Dehydrogenation of Propane Using a Packed-Bed Catalytic Membrane Reactor

Herman Weyten, Klaas Keizer, Annemieke Kinoo, Jan Luyten, and Roger Leysen
Flemish Institute for Technological Research, Process Technology, Boeretang 200, B-2400 Mol, Belgium

In a high-temperature catalytic membrane reactor, a plug-flow reactor is combined with a gas-separative membrane. By selectively removing one of the reaction products, the reaction mixture is prevented from reaching equilibrium, and a higher conversion can be obtained. This concept is only valid for reactions that are limited by the thermodynamic equilibrium, such as the direct dehydrogenation of propane to propene. A tubular H_2-selective silica membrane was characterized [$\alpha(H_2/C_3H_8 = 70-90$ at 500°C] and used as the gas-separative membrane. The membrane reactor was filled with a chromia/alumina catalyst. The kinetics of the catalyst was studied. At 500°C the deactivation of the catalyst is slow, and the propene yield is almost constant for at least 10 h of operation. Under well-chosen process conditions, the propene yield is at least twice as high as the value obtained at thermodynamic equilibrium in a conventional reactor.

Introduction

The direct dehydrogenation of alkanes to alkenes can be found in the literature since the early 1930s. Commercially, however, alkenes are mainly produced by fluid catalytic cracking or as a by-product from pyrolysis/cracking furnaces. Besides economic reasons, two main fundamental problems are responsible for the lack of the commercial application of direct dehydrogenation. First, the dehydrogenation reaction (Eq. 1) is endothermic.

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2. \qquad (1)$$

For the dehydrogenation of propane (C_3H_8), $\Delta H^0_{733\ K}$ is about 130 kJ/mol. This limits the equilibrium conversion (ξ_{eq}) to ~18% at 500°C and ~50% at 600°C at atmospheric pressure. Because of the increase in volume, the reaction is best done at low pressure.

The second reason is that the activity of the commercial catalysts for this reaction is not very high and that deactivation due to coke formation is rather fast (less than 1 hour at 600°C). Platinum/alumina (Pt/Al_2O_3) and chromia/alumina (Cr_2O_3/Al_2O_3) are the two types of catalysts that are commonly used. In some cases, silica or zirconia is used as the support for the catalytic material. Many studies on the dehydrogenation of propane or other alkanes using the cheaper Cr_2O_3 catalyst can be found in the literature (Tauster and Koros, 1972; Suzuki and Kaneko, 1977, 1979; Gorriz et al., 1989, 1992; De Rossi et al., 1994). The main focus is on the reaction mechanisms (Suzuki and Kaneko, 1977, 1979) and on rate of reaction (Gorriz et al., 1989), but all authors mention the problem of coke formation and deactivation of the catalyst as a function of time. Oxidative dehydrogenation can be an alternative, but the mixing of oxygen in the feed stream requires the necessary safety precautions and can also lead to nonselective gas-phase reactions.

In recent years a completely different approach has been considered: the catalytic membrane reactor. In this concept, one of the reaction products (H_2) is removed from the reaction mixture using a gas-separative membrane. By selectively removing the hydrogen, the reaction mixture cannot reach the equilibrium composition and the production of propene should increase (Figure 1).

Although the principle of the catalytic membrane reactor is easily understood, in practice the concept is much more complex. The three aspects of the reactor and their relationship to each other have to be taken into account.

1. The membrane performance: H_2 permeation rate and H_2 selectivity with respect to the feed, sweep gas, and reaction products. The long time stability and performance of the membrane under operating conditions are also very important if this type of reactor is going to be used in industry.

Correspondence concerning this article should be addressed to H. Weyten.
Permanent address of K. Keizer: Inorganic Materials Science, Faculty of Chemical Technology, University of Twente, Enschede, The Netherlands.

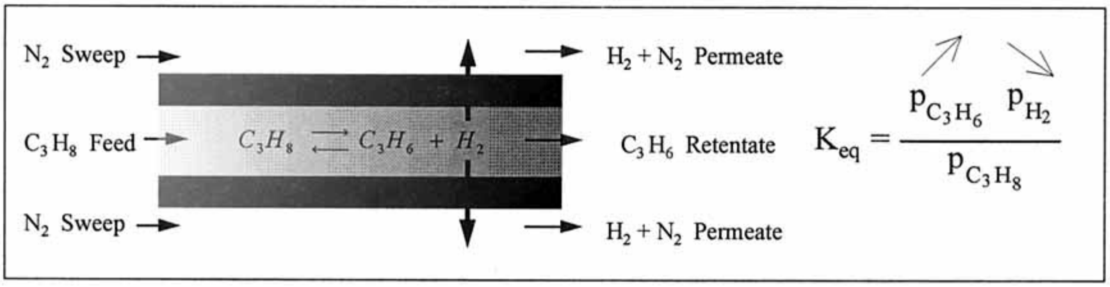

Figure 1. Membrane reactor concept.

2. The catalyst performance: intrinsic activity and selectivity of the catalyst are of course important, but it is often forgotten that the activity and selectivity under operating conditions (when H_2 is removed from the reaction zone) can be different from these intrinsic values.

3. The process parameters have a huge effect on the membrane and catalyst performance, and thus determine the conversion (ξ), yield (Y), and selectivity (σ) of the propane/propene reaction. The relationships between the reaction rate, the flow rate, and the permeation rate are very important in optimizing the process conditions.

Numerous review articles have been published on all three aspects of the catalytic membrane reactor (Armor, 1988; Falconer et al., 1995; Hsieh, 1988; Saracco and Specchia, 1994; Tsotsis et al., 1994). Most authors however focus on the process concept and on the modeling of the process (Bernstein and Lund, 1993; Bernstein et al., 1996; Champagnie, 1992; Itoh et al., 1985; Itoh, 1987; Mohan and Govind, 1986, 1988; Omorjan et al., 1996; Tiscareno-Lechugo et al., 1996; Sun and Khang, 1988; Zaika et al., 1993a,b). In some cases, specific aspects of the membrane and/or of the catalyst are described (Ionnides and Gavalas, 1993; Keizer et al., 1994; Sjinji et al., 1982; Zaspalis et al., 1991).

In this article all three aspects of the high-temperature membrane reactor are discussed: the gas separative membrane (silica/alumina), the catalyst (chromia/alumina), and the influence of the process parameters. The main focus of this study is on the experimental aspects of the catalytic membrane reactor. As a model reaction the direct dehydrogenation of propane (C_3H_8) to propene (C_3H_6) was chosen.

Experiments and Results

Membrane

Different kinds of gas-separative membranes can be used to separate H_2 from a gas mixture. Palladium (Itoh, 1995) or a palladium/silver alloy, porous glass (Sjinji et al., 1982), mesoporous alumina (Zaspalis et al., 1991), and different types of silica (Ioannides and Gavalas, 1993; Lin et al., 1994; Wu et al., 1993, 1995) are the materials that are commonly used for these H_2-selective membranes.

For these experiments a commercial [Media and Process Technology Inc. (MPT)] CVI (Chemical Vapor Infiltration)-type of silica/alumina membrane (Wu et al., 1995) was chosen. This type of membrane can be used at temperatures up to 650°C and is stable when subjected to cyclic treatments of heating and cooling. This tubular membrane has an inner diameter of ~7 mm and an outer diameter of ~10 mm. The total length of the tube is 250 mm. At both ends of the tube there are glass coatings that assure the graphite seals are gastight. The effective surface area of the microporous membrane is approximately 6×10^{-3} m^2. The membrane is mounted in a stainless-steel module.

Permeation (F_0) and permselectivity (α_0)

The permeation (F_0) and permselectivity (α_0) were determined by single-gas, flow-controlled permeation measurements (Figure 2a). For these measurements the pressures at the feed side (p_h) and at the shell side (p_1) are measured for a fixed gas flow at the feed side at a constant temperature. The permeation (F_0 [mol/m^2·Pa·s]) is defined as the gas flux ($\Phi = f/S$ = flow per unit of surface area [mol/m^2·s]) through the membrane divided by the pressure difference ($\Delta p = p_h - p_1$ [Pa]) over the membrane. The permselectivity is the ratio of the permeation values of two gasses measured at the same temperature:

$$F_0 = \frac{\Phi}{\Delta p} = \frac{f}{S \cdot \Delta p} \tag{2}$$

$$\alpha_0(H_2/C_3H_8) = \left[\frac{F_0(H_2)}{F_0(C_3H_8)}\right]_{T = c^{te}} \tag{3}$$

The results of the single-gas permeation measurements are shown in Table 1. For these measurements, vacuum was used at the shell side of the membrane ($p_1 < 10^{-3}$ MPa). The per-

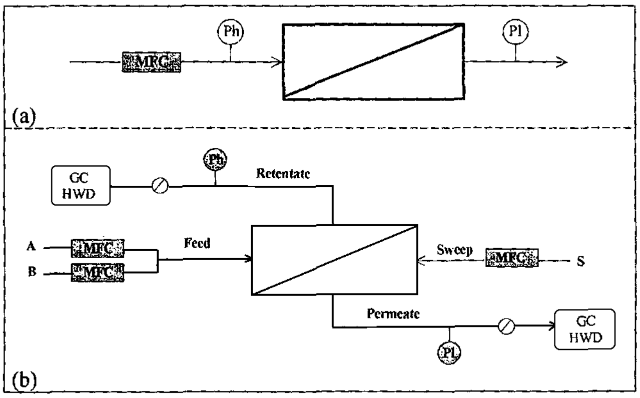

Figure 2. Principle of single gas, flow-controlled permeation measurements (a), and of binary gas separation (b).

Table 1. Permeation and Permselectivity of the MPT Silica Membrane: $p_1 < 10^{-3}$ MPA (Vacuum)

F_0 (10^{-9} mol/m^2·Pa·s)	H_2	He	CH_4	N_2	CO_2	C_3H_8
M	2.02	4.00	16.04	28.01	44.01	44.10
Kin. Dia. (Å)	2.89	2.60	3.80	3.64	3.30	4.30
200°C, $p_h = 0.1$ MPa	15.3	64.0				3.36
$p_h = 0.3$ MPa	16.6	65.6				4.51
400°C, $p_h = 0.1$ MPa	31.3	173		2.05	2.38	2.23
$p_h = 0.3$ MPa	33.1	174		2.63	2.64	2.92
500°C, $p_h = 0.1$ MPa	139	510	2.68	1.87	1.75	1.51
$p_h = 0.3$ MPa	143	519	3.32	2.26	2.20	2.13

α_0	H_2/CH_4	H_2/N_2	H_2/CO_2	H_2/C_3H_8	He/CH_4	He/N_2	He/CO_2	He/C_3H_8
Knudsen (α_{KN})	2.8	3.7	4.7	4.7	2.0	2.6	3.3	3.3
200°C, $p_h = 0.1$ MPa				4.6				19
$p_h = 0.3$ MPa				3.7				15
400°C, $p_h = 0.1$ MPa		15	13	14		84	73	78
$p_h = 0.3$ MPa		13	13	11		66	66	60
500°C, $p_h = 0.1$ MPa	52	74	79	92	190	272	291	338
$p_h = 0.3$ MPa	43	63	65	67	156	230	236	244

meations of H_2 and He are approximately independent of the pressure difference and are activated by temperature. The permeations of the heavier gasses (CH_4, C_3H_8, CO_2, and N_2) increase slightly with increasing pressure gradient, but decrease with increasing temperature. From these measurements it is clear that the diffusion of the lighter gas does not follow the Poiseulle/Knudsen law:

$$F_0 = F_{0,K} + F_{0,P} = K_0 + B_0 \bar{p} \left\{ \begin{array}{l} K_0 \propto \dfrac{1}{\sqrt{MT}} \bar{r} \\ B_0 \propto \dfrac{1}{\eta T} \bar{r}^2 \end{array} \right. \tag{4}$$

(mean pressure $\bar{p} = 1/2\ (p_h + p_l)$ [Pa], M = molecular mass [kg/mol], η = viscosity of the gas [Pa·s], T = temperature [K], and $\bar{r}$ = average pore radius of the membrane [m]).

Gasses with a kinetic diameter (d_{kin}) smaller than ~ 3 Å (H_2 and He) have a much higher permeation than the other gasses. This could indicate that the average pore-size diameter is of the same order of magnitude. The diffusions of these gasses are activated by temperature. The activation energy (E_a) is for both gasses 17–20 kJ/mol. The permeation of the other gasses (CH_4, C_3H_8, CO_2, and N_2) is independent on the kinetic diameter of the gas. The permeation decreases with increasing temperature, but does not follow the Poiseulle/Knuden law (Eq. 4) in the temperature range from 200°C to 500°C. Only at the highest temperature that was measured (500°C), a Knudsen-like dependence of the permeation on the molecular mass ($F_0 \propto 1/\sqrt{M}$) is observed for the heavier gasses. There is, however, a small pressure dependence.

The real transport mechanism is not yet fully understood, but it seems that the dominating separation mechanism through this membrane is *size exclusion* or molecular sieving. The smaller gasses (H_2 and He) can pass through the pores (~ 3 Å), while the larger ones cannot.

Binary gas separation

The principle of the binary gas-separation measurements is shown in Figure 2b. A mixture of two gasses ($A = H_2$ and $B = C_3H_8$) is injected into the module. At the shell side of the membrane, a sweep gas ($S = N_2$) can be used. The pressure difference (Δp) is set by controlling the pressure at the feed side (p_h) and at the sweep side (p_l). The compositions of the permeate and of the retentate are determined by a gas chromatographer that is equipped with a hot wire detector (HWD). The measurements were carried out in a *VELTEROP* membrane test apparatus (MTA) (Figure 3).

The separation factor (α) can be calculated from the molar ratios of the two gasses in the permeate and in the feed:

$$\alpha(H_2/C_3H_8) = \left[\frac{X_{H_2}}{X_{C_3H_8}} \right]_{\text{perm}} \cdot \left[\frac{X_{C_3H_8}}{X_{H_2}} \right]_{\text{feed}} . \tag{5}$$

The experiments were carried out at atmospheric pressure at the shell side ($p_l = 0.1$ MPa) and for a pressure difference (Δp) of 0.1 MPa as the driving force. For the feed composition two $H_2 \div C_3H_8$ mixtures were used: 50% ÷ 50% and 80% ÷ 20%. The experiments were done by using the feed and the sweep gasses in a cocurrent mode. From the results of these measurements (Figure 4) it can be concluded that it is very important to use a sweep gas. The real separation factor (α) is always lower than the permselectivity value (α_0). For this relatively small pressure difference, the real separation factor can approach α_0 if a high sweep flow is used. This means that the H_2 molecules that diffuse through the membrane have to be removed as fast as possible so that the partial pressure of this gas at the shell side is always close to zero. In a cocurrent mode the diffusion through the first section of the membrane is the highest. If the sweep flow is not high enough, the differential partial hydrogen pressure becomes smaller over the length of the membrane, and the separation factor goes down. A simple model confirms this (50% H_2 feed ——, and 80% H_2 feed ---- in Figure 4). When a sweep gas (N_2) is used, there can be back diffusion of this sweep gas from the shell side to the tube side due to the N_2 partial pressure difference in spite of the total pressure difference over the membrane. It is therefore advisable to use an inert sweep gas with a low permeability. The difference between the 50% ÷ 50% and 80% ÷ 20% feed mixtures can only be seen when a small sweep gas flow is used.

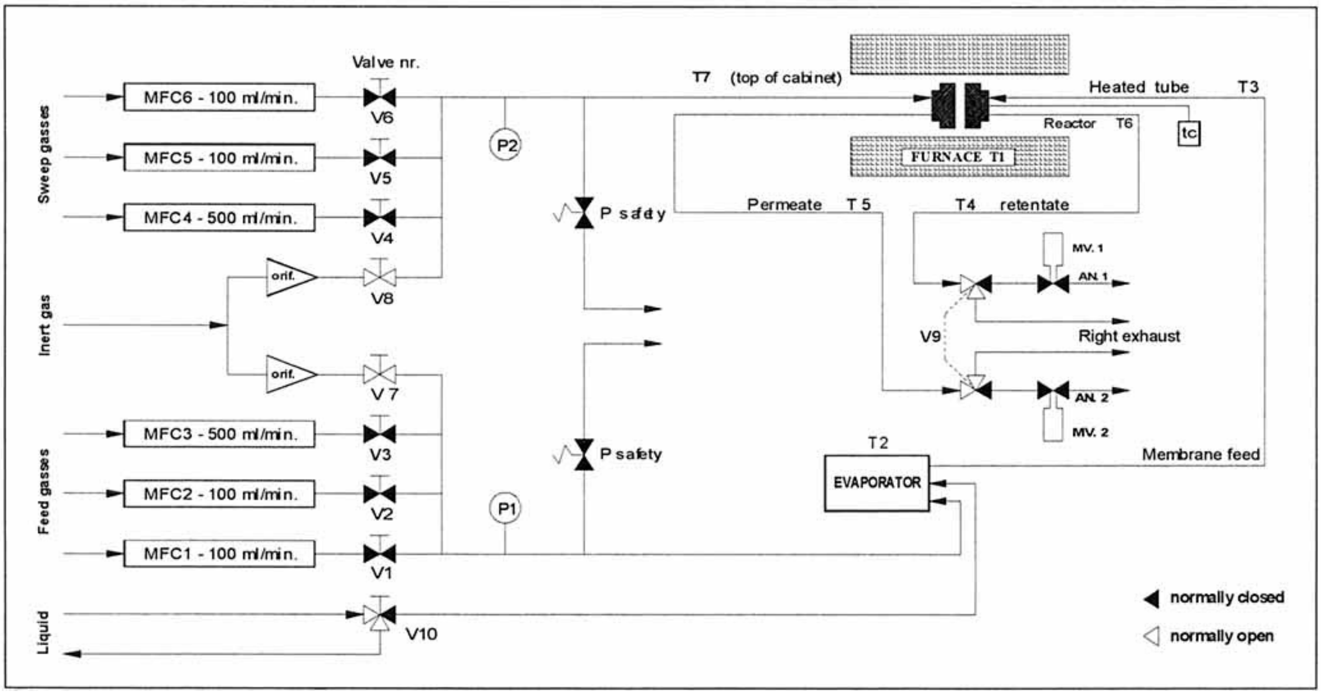

Figure 3. VELTEROP membrane test apparatus (MTA).

Catalyst

For the direct dehydrogenation reaction of propane to propene, three commercial chromia/alumina (Cr_2O_3/Al_2O_3) catalysts were tested. CAT1 is a standard Cr_2O_3/Al_2O_3 catalyst, CAT2 contains a potassium (K) promoter, and CAT3 contains cesium (Cs) and zirconium (Zr). The support of all three catalysts is γ-Al_2O_3. The specific surface area (BET) is between 80 and 90 m^2/g. The catalysts were tested in a conventional plug-flow reactor to study the activity and deactivation behavior (due to coke formation).

Activity and deactivation

In the first set of experiments the propene yield [$Y(C_3H_6)$ (to calculate the propene yield, H_2 and Ar are not taken into account)] was measured as a function of the time-on-stream at 450°C, 500°C, and 600°C and at atmospheric pressure. As the feed gas, a 0.25 vol. % C_3H_8 in Ar mixture was used and was injected in the reactor at a weight–hour–space–velocity (WHSV = mass (g) of C_3H_8 per hour per g catalyst) of 0.07 h^{-1}. The results of these experiments are summarized in Table 2.

At 450°C the activity of the catalyst is very low. The yield is for all three catalysts between 3 and 5%. The WHSV is probably too high compared to the reaction rate to be able to reach equilibrium when a 0.25% C_3H_8 mixture is used. The yield is relatively stable in time, which indicates that the deactivation due to coke formation is not a major problem at 450°C under these reaction conditions.

At 600°C, however, the deactivation of the catalyst is a real problem (Table 2 and ■ in Figure 5b). Due to the coke for-

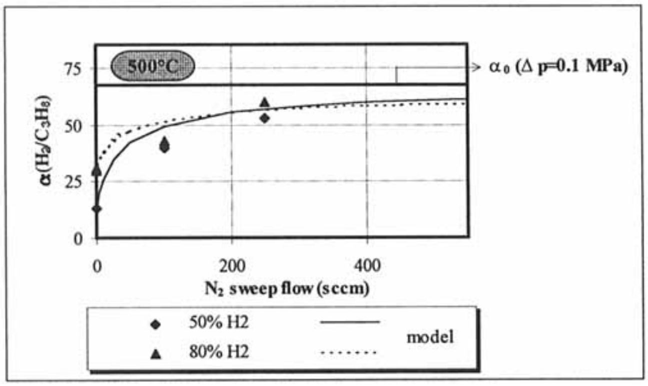

Figure 4. H_2/C_3H_8 separation factor (α) vs. flow (cm^3/min at STP) of the sweep gas (N_2) for $\Delta p = 0.1$ MPa and a feed composition of 50% $H_2 \div$ 50% C_3H_8 and 80% $H_2 \div$ 20% C_3H_8.

Table 2. Propene Yield for Three Commercial Cr_2O_3/Al_2O_3 Catalysts at 0.1 MPa and WHSV = 0.07 h^{-1}

Temp.	Time-on-Stream (min)	Propene Yield (mol %) 450°C	500°C	600°C
Theory				
Pure C_3H_8		9.0	17.9	49.8
0.25% C_3H_8		80.4	93.4	99.2
CAT1	510	5.2	18.7	18.6
	1,560	5.0	16.7	6.4
	2,610	4.9	15.2	2.9
CAT2	510	4.3	18.3	—
	1,560	3.7	13.9	
	2,610	3.7	10.4	
CAT3	510	3.5	16.7	—
	1,560	3.2	13.7	
	2,610	3.0	12.0	

mation, the propene yield drops very fast even with this very low concentration of propane in the feed.

A good compromise is found at 500°C (Table 2 and ■ in Figure 5a). After some time of stabilization, the propene yield of the reactor is relatively stable (at ~17–18% for the three catalysts) for more than 12 h. Then the yield gradually decreases due to the formation of coke. The fact that the yield is much lower than the theoretical value is probably due to the very low concentration of propane in the feed gas. The reaction rate is probably too low to reach equilibrium at the WHSV of 0.07 h^{-1}, although deactivation of the catalyst can also be an additional reason.

The difference between the three catalysts is very small, except for the fact that CAT3 may be a little less active. CAT1 was chosen to be used as a packed bed in the catalytic membrane reactor. The C_3H_6 selectivity in the experiments at 450°C and 500°C is ~85%.

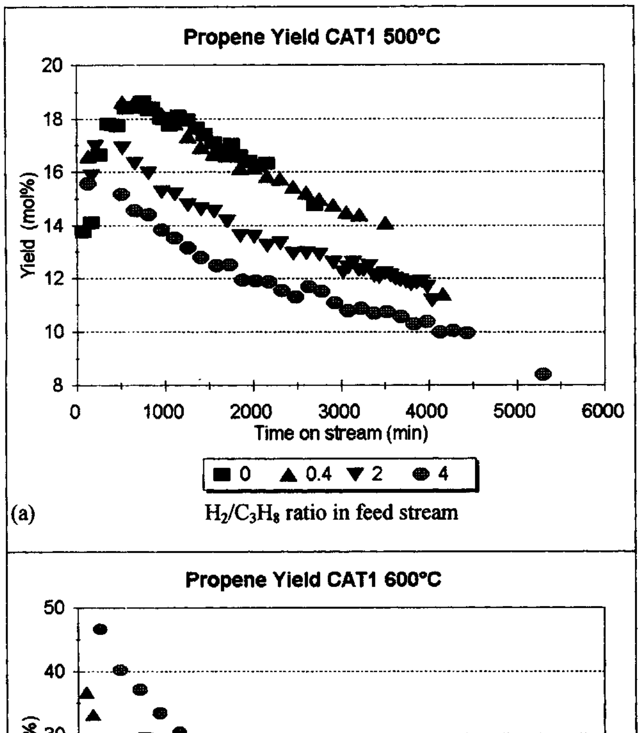

Figure 5. Influence of H_2 in the feed stream on the propene yield vs. time on stream ($p = 0.1$ MPa) for CAT1 at 500°C (a) and at 600°C (b).

Table 3. Theoretical Thermodynamic Propene Yield for a Feed of Pure C_3H_8 and 0.25% C_3H_8 in Ar to Which H_2 Is Added ($p = 0.1$ MPa)

		Theoretical Propene Yield (mol %)	
		Temperature	
Feed	H_2/C_3H_8	500°C	600°C
Pure C_3H_8	0	17.9	49.8
	0.4	9.1	42.2
	2	4.9	32.1
	4	4.0	28.9
0.25% C_3H_8	0	93.4	99.2
	0.4	91.3	99.0
	2	82.5	97.8
	4	73.8	96.4

Influence of the H_2 concentration on the deactivation of the catalyst

In a membrane reactor the H_2 is selectively removed from the reaction zone. Because the H_2 concentration is reduced, the deactivation of the catalyst by coke formation could be enhanced. To study the effect of the H_2 concentration on the deactivation of the catalyst, H_2 was added to the feed (0.25% C_3H_8 in Ar) in a conventional plug-flow reactor. The H_2/C_3H_8 ratios were 0, 0.4, 2, and 4. The results of the experiments at 500°C and 600°C are shown in Figures 5a and 5b.

At 500°C (Figure 5a) the slopes of the curves are approximately the same, which leads to the conclusion that the addition of H_2 to the feed has little or no effect on the deactivation of the catalyst. By adding H_2 to the feed, the C_3H_8 conversion will be reduced, as is predicted by Le Chatelier's law (Table 3). This effect can be seen in Figure 5a. Although the yield is much lower than the theoretical value that is predicted by the thermodynamic equilibrium, the reduction in the C_3H_6 yield due to the addition of H_2 fits very well with the thermodynamic data. For instance, when the H_2/C_3H_8 ratio is 4, then the yield is reduced ~21% compared with $H_2/C_3H_8 = 0$.

At 600°C, however, the effect on the propene yield of adding H_2 to the feed is quite different. Although Le Chatelier's principle predicts a reduction in the C_3H_6 yield, the opposite effect is observed: the yield increases with increasing H_2 concentration in the feed (Figure 5b). The added hydrogen slows down coke formation on the catalyst and has a stabilizing effect on the activity of the catalyst. This effect could cause problems in the membrane reactor. If H_2 is removed from the reaction mixture, coke formation could be a real problem. Because a certain stability of the propane conversion is needed for representative measurements, 500°C was chosen to do the catalytic membrane reactor studies.

The Catalytic Membrane Reactor

After permeation and gas-selectivity measurements, the tubular membrane was filled with (~7.5 g; grain size 200–500 μm) Cr_2O_3/Al_2O_3 catalyst (CAT1). The reactor was mounted in the MTA (Figure 3) with the feed and sweep (N_2) gasses in a cocurrent mode. For these experiments the reactor was run at 500°C, as explained in the previous section. For gasses, the thermodynamic equilibrium constant is K_p. This means that the C_3H_8 conversion depends on the absolute pressure:

$$K_{eq} = e^{-\Delta G/RT} = [K_p]_{\text{atmospheric pressure}} \tag{6}$$

$$K_p = \frac{p_{H_2} \cdot p_{C_3H_6}}{p_{C_3H_8}} = \frac{X_{H_2} X_{C_3H_6}}{X_{C_3H_8}} p_{abs}. \tag{7}$$

These experiments were carried out at atmospheric pressure on both sides of the membrane ($p_h = p_l = 0.1$ MPa). The driving force for the permeation through the membrane is created by using sweep gas (N_2) in cocurrent. The feed for these experiments was pure propane (C_3H_8). The compositions of the permeate and of the retenate were analyzed with the gas chromatographer.

At 500°C, deactivation of the catalyst due to coke formation is relatively slow. The propane conversion (ξ) is stable for at least 10 h; then deactivation of the catalyst makes the conversion go down (Figure 6). The conversion is defined as the difference of the propane concentration between the retentate and the feed:

$$\xi_{C_3H_8} = \frac{(X_{C_3H_8})_{\text{feed}} - (X_{C_3H_8})_{\text{ret.}}}{(X_{C_3H_8})_{\text{feed}}} \times 100\%. \tag{8}$$

(For the calculations, H_2 and N_2 are not taken into account as is usually done). For the yield (Y) and selectivity (σ) of the reaction, only production in the retentate was considered. The products that diffuse through the membrane are not taken into account for the calculations and are considered waste that is not recovered:

$$Y_{C_3H_6} = (X_{C_3H_6})_{\text{ret.}} \times 100\% \qquad \sigma_{C_3H_6} = Y_{C_3H_6}/\xi_{C_3H_8} \times 100\%. \tag{9}$$

Using a WHSV of 0.16 h^{-1}, the C_3H_8 conversion is 23.8%, which is 34% higher than the thermodynamic equilibrium conversion for these reaction conditions (Figure 6). The C_3H_6 selectivity is about 89%, which is also a little higher than what was obtained in the conventional plug-flow reactor.

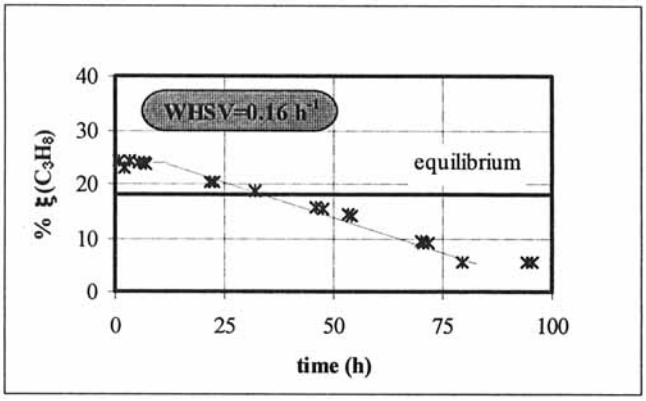

Figure 6. C_3H_8 conversion (ξ) vs. time for WHSV = 0.16 h^{-1} at T = 500°C and p = 0.1 MPa.

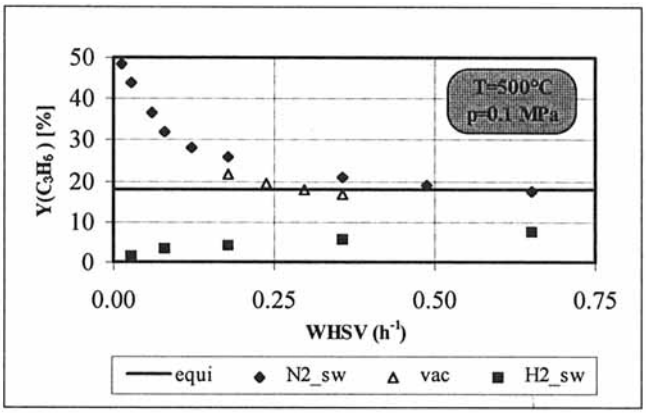

Figure 7. Propene yield (Y) vs. WHSV at T = 500°C and p = 0.1 MPa.

In the first series of experiments the C_3H_8 feed flow was varied. Changing the flow of the feed stream means that the WHSV changes, because the amount of catalyst in the reactor is constant. After each day of operation, the catalyst was regenerated (oxidized) over night using a mixture of 4 vol. % O_2 in N_2 in order to burn off the coke. Before propane was fed into the reactor again, the catalyst was reactivated with H_2 for one hour and then flushed with N_2. The feed was pure propane and a constant N_2 sweep was used at the shell side of the membrane. The driving force for the H_2 transport through the membrane is the partial pressure gradient over the membrane. The effective overall H_2/C_3H_8 separation factor of the membrane (α) at 500°C under these operating conditions is only 6–8, about 10 times lower than the permselectivity.

Figure 7 (◆ N_2 sw) shows the results of these measurements: the propene yield as a function of the WHSV. From this figure it is clear that the concept of the membrane reactor works. By selectively removing one of the products (H_2) from the reaction mixture, the C_3H_6 yield can be improved to values higher than the thermodynamic equilibrium composition. Because of the relatively low H_2/C_3H_8 and H_2/C_3H_6 separation factors, some C_3H_8 and C_3H_6 also diffuse through the membrane. Only the retentate gas mixture was considered for the yield in Figure 7. This means that the propene in the permeate is not taken into account and that the real value is even higher. Lower C_3H_8 and C_3H_6 permeabilities could improve the C_3H_8 conversion and the C_3H_6 yield even more. The increase in C_3H_6 yield is, however, only noticed for low values of the WHSV (< 0.32 h^{-1}, or a feed stream flow of < 60 sccm C_3H_8, in this case). The equilibrium composition is found at high WHSV. This means that, under these reaction conditions, the reaction rate is high enough (compared to the flow rate) to reach equilibrium and that the conversion is limited by the thermodynamics of the reaction. It also means that the permeation rate of hydrogen through the membrane is too low to effectively remove enough H_2 from the reaction mixture to make a difference when the residence time of the gas in the reactor is short. By using a membrane with a higher H_2 permeation, it should be possible to get conversions that are higher than the equilibrium value at higher WHSV.

Obviously, using a low WHSV means that the propene

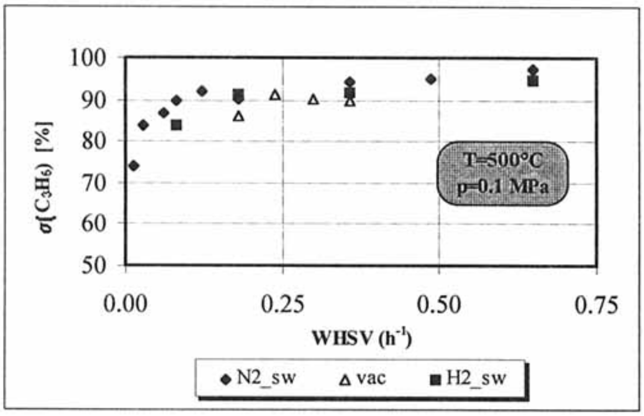

Figure 8. Propene selectivity (σ) vs. WHSV at T = 500°C and p = 0.1 MPa.

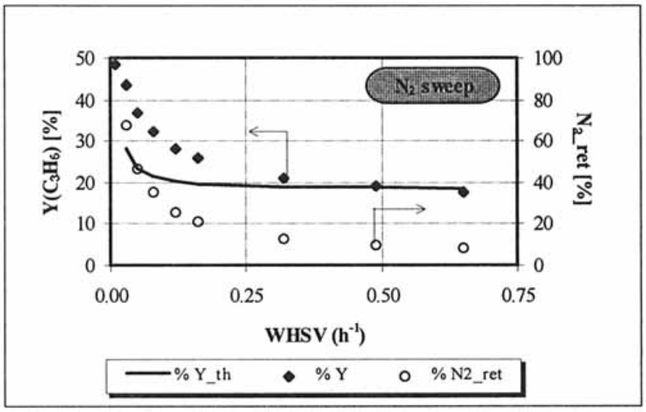

Figure 9. Experimental (◆) vs. theoretical (——) C_3H_6 yield [with N_2 concentration in the retentate (○)] vs. WHSV.

production rate (the amount C_3H_6 that is produced per hour) will be small, but it also has another disadvantage. A low WHSV means that the residence time of the gas in the reactor is long. Because the catalyst is not 100% specific, the selectivity will go down (Figure 8). The decrease in selectivity is, however, not drastic. Only at the smallest WHSV values (feed flow of 2.5 sccm^3), the selectivity is lower than 80%. The main by-products are methane (CH_4), ethane (C_2H_6), and ethene (C_2H_4) that result from the catalytic cracking reactions. This is not surprising when the theoretical composition at equilibrium is calculated from thermodynamic data (Table 4). It is also quite obvious that this thermodynamic approximation does not represent reality, because then the main reaction product should be methane. The kinetics and the catalyst make the reaction selective for the production of mainly propene. In the worst case (WHSV = 0.01 h^{-1}), only ~ 10% of the hydrocarbons is methane. For higher WHSV, this amount is $\leq 5\%$.

When a sweep gas is used, a certain amount of the N_2 can be found in the retentate caused by back diffusion. This means that the reaction mixture is being diluted with N_2. By diluting the reaction mixture, the theoretical yield is higher than 18% (Tiscareno-Lechugo et al., 1996), the 18% being the thermodynamic C_3H_6 yield for pure gas. This dilution effect cannot, however, be responsible for the increase in conversion that is observed in Figure 7. Using the N_2 concentration that is measured in the retentate (○ in Figure 9), the theoretical thermodynamic equilibrium can be calculated (——). At low WHSV the back diffusion of the sweep gas is very significant, because the residence time of the mixture in the reactor is relatively long and the permeation of N_2 through the membrane is relatively high for this membrane. At higher WHSV The back diffusion is less of a problem. At low WHSV the experimental values for the propene yield are, however, still always higher than this theoretical thermodynamic equilibrium. This indicates that the dilution effect can only explain a small part of the increase in conversion. The additional increase must be caused by the removal of H_2 from the reaction mixture, and proves that the concept of the membrane reactor works. In reality the effect of H_2 removal is even larger than shown in Figure 9. To calculate the theoretical thermodynamic equilibrium in Figure 9 (——), the N_2 concentration in the retentate was used. It was assumed that this concentration is constant in the total reactor. In fact, this is the N_2 concentration at the end of the reactor. The N_2 concentration is zero at the beginning and increases toward the end. This means that the picture that is shown in Figure 9 is the most pessimistic one.

Table 4. Theoretical Thermodynamic Equilibrium Composition at 500 and 600°C

Temperature		500°C (mol %)	600°C (mol %)
Hydrogen	H_2	*< 0.1*	*0.2*
Methane	CH_4	56.0	56.4
Ethane	C_2H_6	1.9	1.2
Ethene	C_2H_4	15.1	22.1
Ethyne	C_2H_2	0.2	1.2
Propane	C_3H_8	*0.2*	*< 0.1*
Propene	C_3H_6	*25.5*	*16.3*
Propyne	C_3H_4	1.1	2.6

When a diluted feed stream of 50% C_3H_8 in N_2 was used, the results of the measurements were approximately the same as those found for the pure C_3H_8 feed. The concentration of N_2 in the retentate was approximately the same for both series of experiments. This could mean that under these conditions a kind of steady state is reached between diffusion and back diffusion of N_2.

When a vacuum ($p_1 < 10^{-3}$ MPa) is used at the shell side of the membrane instead of a sweep gas, the reaction mixture cannot be diluted. The results of these measurements are also shown in Figures 7 and 8 (Δ vac). The C_3H_6 yield is a little lower than when the N_2 sweep (◆) is used. This difference could be the result of the dilution effect, but the difference is only very small. The conversion is still higher than what could be expected from the thermodynamic equilibrium. With our equipment it is not possible to measure the composition of the retentate accurately if the feed stream flow is lower than 30 sccm (WHSV = 0.18 h^{-1}) and still maintain a process pressure of 0.1 MPa when using vacuum instead of a sweep gas.

For the last series of experiments shown in Figures 7 and 8 (■ H_2 sw) a constant sweep of hydrogen was used. Due to the partial pressure difference across the membrane, part of

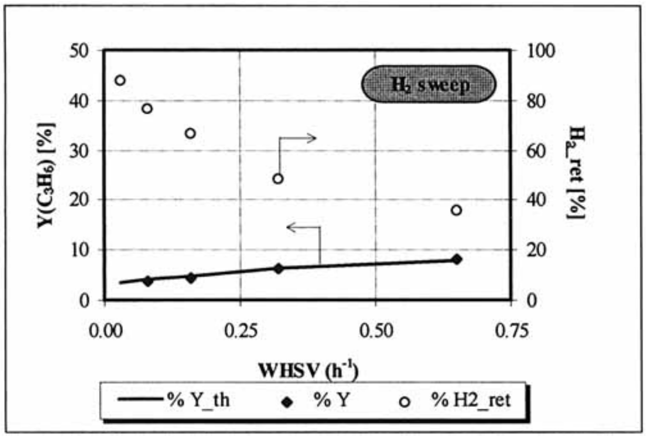

Figure 10. Experimental (♦) vs. theoretical (——) C_3H_6 yield [with H_2 concentration in the retentate (○)] vs. WHSV.

the H_2 will diffuse from the shell side into the reaction mixture. Because one of the reaction products is added to the reaction mixture, the equilibrium will be forced back according to Le Chatelier's principle, and the conversion has to go down. In this mode of operation the effect of the membrane reactor is bypassed; it is even reversed.

At high WHSV the residence time of the gas in the reactor is short. Because the H_2 diffusion rate is rather low compared to the flow rate, the effect of H_2 dilution is less noticeable, but the C_3H_8 conversion is only about half the theoretical value of a pure propane feed. At low WHSV much more H_2 finds its way to the reaction mixture, and there is almost no propene production left. Using the H_2 concentration that is measured in the retentate (○ in Figure 10), a theoretical thermodynamic equilibrium can be calculated (——) in the same way that was done for N_2 dilution. Although this method is only a very rough approximation (where only H_2 and the C_3H_8 are being considered), the propene yields that are measured agree very well with the calculated values. This proves that the principle of the membrane reactor is nothing more than Le Chatelier's law.

Conclusions

In this article the direct dehydrogenation of propane is described using a "packed-bed catalytic membrane reactor" (PBMR). The objective of the experiments was to show that the single-step conversion of this type of endothermic reaction, which is limited by the thermodynamic equilibrium, can be enhanced. It was proven that at 500°C, the conversion could be improved from the equilibrium value (~ 18%) to about twice as high. This increase is, however, only significant for relatively small values of the WHSV ($< 0.25\ h^{-1}$). The problem is that three aspects come together in a membrane reactor that make the process complex and vulnerable to weak links.

The three aspects that are important for the successful operation of the catalytic membrane reactor are (1) the membrane performance, (2) the catalytic activity and catalyst deactivation, and (3) the process performance. The membrane performance and the catalyst properties were studied in detail. From the results of these experiments, the process parameters were adapted to assure reproducible measurements of the propane dehydrogenation experiments in the membrane reactor.

The commercial silica membrane has a moderate H_2 permeance ($\sim 1.4\ 10^{-7}$ mol/m^2·Pa·s) and a limited H_2/C_3H_8 permselectivity ($\alpha_0 = 70-90$) at 500°C. Both of these properties are very important for the performance of the membrane reactor. A high H_2 transport through the membrane is necessary if a high propane flow rate (high WHSV) is to be used. On the other hand, it is necessary to have a high H_2 selectivity so that almost no reactant or reaction products can diffuse through the membrane to the shell side and be lost. The membrane that is used for these experiments is not perfect, but it is one of the best commercial silica membranes that exist and that can operate at 500°C–600°C. It is possible that the Pd/Ag composite membranes, which came on the market recently, have better permeability and selectivity. Tests under process conditions will have to be done to determine the characteristics and stability of these membranes under these conditions.

The commercial catalysts for propane dehydrogenation have existed for a long time. Although much research has been done on these catalysts, the long time stability is still a big problem. The deactivation of the catalyst is very fast because of coking. This is one of the main reasons why direct dehydrogenation is still not commonly used in industry. Burning coke is one of the sources of heat for the strongly endothermic reaction. This strongly endothermic behavior is also one of the reasons why the reaction cannot be done adiabatically. In a membrane reactor, H_2 is continuously removed from the reaction mixture. The influence of the H_2 concentration on the deactivation of the catalyst was studied at different temperatures. We concluded from the results of these measurements that 500°C is the best temperature at which to study the reaction and to get reproducible measurements over a period of more than 15 h, when the catalyst has to be regenerated.

The theoretical concept of the catalytic membrane reactor is already well known. This article experimentally shows that this concept really works and combines the reactor experiments with the characteristics of the membrane and of the catalyst. It also shows that it helps to use a catalyst that is more active at a lower temperature and that does not deactivate so fast. But there is an urgent need for better membranes to improve the results further and get higher conversion at a higher WHSV.

Acknowledgments

The authors thank Prof. Dr. Jacobs (University of Leuven (KUL)) for the help in characterizing the catalyst.

Literature Cited

Armor, N. J., "Catalysis with Permselective Inorganic Membranes," *Appl. Catal.*, **49**, 1 (1988).

Bernstein, L. A., and C. R. F. Lund, "Membrane Reactors for Series and Series-Parallel Reactions," *J. Memb. Sci.*, **77**, 155 (1993).

Bernstein, L. A., M. C. Reo, and C. R. F. Lund, "A Batch Membrane Reactor for Laboratory Studies," *J. Memb. Sci.*, **118**, 93 (1996).

Champagnie, A. M., T. T. Tsotsis, R. G. Minet, and E. Wagner, "The Study of Ethane Dehydrogenation in a Catalytic Membrane Reactor," *J. Catal.*, **134**, 713 (1992).

De Rossi, S., G. Ferraris, S. Fremiotti, E. Garrone, M. C. Campa, and V. Indovina, "Propane Dehydrogenation on Chromia/Silica and Chromia/Alumina Catalyst," *J. Catal.*, **148**, 36 (1994).

Falconer, J. L., R. D. Nobel, and D. P. Sperry, "Catalytic Membrane Reactors," *Membrane Separation Technology*, Chap. 14, R. D. Nobel and S. A. Stern, eds., Elsevier, New York (1995).

Gorriz, O. F., L. A. Arrua, L. E. Cadus, and J. B. F. Rivarola, "Catalytic Dehydrogenation of Propane to Propylene," *Latin Amer. Appl. Res.*, **19**, 31 (1989).

Gorriz, O. F., V. C. Corberan, and J. L. G. Fierro, "Propane Dehydrogenation and Coke Formation on Chromia-Alumina Catalyst," *Ind. Eng. Chem. Res.*, **31**, 2670 (1992).

Hsieh, H. P., "Inorganic Membrane Reactors," *Catal. Rev., Sci. Eng.*, **33**, 1 (1988).

Ionnides, T., and G. R. Gavalas, "Catalytic Isobutane Dehydrogenation in a Dense Silica Membrane Reactor," *J. Memb. Sci.*, **77**, 207 (1993).

Itoh, N. Y., Shindo, K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, "Simulation of a Reaction Accompanied by Separation," *Int. Chem. Eng.*, **25**, 138 (1985).

Itoh, N., "A Membrane Reactor Using Palladium," *AIChE J.*, **33**, 1576 (1987).

Itoh, N., "Limiting Conversions of Dehydrogenation in Palladium Membrane Reactor," *Catal. Today*, **25**, 251 (1995).

Keizer, K., V. T. Zaspalis, R. S. A. De Lange, M. P. Harold, and A. J. Burggraaf, "Membrane Reactors for Partial Oxidation and Dehydrogenation Reactions," *Membrane Processes in Separation and Purification*, J. G. Crespo and Böddeker, eds., Kluwer, Dordrecht, The Netherlands, p. 415 (1994).

Lin, C. L., D. L. Flowers, and P. K. T. Liu, "Characterisation of Ceramic Membranes: II. Modified Commercial Membranes with Pore Size under 10 Å," *J. Memb. Sci.*, **92**, 45 (1994).

Mohan, K., and R. Govind, "Analysis of a Cocurrent Membrane Reactor," *AIChE J.*, **32**, 2083 (1986).

Mohan, K., and R. Govind, "Studies on a Membrane Reactor," *Sep. Sci. Technol.*, **23**, 1715 (1988).

Omorjan, R. P., G. M. Clirc, and M. N. Tekic, "A Simple Analytical Analysis of the Performance of a Two-Membrane Reactor," *J. Memb. Sci.*, **118**, 17 (1996).

Saracco, G., and V. Specchia, "Catalytic Inorganic Membrane Reactors: Present Experience and Future Opportunities," *Catal. Rev., Sci. Eng.*, **36**, 304 (1994).

Sjinji, O., M. Misono, and Y. Yonedo, "The Dehydrogenation of Cyclohexane by Use of a Porous Glass Reactor," *Bull. Chem. Soc. Japan*, **55**, 2760 (1982).

Sun, Y.-M., and S.-J. Khang, "Catalytic Membrane Reactor for Simultaneous Reaction and Separation Applied to a Dehydrogenation Reaction," *Ind. Eng. Chem. Res.*, **27**, 1136 (1988).

Suzuki, I., and Y. Kaneko, "Dehydrogenation of Propane over Chromia-Alumina-Potassium-Oxide Catalyst," *J. Catal.*, **47**, 239 (1977).

Suzuki, I., and Y. Kaneko, "Pressure Jump Method in the Dehydrogenation of Propane over Chromia-Alumina-Potassium-Oxide," *React. Kinet. Catal. Lett.*, **10**, 213 (1979).

Tauster, S. J., and R. M. Koros, "Removal of Coke Precursors with Hydrogen: Studies with Alternating Pulses of Propane and Hydrogen," *J. Catal.*, **27**, 307 (1972).

Tiscareno-Lechugo, F., C. G. Hill, Jr., and M. A. Anderson, "Effect of Dilution in the Experimental Dehydrogenation of Cyclohexane in Hybrid Membrane Reactors," *J. Memb. Sci.*, **118**, 85 (1996).

Tsotsis, T., A. M. Champpagnie, R. G. Minet, and P. K. T. Liu, "Catalytic Membrane Reactors," *Computer Aided Design of Catalysis*, E. R. Barker and Periera, eds. (1994).

Wu, C. S., D. L. Flowers, and P. K. T. Liu, "High Temperature Separation of Binary Gas Mixtures Using Microporous Ceramic Membranes," *J. Memb. Sci.*, **77**, 85 (1993).

Wu, J. C. S., H. Sabol, G. W. Smith, D. L. Flowers, and P. K. T. Liu, "Characterisation of Hydrogen-Permselective Microporous Ceramic Membranes," *J. Memb. Sci.*, **96**, 275 (1995).

Zaika, Z. D., R. G. Minet, and T. Tsotsis, "A High Temperature Catalytic Membrane Reactor for Propane Dehydrogenation," *J. Memb. Sci.*, **77**, 221 (1993a).

Zaika, Z. D., R. G. Minet, and T. Tsotsis, "Propane Dehydrogenation in a Packed Bed Membrane Reactor," *AIChE J.*, **39**, 526 (1993b).

Zaspalis, V. T., W. Van Praag, K. Keizer, J. G. Ommen, J. R. H. Ross, and A. J. Burggraaf, "Reactor Studies Using Alumina Separation Membranes in Relation to the Dehydrogenation of Methanol and n-Butane," *Appl. Catal.*, **74**, 223 (1991).

Manuscript received Dec. 12, 1996, and revision received Mar. 11, 1997.