sectional view of a film made by paste-painting is shown in Fig. 5, which shows a dense 15-μm-thick HTM film on top of a porous alumina substrate.
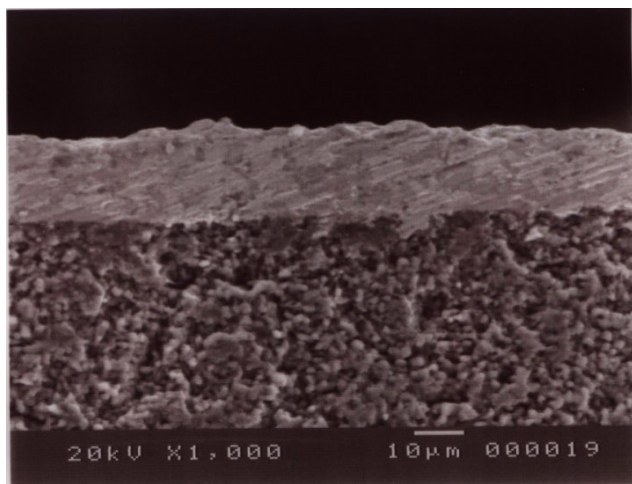

Fig. 5 Cross-sectional view of 15-μm-thick HTM film on porous alumina substrate.

Figure 6 shows the hydrogen flux for a 15-μm-thick HTM made by paste-painting. The flux ($\approx$33 cm^3/min-cm^2) at 900°C is much higher than could be obtained with the 0.25-mm-thick HTM for the dehydrogenation experiment, based on thickness. The flux at 500°C ($\approx$21 cm^3/min-cm^2) was even much higher than expected for a 0.25-mm-thick HTM at 900°C. These results suggest that dehydrogenation should be favorable results at temperatures <850°C.
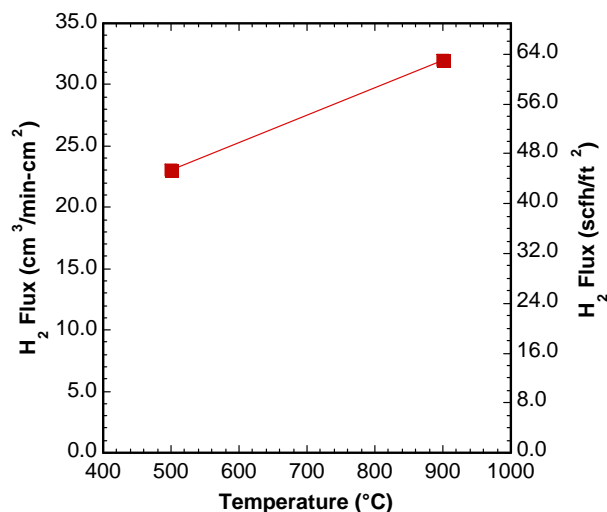

Fig. 6 Hydrogen flux at 900°C for 15-μm-thick HTM film on top of porous alumina. Feed gas was 100% H_2, and sweep gas was N_2.

In order for the new approach for producing ethylene to be practical, HTMs must be available in a shape that has a large active area, such as tubes; therefore, we adapted the paste-painting technique to fabricate dense HTMs on porous tubes. To this point, we have fabricated small ($\approx$8-10 cm in length with outside diameter of $\approx$1 cm) tubes for demonstration purposes. Tubes made by this method typically contain a dense HTM film with a thickness of $\approx$25-60 μm. Figure 7 shows two cross-sectional views of a tubular HTM with a membrane thickness of $\approx$60 μm.
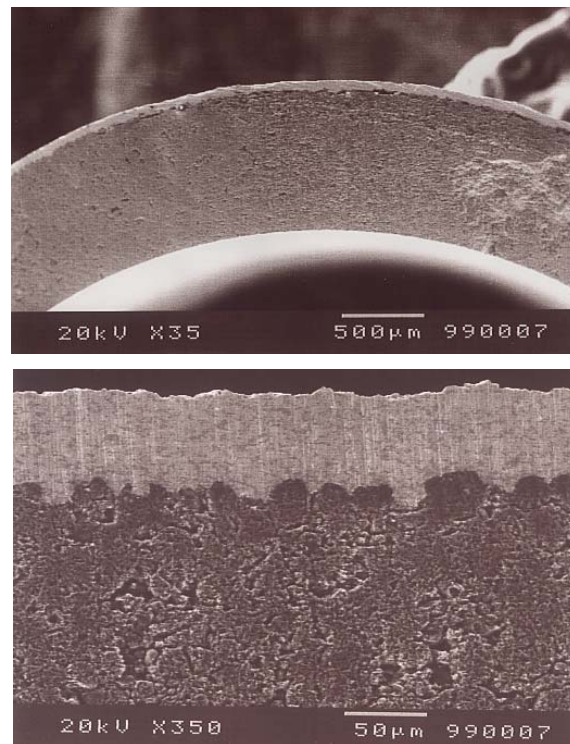

Fig. 7 Cross-sectional views at two magnifications of $\approx$60-μm-thick HTM film on porous alumina tube.

Figure 8 plots the hydrogen permeability for an HTM tube. The tube had a dense HTM film with a thickness of ≈60 μm, and the film contained 60 vol.% Pd. Concentration polarization effects were possible, because the surface area of the tube (≈25 cm^2) was much larger than that of disk membranes (≈1 cm^2), and because the porous support might facilitate the establishment of a boundary layer at the membrane surface. To test for concentration polarization effects, the permeability was measured with both 4 and 90% H$_2$/balance He as the feed gas, and various feed and sweep gas flow rates were used. Hydrogen permeability is obtained from the hydrogen flux using the equation

$$\Phi\left(\frac{mol}{m-s-Pa^{1/2}}\right) = \frac{6.81 \times 10^{-5} \cdot F\left(\frac{cm^3}{min-cm^2}\right) \cdot l(cm)}{\Delta pH_2^{1/2}(Pa^{1/2})}$$

where l is the membrane thickness, F is the hydrogen flux, and $\Delta pH_2^{1/2}$ is related to the partial pressure of hydrogen on the feed and air side of the membrane, as given below
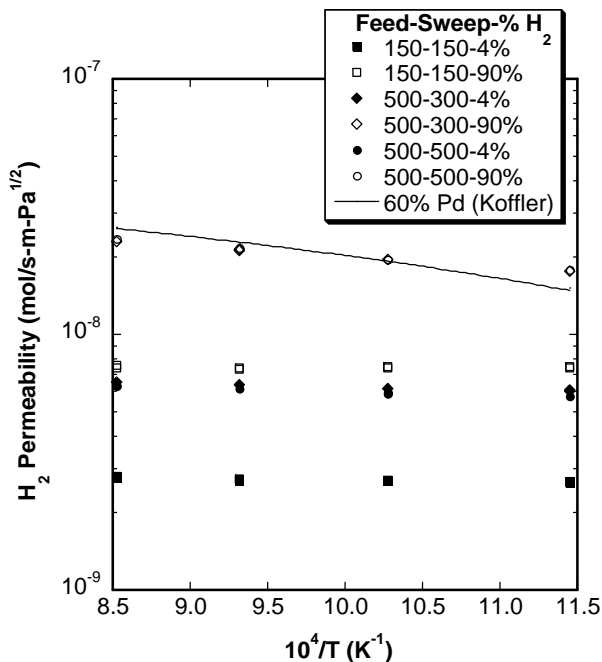
$$\Delta pH_2^{1/2} = \sqrt{pH_2(feed)} - \sqrt{pH_2(air)}$$

Fig. 8   Hydrogen permeability for ≈60-μm-thick HTM on porous alumina support tube. Inset gives feed flow rate (ml/min), sweep flow rate (ml/min), and hydrogen concentration in feed gas (%).

Two observations suggest that the hydrogen flux is influenced by concentration polarization during the measurements. First, the permeability values are essentially independent of temperature when 4% H$_2$/balance He is used as the feed gas (solid symbols), and second, the permeability depends strongly on the hydrogen concentration in the feed gas, especially at high temperatures. The solid line represents the expected permeability, based on the Pd-content in the HTM film (60 vol.%) and the reported permeability value for Pd [4]. The agreement between our measured permeability values and the expected values indicates that the concentration polarization effects were overcome at high flow rate and high hydrogen concentration.

4   CONCLUSIONS

We have demonstrated a new way to make ethylene via ethane dehydrogenation using a dense HTM to drive the unfavorable equilibrium conversion. This new process should reduce energy costs and overall costs, in addition to greatly reducing the production of greenhouse gases. Preliminary results obtained at 850°C with a relatively thick HTM show that this approach provides ethylene yields well above the thermodynamic equilibrium limit. Because the ethylene production rate depends directly on the rate at which hydrogen is removed from the dehydrogenation zone, we developed a technique for fabricating thinner HTMs with significantly higher hydrogen fluxes. HTMs with higher hydrogen flux would enhance the process by allowing dehydrogenation to be performed at a lower temperature, which would suppress unwanted side reactions, eliminate NO$_x$ production on the air side, and prolong membrane life.

ACKNOWLEDGEMENTS

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