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Catalytic Dehydrogenation of Propane in Hydrogen Permselective Membrane Reactors

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Propane dehydrogenation was studied in hydrogen permselective packed-bed membrane reactors and conventional packed-bed reactors. Two different types of developmental membranes were investigated: microporous silica-based membranes and a palladium thin film supported by a porous ceramic substrate. The membrane reactors were operated at liquid hourly space velocities (LHSVs) similar to those used in commercial reactors for propane dehydrogenation. Although the initial hydrogen permselectivity of the palladium membrane was substantially higher than that of the silica-based membranes, this membrane deactivated and eventually failed after several hours of exposure to reaction conditions. Moderate improvements in propylene yield were obtained with the silica-based membrane reactors. A propylene yield of 39.6% was obtained at an LHSV of 3 and a temperature of 823 K compared to a yield of 29.6% in a conventional packed-bed reactor operated with the same flow rate. The reaction selectivity for propylene was generally above 97 mol % in both the conventional and membrane reactors, however, catalyst deactivation rates were generally higher in the membrane reactors.

Introduction

Catalytic dehydrogenation is a potential method for obtaining alkenes for polymerization and other organic syntheses from low-cost saturated carbon feedstocks. One example of this process is the selective production of propylene from propane. Thermodynamic limitations on conversion are a significant problem when conventional packed-bed reactors are used in propane dehydrogenation. While the propane conversion may be increased by operating at higher temperatures, this results in an increase in the rate of catalyst deactivation and a decrease in the reaction selectivity for propylene. Propane dehydrogenation in a hydrogen permselective membrane reactor may be a potential method for increasing conversion while maintaining an acceptable catalyst deactivation rate and reaction selectivity.

During the past decade, there has been intensive research into inorganic membrane reactors for a variety of different reactions. Review articles by Zaman and Chakma (1994), Hsieh (1991), Armor (1989), and Shu et al. (1991) discuss the basic principles and potential applications for membrane reactors. Some of the many potential applications include steam reforming of methane, water−gas shift, hydrogen sulfide decomposition, and dehydrogenation of various hydrocarbons including cyclohexane, ethylbenzene, ethane, propane, and isobutane. Since these reactions produce hydrogen, improvements in reactor performance are obtainable when using a membrane with high hydrogen permeability and permselectivity.

Propane dehydrogenation in packed-bed membrane reactors was previously studied by Ziaka et al. (1993a,b) and Sheintuch and Dessau (1996). Ziaka and coworkers used commercially available ceramic membranes with Knudsen diffusion permselectivity. Moderate improvements in propylene yield and reaction selectivity were obtained with the membrane reactors compared to conventional reactors operated under the same conditions. Sheintuch and Dessau utilized commercially available palladium−ruthenium and palladium−silver alloy tubes with essentially infinite hydrogen permselectivity. The wall thicknesses for the palladium−ruthenium and palladium−silver tubes were 254 and 76 μm, respectively. A propylene yield of 70% was obtained with the palladium−ruthenium tube at 823 K compared to the equilibrium yield of 32%. The equilibrium shift was significant, but the reactor was operated with a relatively low weight hourly space velocity (WHSV) of 0.12. In contrast, the commercial Oleflex process for propane dehydrogenation operates with a WHSV of approximately 2.0 (Ward et al., 1994). To attain similar propylene yields at higher flow rates requires a membrane with a substantially higher hydrogen permeance.

In this study, we investigated propane dehydrogenation with supported palladium and sol−gel-derived silica-based membranes. Additional details regarding

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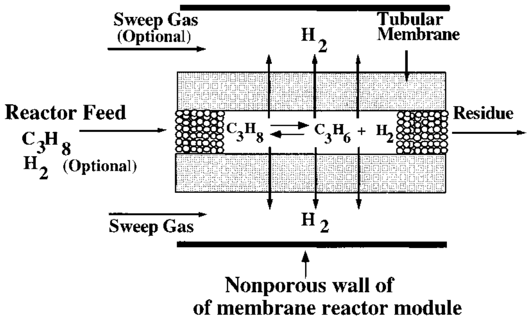

Figure 1. Cross section of a packed-bed membrane reactor for the catalytic dehydrogenation of propane to propylene.

the silica-based and supported palladium membranes are available from Sehgal et al. (1994) and Collins and Way (1993). The membranes are each composed of a thin, hydrogen permselective film supported by a porous ceramic tube. The silica-based membranes consist of a thin ultramicroporous layer of silica deposited on the surface of a commercially available ceramic support tube. A pore size of molecular dimensions is achieved in the silica film by carefully controlling the membrane fabrication conditions. Hydrogen permselectivities that are well above the Knudsen diffusion values currently obtained with commercially available ceramic membranes are achievable with the silica-based membranes since gas transport in the silica film occurs by molecular sieving rather than Knudsen diffusion. Although the permeability of the silica film is substantially lower than that of commercially available ceramic membranes, reasonable hydrogen fluxes are still obtained because the film thickness is on the order of 0.1 μm. The advantage of using a supported palladium membrane instead of a thick-walled palladium tube is that a significant increase in hydrogen flux may be obtained while maintaining an infinite, or extremely high, hydrogen permselectivity. The cost of a supported palladium membrane is also substantially lower than that of a thick-walled tube.

The objective of our study was to investigate membrane reactor performance at space velocities similar to those used in commercial conventional reactors. As mentioned above, developmental membranes that have a higher hydrogen permeance than palladium alloy tubes and greater hydrogen permselectivity than commercially available ceramic membranes were evaluated in the study. The membranes were developed to try to achieve the high fluxes usually needed for industrial applications while retaining the high hydrogen permselectivities required to minimize downstream separation problems. We have tested two different types of membranes in this study because there may be certain advantages in terms of stability, cost, or performance under reaction conditions associated with using either a dense palladium or a porous silica-based membrane. Experiments were performed over a range of temperatures and LHSVs and for extended time periods in order to evaluate the reactor performance and to determine the stability of the membranes and catalyst.

Figure 1 presents a schematic diagram of the membrane reactor design we employed for propane dehydrogenation. The reactor utilized a shell and tube type configuration, with the tube side consisting of a tubular membrane packed with catalyst. A nitrogen sweep gas was passed through the shell side to obtain the partial pressure driving force required for hydrogen permeation.

Experimental Section

Membrane Preparation. Both the silica-based and palladium–ceramic membranes consisted of silica or palladium films deposited on the inside surface of asymmetric, tubular porous ceramic supports. The ceramic supports were Membralox T-170 alumina tubes obtained from U.S. Filter Corp., Warrendale, PA. The inside and outside diameters of the ceramic supports were approximately 0.7 and 1.0 cm, respectively. The alumina supports consisted of a macroporous tube with an inner surface covered by a thin, multiple-layer microporous region. For the palladium–ceramic membrane, the top layer of the support tube was α-alumina with a pore diameter of 200 nm. In the case of the silica-based membranes, the top layer of the support tube was γ-alumina with a pore diameter of 5 nm.

For ease of handling and testing, the membrane supports (supplied by U.S. Filter Corp. in lengths of 25 cm) were cut into 6 cm sections using a diamond wafering saw. The membrane supports were then cleaned, and the ends were resealed with a high-temperature glaze. After sealing, the total active length for permeation was generally about 4.5–5 cm.

Electroless plating was used to fabricate the palladium membrane. Conditions for the electroless plating operation were similar to those described by Collins and Way (1993). The thickness of the palladium film was approximately 12 μm.

A polymeric silica sol was used to fabricate the silica-based membranes. The silica films were deposited on the supports by a sol–gel process that combines the features of slip-casting and dip coating. The supports were calcined at 823 or 873 K following deposition of the silica film. Additional information regarding sol preparation and membrane coating procedures is presented by Sehgal and co-workers (1994) and Sehgal (1996).

Membrane and Conventional Reactor Experiments. The catalyst used in the membrane and conventional reactor experiments was a platinum-loaded aluminosilicate molecular sieve developed by Amoco Corp. Catalyst preparation procedures were similar to those described by Kaminsky and co-workers (1993).

Propane dehydrogenation experiments were conducted in packed-bed membrane reactors and in a conventional packed-bed reactor operated under the same conditions. The conventional reactor design was similar to the membrane reactor design except a quartz tube with 0.7 cm i.d. replaced the membrane. Membrane reactors were packed with catalyst along their entire active length. The membrane module consisted of a shell and tube design similar to the one described by Collins and Way (1993, 1994). The ends of the membrane were connected to nonporous alumina tubes using Swaglok compression fittings with seals (ferrules) made from GRAFOIL ribbon (graphite-based packing material). Temperature was measured at the inlet and outlet of the membrane with Type K thermocouples. The thermocouples were placed in quartz thermowells to minimize metal contact with the hydrocarbon gas stream. The body of the Swaglok fitting was also drilled through in order to seal the ends of the nonporous alumina tubes against the ends of the membrane. This further reduced metal contact with the hydrocarbon gas stream, minimizing undesirable reactions on exposed metal surfaces that were not part of the membrane. The membrane module was placed inside a Model 3210, three-zone split tube furnace manufactured by Applied

Table 1. Initial Pure Gas Permeance Values for Silica and Palladium Membranes at 773 K

	palladium memb[a]	Silica Memb. No. 1	Silica Memb. No. 2	Silica Memb. No. 3
H_2 permeance (mol/m^2·s·Pa)	8.09×10^{-7}	5.25×10^{-7}	1.05×10^{-6}	1.07×10^{-6}
N_2 permeance (mol/m^2·s·Pa)	1.05×10^{-9}	5.16×10^{-8}	8.20×10^{-8}	5.70×10^{-8}
α_{H_2/N_2}	770	10.2	12.8	18.8

[a] H_2 permeance value for palladium membrane is listed with units of mol/m^2·s·Pa instead of mol/m^2·s·$\sqrt{\text{Pa}}$ in order to compare it with the silica membranes. The reported H_2 permeance and the hydrogen/nitrogen permselectivity are based on measurements made with P_t = 153 000 Pa and P_s = 85 000 Pa and are only valid for those conditions.

Test Systems, Inc. (Butler, PA). The measured temperature difference between the membrane inlet and outlet was generally less than 2 K.

The experimental system was also similar to the system described by Collins and Way (1993, 1994). Brooks 5850E mass flow controllers were used to regulate the inlet gas flow rates and compositions. The purities of the propane, hydrogen, and nitrogen source gases were >99.5%, >99.999%, and >99.999%, respectively. The compositions of residue and permeate streams were measured with a Hewlett-Packard 5890 Series II GC equipped with flame ionization (FID) and thermal conductivity (TCD) detectors. Residue and permeate stream flow rates were measured with bubble flow meters. The pressure was measured at various points using digital pressure gauges manufactured by PSI-Tronix (Tulare, CA).

Experiments were conducted at temperatures ranging from 773 to 848 K. The reaction side pressure was approximately 100 kPa, and the sweep side pressure was approximately 90.5 kPa. (Note that atmospheric pressure in Albuquerque, NM, is approximately 85 kPa.) The reactor feed composition was either pure propane or a mixture of 80 mol % propane and 20 mol % hydrogen. The ratio of the inlet sweep gas to inlet reactor feed gas flow rates (FR) was varied from 2 to 8. In later sections of this paper, the reactor feed rates are expressed in terms of the liquid hourly space velocity (LHSV). The LHSV is calculated on the basis of the volume amount, as a liquid at standard conditions, of propane charged to the reactor per hour divided by the volume of the catalyst bed (Imai and Hung, 1984). The weight hourly space velocity (WHSV = g of propane/g of catalyst/h) is another common term for expressing flow rate. For the Amoco catalyst, WHSV values can be calculated by multiplying the LHSV values by 1.06.

The collected effluent flow rate and composition data were analyzed to determine the yield to propylene and reaction selectivity for propylene. The propylene yield and reaction selectivity are defined as follows:

$$\text{yield to propylene} = \frac{\text{moles of propylene generated}}{\text{moles of propane entering reactor}} \times 100 \quad (1)$$

$$\text{propylene reaction selectivity} = \frac{\text{moles of propylene generated}}{\text{moles of propane reacted}} \times 100 \quad (2)$$

Propane and propylene that exit the system in both the residue stream and permeate stream are included in eqs 1 and 2. The reaction selectivity is not 100% because small amounts of methane, ethane, ethylene, and carbon are produced in addition to hydrogen and propylene.

Catalyst deactivation occurred to varying degrees in all of the membrane and conventional reactor experiments reported in this paper. The catalyst was reactivated by passing air through the system at 723 or 748 K for several hours to burn off carbon. After purging with nitrogen, hydrogen or a hydrogen/nitrogen mixture was flowed through the system for several hours prior to reinitiating reactor experiments. Following catalyst reactivation, the same time schedule was followed for the membrane and conventional reactor experiments in order to compare their performance. Information regarding experimental schedules is presented in the Results and Discussion section.

Gas permeability experiments were conducted with hydrogen and nitrogen prior to initiating the membrane reactor experiments and several times between the membrane reactor experiments. The gas permeances were determined by flowing pure gas through the membrane at various pressures and measuring the permeate flow rate with a bubble flow meter. No sweep gas was used in the gas permeation experiments, and the permeate side pressure was slightly above atmospheric pressure. Ideal hydrogen/nitrogen permselectivity values were calculated by dividing the hydrogen permeance by the nitrogen permeance.

Results and Discussion

Results of Gas Permeation Experiments. Table 1 summarizes results of the initial gas permeation experiments which were performed for each membrane tested in the membrane reactor studies. As shown in Table 1, the palladium membrane had the best initial performance because its hydrogen permeance was similar to that of the silica-based membranes, and it had the highest hydrogen/nitrogen permselectivity. The small amount of nitrogen permeation is attributable to defects in the palladium membrane and/or leakage through the GRAFOIL seals used in the membrane module (Collins and Way, 1993). The hydrogen/nitrogen permselectivity values for the three silica-based membranes were substantially lower than that of the palladium membrane but well above the Knudsen diffusion value of 3.74 which indicates that gas transport through the pores of these membranes was occurring by molecular sieving.

Molecular sieving (also known as micropore or configurational diffusion) occurs when the pore diameter of the membrane is comparable to the kinetic diameter of the gas molecules. Molecular sieving is an activated transport mechanism and is characterized by an increase in the permselectivity above the Knudsen diffusion value. Theoretically, complete separation can be achieved by exclusion of the larger gas if the membrane has a pore diameter in between the kinetic diameters of two gases. The silica-based membranes tested in this study are composed of an amorphous silica film that contains a pore size distribution rather than a single pore size. Size exclusion (i.e., infinite hydrogen permselectivity) was not achieved with these membranes since some of the pores were larger than the kinetic diameters of the gases tested in the experiments.

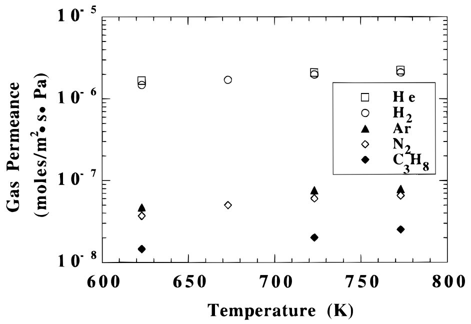

Figure 2. Gas permeances versus temperature for Silica Membrane No. 4.

No gas permeation experiments were conducted with propane and propylene during the membrane reactor studies since the membrane tubes were packed with catalyst. However, we have conducted gas permeation experiments with helium, hydrogen, argon, nitrogen, and propane in the absence of catalyst with a silica-based membrane (Silica Membrane No. 4) that was similar to the membranes shown in Table 1. Results of the gas permeation experiments conducted with Silica Membrane No. 4 over a temperature range of 623−773 K are shown in Figure 2. Several characteristics of molecular sieving are shown in Figure 2. The gas permeance values increased with increasing temperature which indicates that activated transport was occurring in the membrane. In addition, the permeance values at each temperature followed the exact order of the kinetic diameters of the gas molecules. Helium, which has the smallest kinetic diameter (2.6 Å), permeated the fastest, followed by hydrogen (2.89 Å), argon (3.4 Å), nitrogen (3.64 Å), and finally propane (4.3 Å) (kinetic diameters are from Breck, 1973). Permselectivity values for the membrane were also well above the Knudsen diffusion values. The hydrogen/propane and hydrogen/nitrogen permselectivities at 773 K were 83 and 32, respectively, compared to the Knudsen diffusion values of 4.7 and 3.7. Although propylene was not included in the permeation experiments, the hydrogen/propylene permselectivity should be higher than the hydrogen/propane value since propylene has a larger kinetic diameter than propane.

Although there is currently no direct method to measure the pore size distribution of the supported submicron-thick membrane layer in the silica-based membranes, we believe that the large observed differences in the high-temperature permeance values for gases with only relatively small differences in kinetic diameters indicate that the diameter of most of the pores is below 5 Å. Samuel and co-workers (1996) have recently developed a cantilever beam stress measurement experiment in which the pore size and pore size distribution of a porous film deposited on one side of a silicon wafer can be ascertained by exposing the film to probe vapors of varying kinetic diameters. The results of stress measurement experiments performed on wafers coated with the silica sols used to make the membranes tested in this study support the above conclusions regarding the small pore size of the silica-based membranes (see Sehgal, 1996, for additional details).

Membrane Stability. Hydrogen permeation rates were monitored during the membrane reactor experiments to evaluate membrane performance and stability under reaction conditions. The hydrogen permeation rates measured during experiments conducted with the palladium membrane and Silica Membrane No. 1 are summarized in Figure 3. The reactor feed gas composition for these experiments was 80 mol % propane and 20 mol % hydrogen, and the FR value was 2. The reactors were held at each temperature for approximately 3 h, and the starting temperature was 773 K. The average hydrogen permeation rate for each temperature is shown in the figure.

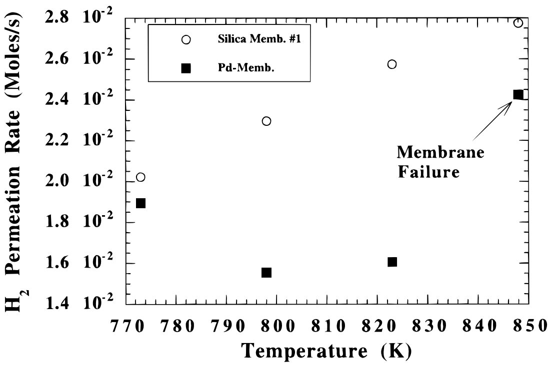

Figure 3. Hydrogen permeation rates measured in membrane reactor experiments conducted with Silica Membrane No. 1 and palladium membrane (LHSV = 2.26).

The hydrogen permeation rate should increase as the temperature is raised since more hydrogen is generated from the reaction, and the hydrogen permeances of both the silica-based and palladium membranes increase with increasing temperature. As shown in Figure 3, the hydrogen permeation rate of the silica-based membrane did increase with increasing temperature, as expected. However, in the palladium membrane, the hydrogen permeation rate initially decreased with increasing temperature. In addition, hydrogen permeation rates in the palladium membrane were lower than those in the silica-based membrane even though its initial hydrogen permeance was higher than that of the silica-based membrane.

The palladium membrane deactivated when it was exposed to reaction conditions, resulting in a significant reduction in the hydrogen permeance. The deactivation of the palladium membrane resulted from the deposition of carbonaceous matter or “coking” on the surface of the palladium film. It is well established that hydrogen permeates through palladium by a multistep process which includes the reversible dissociative chemisorption of molecular hydrogen on the membrane surface (Shu et al., 1991). Coking of the membrane surface inhibits the hydrogen dissociation reaction, resulting in a reduced hydrogen permeation rate. We have visually observed the deposition of carbonaceous matter on a 0.5 cm long sample of a supported palladium film that was suspended inside a quartz tube. No observable carbon deposition occurred when a mixture of propane and hydrogen was passed through the quartz tube at 823 K. After propylene was added to the gas mixture, carbonaceous matter was observed on the palladium surface and this material filled the entire palladium membrane tube after 4 h. We have also performed permeation experiments in which propylene was added to a gas mixture of propane and hydrogen and observed a significant reduction in the hydrogen permeation rate following the addition of propylene. Therefore, we currently believe that the deactivation of the palladium membrane was primarily due to coke deposition produced from the cracking of propylene.

Propane and propylene permeation (leakage) rates in the palladium membrane were minimal and approxi-

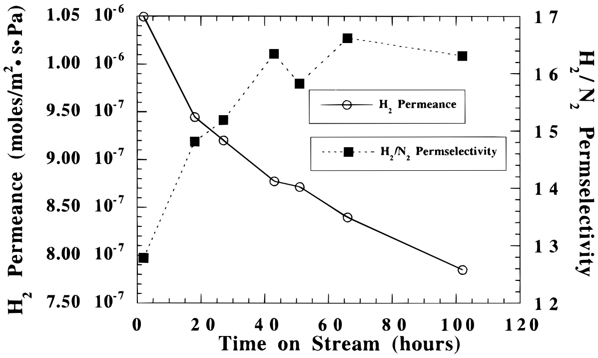

Figure 4. Hydrogen permeance and permselectivity of Silica Membrane No. 2 versus time on stream. Temperature ranged from 723 to 798 K during the 100 h test period. Note: Lines are drawn for visual guidance.

mately constant with time at 773 K; however, after the temperature was raised to 798 K, propane and propylene leakage rates increased significantly while the hydrogen permeation rate decreased. Propane and propylene leakage rates continued to increase with both time and temperature. At 848 K, approximately 10% of the propane in the reactor feed leaked out of the reaction side of the membrane module while only 0.2% leaked at 773 K. This 50-fold increase in the leakage of propane and propylene after less than 12 h of operation, which we have classified as a membrane failure, is attributable to defects that developed in the palladium film at the higher temperatures. The defects or holes were clearly observable in SEM micrographs taken of the palladium membrane. The increase in hydrogen permeation rates observed at 823 and 848 K was due to leakage of hydrogen through the defects, rather than hydrogen permeation through the palladium film.

At this time we do not fully understand the mechanism of defect development in the palladium film. A possible explanation is that carbon diffusion into the palladium film is accelerated when the temperature is raised and that the stress produced from the carbon incorporation may have produced the defects.

Each of the silica-based membranes was tested over a period of several days in the membrane reactor experiments. During these tests, gas permeation experiments with hydrogen and nitrogen were conducted several times, and results for Silica Membrane No. 2 are summarized in Figure 4. The temperature was 773−798 K during most of the 100 h test period. A mixture of hydrogen and nitrogen was flowed through the system between membrane reactor tests, and the membrane was cooled to 723 K after approximately 48 h to reactivate the catalyst. As shown in Figure 2, the hydrogen permeance decreased by approximately 34% over the 100 h test period while the hydrogen/nitrogen permselectivity actually increased during the first 40 h of testing and then remained relatively constant. Similar drops in hydrogen permeance were observed for Silica Membrane Nos. 1 and 3. Therefore, the silica-based membranes are not stable over long time periods at high temperatures.

The impact of the decreasing hydrogen permeances on the silica membrane reactor experimental results is minimal because the propylene yield is not sensitive to small changes in hydrogen permeance. Alternative fabrication methods designed to improve the stability of the silica-based membranes are under investigation in our laboratories.

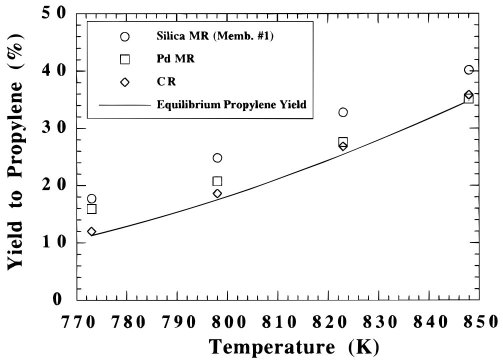

Figure 5. Propylene yields from membrane reactor experiments conducted with Silica Membrane No. 1 and palladium membrane (LHSV = 2.26, FR = 2). Reactor feed stream to membrane and conventional reactors consisted of a 80 mol % propane, 20 mol % hydrogen mixture.

Results of Membrane Reactor Experiments. Results of membrane reactor experiments (LHSV = 2.26) conducted with the palladium membrane and Silica Membrane No. 1 are summarized in Figure 5. The conventional reactor (CR) propylene yields shown in Figure 5 are from experiments performed with the same reactor feed composition and flow rate as the membrane reactors. Propylene yields from the conventional reactor experiments were slightly higher than the calculated equilibrium yield, possibly due to slight deviations from isothermal operation or errors in temperature measurement. Propylene yields from the silica membrane reactor were higher than those from the palladium membrane reactor due to its higher hydrogen permeation rate. The propylene yield in the silica membrane reactor was 1.48 times higher than the conventional reactor yield at 773 K and 1.12 times higher at 848 K. Hydrogen concentrations in the residue stream from the silica membrane reactor ranged from 14 mol % at 773 K to 22.5 mol % at 575 K. Therefore, most or all of the hydrogen generated during propane dehydrogenation was removed by the membrane. One reason for the greater equilibrium shift at 773 K is that operation at this temperature resulted in the lowest hydrogen concentration in the residue stream.

As shown in Table 1, the hydrogen permselectivity of Silica Membrane No. 1 was significantly lower than that of the palladium membrane. Therefore, some permeation of propane and propylene occurred as well as backpermeation of the nitrogen sweep gas. Permeation losses of propane and propylene ranged from approximately 5 mol % at 773 K to less than 3 mol % at 848 K. Nitrogen concentrations measured in the residue stream ranged from 11 mol % at 773 K to 9 mol % at 848 K. When backpermeation of the sweep gas occurs, there is some concern as to whether the observed equilibrium shift is due to dilution or due to the selective removal of hydrogen. Due to the low nitrogen concentrations in the residue stream, we believe that the impact of dilution on the observed equilibrium shifts for the silica membrane was minimal.

A pure propane feed gas (propane concentration > 99.5 mol %) was used in the membrane reactor experiments conducted with Silica Membranes Nos. 2 and 3. Figure 6 shows the propylene yields achieved at 798 K with Silica Membrane No. 2 as a function of the LHSV (FR = 2). Experiments were initiated at the highest LHSV with freshly reactivated catalyst before proceeding to measurements of the reactor performance at the lower LHSVs. Approximately 1.75 h were spent at each

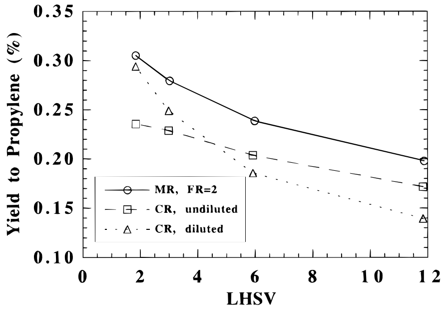

Figure 6. Propylene yield versus LHSV at 798 K for Silica Membrane No. 2 and conventional reactors. Pure propane feed to membrane reactor and undiluted conventional reactor. The diluted reactor feed stream consisted of a combined mixture of membrane reactor tube side and sweep side feed streams. Note: Lines are drawn for visual guidance.

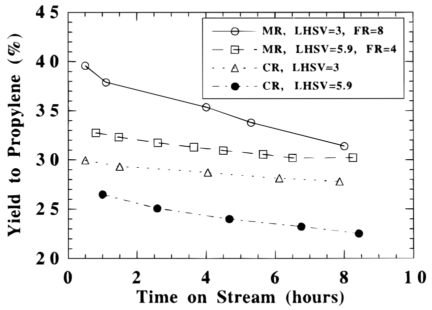

Figure 7. Propylene yield versus time on stream at 823 K for Silica Membrane No. 3 and conventional reactors. Pure propane feed to membrane and conventional reactors. Note: Lines are drawn for visual guidance.

flow rate. In Figure 6, we compare the performance of the membrane reactor to the performance achieved with two different conventional reactors operated under the same time schedule as the membrane reactor. The reactor feed to the first conventional reactor was the same composition (pure propane) fed to the tube side of the membrane reactor. The feed stream to the second conventional reactor consisted of a mixture of propane and nitrogen. The composition and flow rate of this feed stream was the same as that obtained from mixing the tube side and sweep side feeds to the membrane reactor. Harold and co-workers (1994) have suggested that membrane reactor performance should be compared to the performance of conventional reactors operated with such a diluted feed stream.

Figure 6 shows that propylene yields in the membrane reactor were greater than those in the two conventional reactors for all LHSVs. At the higher LHSVs, the conventional reactor with the diluted feed had the lowest propylene yield. The lower conversion is due to the reduced contact time that results from increasing the total flow rate to the reactor. At an LHSV of 3, propylene yield in the membrane reactor was 1.22 times higher than that in the undiluted conventional reactor and 1.13 times higher than that in the diluted conventional reactor.

Propylene yields obtained with Silica Membrane No. 3 at 823 K are shown in Figure 7 as a function of time, LHSV, and FR. The propylene yield should increase when the membrane reactor is operated with a high sweep gas flow rate (FR) since more hydrogen can be removed from the reaction zone, resulting in a greater equilibrium shift. A propylene yield of 39.6 mol % was initially achieved when the membrane reactor was operated with an LHSV of 3 and FR of 8 compared to an initial conventional reactor yield of 29.6 mol % for the same LHSV. However, the propylene yield in the membrane reactor operated under these conditions dropped significantly with time on stream due to catalyst deactivation. Catalyst deactivation occurs when carbonaceous matter from undesired side reactions such as propylene cracking is deposited on the catalyst. The deactivation rate was accelerated in the membrane reactor because hydrogen, which inhibits the formation of carbonaceous species, was removed from the reaction side and the concentration of the more reactive unsaturated product (propylene) was increased. The hydrogen concentration in the residue stream from the membrane reactor was approximately 9 mol %, while the propylene concentration in the residue stream ranged from an initial value of approximately 30 mol % down to 25 mol % after 8 h of operation. In comparison, the hydrogen concentration in the outlet stream from the conventional reactor operated with the same LHSV of 3 was substantially higher at 23 mol % and the propylene concentration was lower at 22 mol %. Therefore, the combination of lower hydrogen concentrations and higher propylene concentrations appears to have significantly increased the rate of catalyst deactivation in the membrane reactor.

Catalyst deactivation was slower when the membrane reactor was operated with a higher LHSV and lower FR value (see Figure 7). In these experiments, hydrogen and propylene concentrations in the residue stream were approximately 15 and 25 mol %, respectively. It is important to note that the propylene yield obtained when the membrane reactor was operated with an LHSV of 5.9 was higher than the yield obtained with the conventional reactor operated with an LHSV of 3 and that the catalyst deactivation rates in the two reactors were similar. This result basically shows that a membrane reactor can maintain a higher yield than a conventional reactor nearly twice its size over a prolonged time period.

Sheintuch and Dessau (1996) also reported a decrease in propylene yield with time on stream in experiments conducted at 798 K with a palladium−silver alloy tube. They attributed the drop in yield to both membrane deactivation and catalyst deactivation. Therefore, improvements in catalyst and/or membrane stability are needed in order to maintain the propylene yields that are achievable with a membrane reactor.

The reaction selectivity for propylene was very high in both the membrane and conventional reactors. Reaction selectivities in the membrane reactors were generally above 97 mol %. Reaction selectivities in the conventional reactors were essentially the same as those in the membrane reactors when a pure propane feed gas was used but were slightly lower than the membrane reactor for the 80 mol % propane, 20 mol % hydrogen feed stream.

Implications for Commercialization of Propane Dehydrogenation Membrane Reactors. Overall, moderate improvements in propylene yields were obtained with the membrane reactors compared to conventional reactors operated under similar conditions. However, further improvements in membrane stability and permselectivity as well as catalyst stability are needed before membrane reactors can be considered as a realistic alternative to existing conventional reactor technology for propane dehydrogenation. It is reasonable to assume that improvements in the hydrogen/propane and hydrogen/propylene permselectivities can be obtained while still maintaining the desired hydrogen permeance since the kinetic diameters of propane (4.3 Å) and propylene (4.5 Å) are somewhat larger than that of hydrogen (2.89 Å). As discussed above, we have achieved a hydrogen/propane permselectivity of 83 and reasonable hydrogen permeance with Silica Membrane No. 4 at 773 K. The kinetic diameter of nitrogen is somewhat lower than that of propane at 3.64 Å, and this difference in kinetic diameter appears to have a significant impact on the hydrogen/nitrogen permselectivity since the largest high-temperature hydrogen/nitrogen permselectivity that we have obtained is only 32. Similar permselectivity problems exist with other sweep gas candidates such as argon (kinetic diameter = 3.4 Å) and air. Therefore, sweep gas backpermeation and the resulting downstream separations problem are a major concern.

The need for a sweep gas could be eliminated by operating the permeate side under a reduced pressure. In the Houdry Catofin commercial process for propane dehydrogenation, the conventional reactor operates at reduced pressures ranging from approximately 14 to 69 kPa (Ward and Hagen, 1992). In a membrane reactor, only the permeate side would need to be under reduced pressure, so vacuum equipment requirements and costs may be reduced.

Retrofitting membrane separators into an existing conventional reactor operation is another possible approach for incorporating membrane technology in the propane dehydrogenation process. In the commercial Oleflex process for propane dehydrogenation, staged conventional reactors with interstage heaters are used (Pujado and Vora, 1990). Retrofitting hydrogen permselective membrane separators in between the reactor stages should increase the propylene yield. Using conventional reactors with interstage membrane separators instead of membrane reactors would "decouple" the reaction and separation processes, permitting the use of membranes with lower hydrogen permeances and higher permselectivities. If membranes with very high hydrogen permselectivities were used, this reactor design may permit the use of air on the sweep side in order to oxidize the permeated hydrogen. The membrane could then act as both a separator and heat exchanger. In addition, air would be a less expensive sweep gas than nitrogen or argon.

Thermodynamic equilibrium for propane dehydrogenation strongly favors operation at atmospheric pressure or below. However, operation at higher pressures is attractive for refineries since it reduces the volume of gas required to be handled. High-pressure operation may also reduce sweep gas or vacuum equipment requirements for the permeate side because part of the partial pressure driving force required for hydrogen permeation would be available from the transmembrane pressure difference. Sweep gas backpermeation would also be reduced in porous membrane reactors operated at high transmembrane pressure differences. Sheintuch and Dessau (1966) reported a propylene yield from a palladium−silver membrane reactor operated at 788 kPa and approximately 848 K that was similar to that achieved in a conventional reactor operated at atmospheric pressure. This result is significant because it shows that a membrane reactor may be able to overcome the severe thermodynamic limitations on conversion that are present at high pressure to achieve a reasonable propylene yield. Developmental silica-based membranes with improved hydrogen permselectivity are needed to operate a porous membrane reactor at high pressure so that permeation losses of propane and propylene are acceptable. In addition, a greater fraction of the hydrogen generated in a high-pressure reactor must be removed in order to obtain a reasonable propylene yield. Therefore, improvements in catalyst stability may also be required in order to operate at high pressure with acceptable catalyst deactivation rates.

Conclusions

Moderate shifts in the equilibrium propylene yield were obtained when silica-based membranes were tested in the packed-bed membrane reactors. While the reaction selectivity for propylene was similar in both the membrane and conventional reactors, catalyst deactivation rates were generally higher in the membrane reactors. Improvements in both catalyst and membrane stability are needed for the silica-based membrane reactors to be a feasible alternative for propane dehydrogenation. In addition, in order to optimize the reactor performance, it is desirable to improve the hydrogen permselectivity of the silica-based membranes without significantly decreasing the hydrogen permeance.

The supported palladium membrane was not stable when exposed to the reaction conditions for propane dehydrogenation. However, palladium-based membranes could provide superior performance due to their potential for infinite hydrogen permselectivity if the stability problems can be solved. Additional research is needed to determine whether improvements in the membrane stability may be obtained by using palladium alloys or novel reactor designs.

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Nomenclature

FR = ratio of the inlet sweep gas flow rate to the inlet tube (reactor) side flow rate, dimensionless
P_t = total pressure on the tube (reaction) side of the membrane reactor, Pa
P_s = total pressure on the sweep side of the membrane reactor, Pa
$\alpha_{H_2/i}$ = hydrogen permselectivity relative to gas i
CR = conventional reactor
MR = membrane reactor

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