Propane Dehydrogenation in a Packed-Bed Membrane Reactor

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Membrane reactors combine reaction and separation in one-unit operation, the membrane selectively removing one or more of the reactant or product species. These reactors have been used with thermodynamically or kinetically limited reactions. They help increase their yields through the use of membranes, which allow product/reactant species to permeate out of the reaction zone. The concept started in the 1950s; however, most applications have been developed recently with significant developments in membrane materials and modules. A number of the past applications are in the field of biotechnology (for a review, see Chang and Furusaki, 1991). These are typically low-temperature applications ($< 100°C$) and primarily make use of organic/polymeric membranes. The interest in the use of membrane reactors in high-temperature catalytic applications has been recently rekindled with the development of good quality inorganic membranes (for recent reviews, see Armor, 1989; Hsieh, 1991).

The early applications of high-temperature catalytic membrane reactors involved the use of thin metallic (Pd and Pd alloy) membranes. These reactors were pioneered by Gryaznov and coworkers who studied many hydrogenation/dehydrogenation reactions (for a recent review, see Shu et al., 1991). Pd membranes are useful because they are permeable to hydrogen and virtually impermeable to any other gases. They have yet to find broad industrial application, however, because of their low permeabilities, high cost, their susceptibility to metal sintering, imbrittlement and sulfur poisoning, and deactivation by coke. Efforts to alleviate some of these problems are currently in progress. Successes have also been reported with the use of various nonporous oxygen anionic conductor materials (for a recent review, see Eng and Stoukides, 1992). They have been used in membrane reactors for oxidative methane coupling for the decomposition of various oxygen containing compounds (NO, SO_2, CO, CO_2, H_2O) and for various partial oxidations.

The early applications of catalytic microporous membrane reactors involved the use of porous glass membranes. Reactions studied include cyclohexane, methanol and isobutane dehydrogenation, and H_2S and HI decomposition. These membranes are generally reported to be brittle and not to have desirable resistance to thermal and mechanical stresses. High-temperature catalytic reactors, using porous ceramic membranes, are a more recent development. Earlier applications (that is, three to four years old) involved the use of anodic aluminas (Davidson and Salim, 1988). These materials, though ideally suited for academic investigations of transport and reaction because of their straight, nonintersecting pores, do not appear to have the desired mechanical properties for industrial membrane reactor applications. More recent applications have involved the use of Sol-Gel alumina, zirconia and titania membranes. Reactions studied include butane and methanol dehydrogenation (Zaspalis et al., 1991a,b,c), cyclohexane dehydrogenation (Okubo et al., 1991), ethylbenzene dehydrogenation (Wu et al., 1990), the NH_3 + NO reaction (Zaspalis et al., 1991d), and the Clauss process (Sloot et al., 1990). Harold and Cini (1989) have proposed the use of multiphase membrane reactors.

Our group has reported on the use of catalytic membrane reactors for ethane dehydrogenation (Champagnie et al., 1990, 1992) and methane steam reforming (Minet et al., 1992). A general model for the catalytic membrane reactor has been developed and applied to ethane dehydrogenation (Tsotsis et al., 1992). Here, we report results of our studies with propane dehydrogenation in a packed-bed membrane reactor. To the best of our knowledge, this is the first open literature report for this reaction being carried out in a packed-bed membrane reactor. A British patent application by Bitter (1988) has proposed the use of microporous ceramic membranes for numerous dehydrogenation reactions including the propane to propylene reaction. Bitter's conceptual reactor system includes a packed-bed dehydrogenation reactor preceding the membrane reactor followed by a packed-bed dehydrogenation reactor to treat the membrane permeate. The experimental details are rather sketchy, and we are not aware of any publications associated with this patent or of any companion U.S. patent.

Experimental Apparatus and General Discussion

A typical example of a thermodynamically-limited reaction is propane dehydrogenation to propylene. Propylene is a valuable commodity chemical for the production of isopropyl alcohol, an important gasoline blending component, and as a

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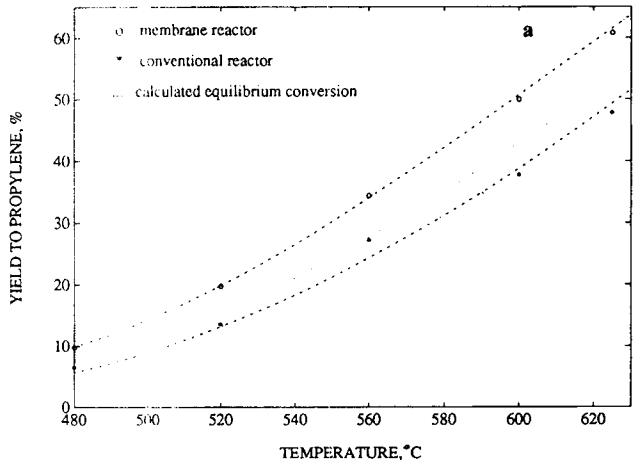

Figure 1a. Yield to propylene vs. temperature.

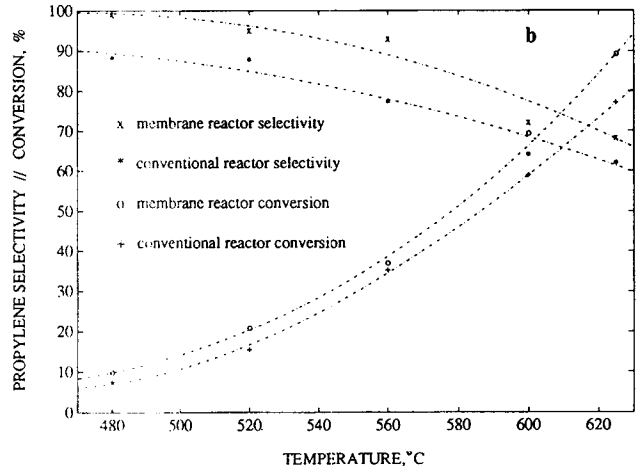

Figure 1b. Propane conversion and selectivity to propylene vs. temperature.

Reactor residence time, $\tau \approx 2$ s; tubeside pressure, $P_T \approx 2$–3 psig (115.1–122 kPa); shellside pressure, P_S = atmospheric (101.3 kPa); sweep ratio, $Fr = 0$.

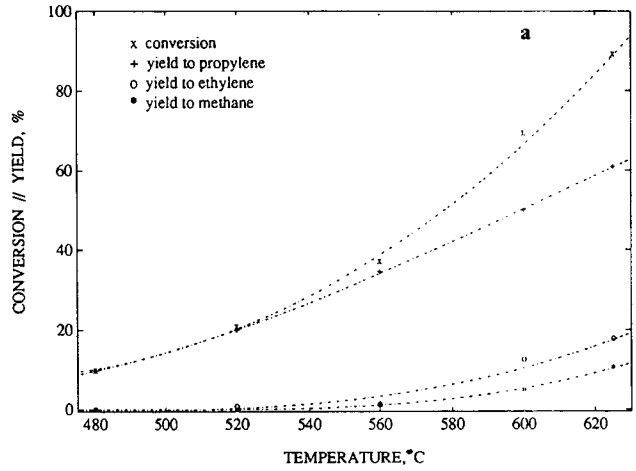

Figure 2a. Membrane reactor conversion and product yield vs. temperature.

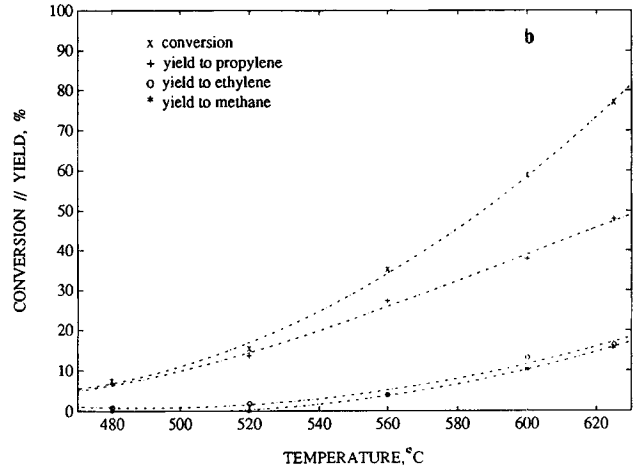

Figure 2b. Conventional reactor conversion and product yield vs. temperature.

Reactor residence time, $\tau \approx 2$ s; tubeside pressure, P_T = 2–3 psig (115.1–122 kPa); shellside pressure, P_S = atmospheric (101.3 kPa); sweep ratio, $Fr = 0$.

polymer grade chemical. Propylene has been produced primarily as a product of fluid catalytic cracking (FCC) units or as a byproduct of pyrolysis/cracking furnaces. Though catalytic dehydrogenation units have been operated since the late 1930s and there has been a surge of interest in them more recently, they still do not play a dominant role in the overall propylene production picture. The problem lies with the thermodynamics of the process. To obtain reasonable yields in the direct dehydrogenation of propane, one requires higher temperatures, but higher temperatures result in losses both in selectivity and overall catalyst activity. There is, therefore, strong incentive for a process that would overcome the equilibrium limitations without concommitant losses in catalyst activity and selectivity. Membrane reactor technology appears promising. The experimental results presented here, using the simplest of all membrane reactor configurations, a packed-bed membrane reactor (PBMR), show that the concept, that is, overcoming the equilibrium yield limitations, by using a membrane reactor is feasible.

The experimental apparatus used in the propane dehydrogenation experiments is similar to the ethane dehydrogenation apparatus described in greater detail elsewhere (Champagnie et al., 1990, 1992). The experimental system consists of the reactant gas delivery system, the high-temperature membrane reactor, and the product collection and measurement devices. The multilayered composite porous alumina tube has an inner diameter of 7 mm, an outer diameter of 10 mm, and a length of 25 cm. It is available commercially under the trade name Membralox and consists of three layers with pore diameters of 40 Å, 2,000 Å and 8,000 Å, supported on a macroporous layer with pore diameter of 15 μm. The membrane reactor consists of a stainless steel shell, with ports for the sweep gas inlet and outlet (see Champagnie et al., 1990, 1992). The ceramic tube is placed inside this shell and sealed at the ends by graphite string and compression fittings. The entire reactor was operated under reasonably isothermal conditions with temperature gradients along the reactor length of less than 2°C.

For the PBMR experiments, the internal volume of the membranes (~ 10 cm^3) was filled with 14-mesh commercial 5%

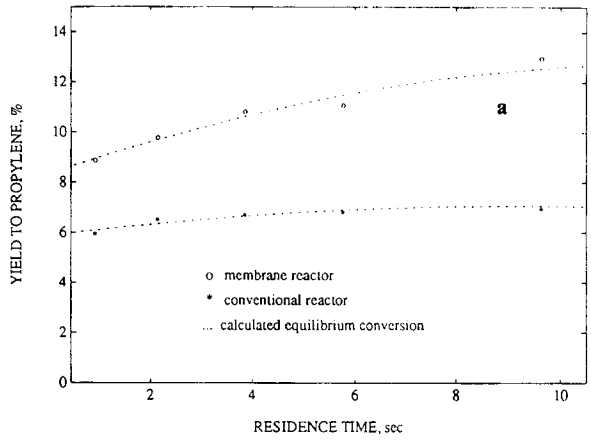

Figure 3a. Yield to propylene vs. residence time.

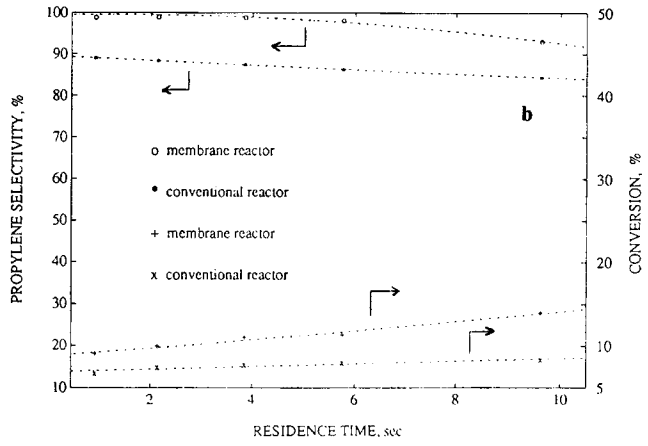

Figure 3b. Propane conversion and selectivity to propylene vs. residence time.

Tubeside pressure, P_T = 2-3 psig (115.1-122 kPa); shellside pressure, P_S = atmospheric (101.3 kPa); sweep ratio, Fr = 0; temperature, T = 480°C.

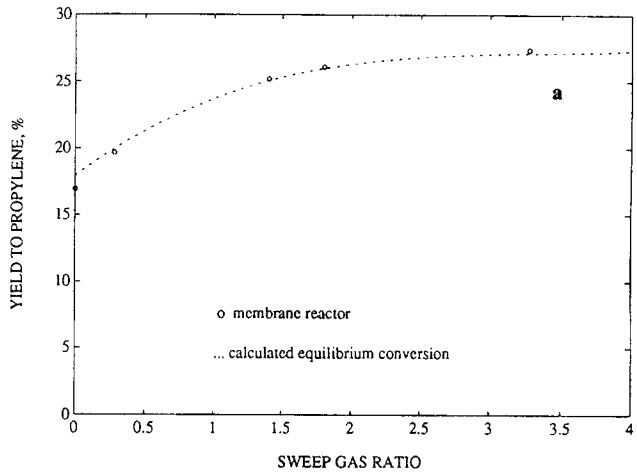

Figure 4a. Yield to propylene vs. sweep gas ratio.

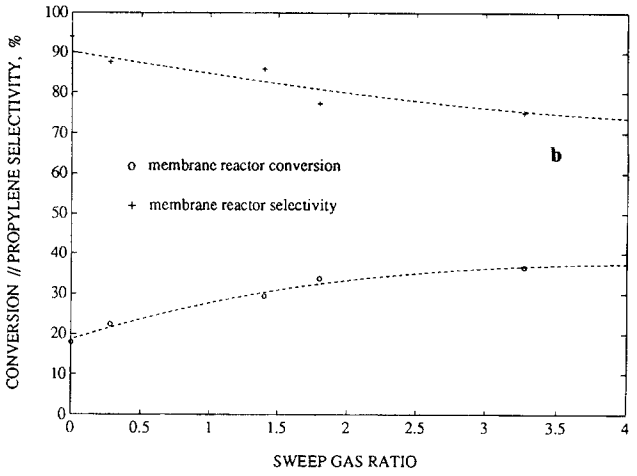

Figure 4b. Propane conversion and selectivity to propylene vs. sweep gas ratio.

Reactor residence time, $\tau \approx 2$ s; tubeside pressure, P_T = 2-3 psig (115.1-122 kPa); shellside pressure, P_S in the range 0-1.6 psig (0-112.33); temperature, T = 480°C.

$Pt/\gamma\text{-}Al_2O_3$ catalyst (Johnson Matthey Company). Mg was also added to the catalyst by a wet impregnation technique [using a $Mg(NO_3)_2 \cdot 6H_2O$ in NH_4OH solution] to improve upon its sintering and coking characteristics. The catalyst was dried *in situ* in the reactor at 130°C overnight and then calcined in two stages: first at 400°C under flowing synthetic air for 12 h and then at 550°C under flowing hydrogen for 24 h. Hydrogen was added to the propane and argon reactant feed mixtures to prevent catalyst deactivation due to coking. The gas stream compositions were analyzed on-line using a UTI 100C mass spectrometer with an attached atmospheric pressure mass sampling unit. The catalyst was kept overnight in flowing hydrogen at a temperature of 550°C. During the experimental runs reported here, catalytic activity remained constant.

Experimental Results and Discussion

Before the initiation of the membrane reactor experiments, kinetic investigations were performed by standard techniques to derive the various reaction rate expressions and to calculate the values of the pertinent kinetic constants. The kinetic experiments were performed in the membrane reactor with the shellside inlet and outlet closed. The permeability of all species involved in the reactions were also measured. The rate expression and constants and the permeability values are used in a mathematical model of the PBMR of use in the scale-up and optimization of such reactors. The description of this model goes beyond the scope of this note and will be presented elsewhere.

In the propane dehydrogenation experiments in a PBMR reported here (unless otherwise noted), we used a single-feed composition consisting of 80 mol % propane and 20 mol % hydrogen. The experiments were carried out in the temperature range of 480-625°C. Figure 1a shows reactor yield of propane to propylene as a function of temperature for both the membrane reactor (without argon sweep gas) and the conventional reactor (that is, the same reactor operating with the shellside inlet and outlet closed). Conversion, yield to propylene and propylene selectivity are defined here as follows (similar definitions for yield and selectivity also hold for other species):

$$X = \text{Conversion} = \frac{\text{Propane}|_{\text{in}}^{\text{tubeside}} - \text{Propane}|_{\text{out}}^{\text{shellside + tubeside}}}{\text{Propane}|_{\text{in}}^{\text{tubeside}}} \quad (1)$$

$$Y_{C_3H_6} = \textit{Yield to Propylene} = \frac{\text{Propylene}\,|_{\text{out}}^{\text{shellside + tubeside}}}{\text{Propane}\,|_{\text{in}}^{\text{tubeside}}} \quad (2)$$

$$S_{C_3H_6} = \text{Propylene Selectivity} = \frac{Y_{C_3H_6}}{X} \quad (3)$$

Shown on the figure is also the calculated equilibrium conversion of propane to propylene (assuming propylene to be the only hydrocarbon product) at the pressure, temperature conditions, and composition of the tubeside inlet. The propylene selectivity, together with the propane conversion, is shown in Figure 1b. The conversion for both reactors increases with the temperature, but, as expected, their propylene selectivities decrease. Remarkably, the membrane reactor not only results in better conversions, but also improves upon the propylene selectivity. Figure 2a shows the yield of various gaseous products as a function of temperature for the membrane reactor while Figure 2b corresponds to the conventional reactor. Ethane was also observed, but in trace amounts. Figure 3a shows propylene yield at a temperature of 480°C as a function of tubeside residence time for the membrane (in the absence of argon sweep gas) and conventional reactors. For the membrane reactor, at a residence time of 10 s, the yield to propylene is 1.8 times higher than the corresponding equilibrium conversion. This conversion increase (as the residence time increases), however, is accompanied by a small loss in propylene selectivity, as shown in Figure 3b. Figure 4a shows propane conversion to propylene at a temperature of 480°C as a function of the sweep ratio Fr, that is, the ratio of the Ar sweep flow rate in the shellside to the propane flow rate in the feedside. The feedside inlet gas consisted of a C_3H_8:Ar:H_2 mixture of 1:1:0.2. Note that increasing the sweep ratio increases the conversion. Again, this increase in conversion is followed by a loss in selectivity (see Figure 4b).

Conclusions

Our experimental studies of propane dehydrogenation in a membrane reactor show that through the use of the membrane reactor we can attain conversions and yields higher than those attained in the conventional packed-bed reactor. Certainly, the conversions and yields reported can be further improved by reactor and catalyst optimization. Work in this area is continuing.

Acknowledgment

We thank Medalert, Inc. for their support. We also acknowledge ALCOA for providing us with the Membralox membranes and Dr. Paul K. T. Liu for many helpful discussions.

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Manuscript received May 18, 1992, and revision received Aug. 24, 1992.