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Membrane performance: the key issues for dehydrogenation reactions in a catalytic membrane reactor

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Abstract

In a high-temperature membrane reactor, one of the reaction products is selectively removed from the reaction mixture, thus preventing the mixture from reaching equilibrium. In a previous study [1], a CVI-silica membrane was used for the direct dehydrogenation of propane in a high-temperature catalytic membrane reactor. This H_2 selective membrane had only a moderate permeation ($\sim 140\times 10^{-9}$ mol/m^{2}Pa s) and a limited H_2/C_3H_8 permselectivity ($\alpha_0 \approx 70$–90 at 500°C). These experiments proved that (at 500°C) the propane conversion could be improved from the equilibrium value (~18%) to a value which is about twice as high. The increase was however only significant for relatively small values of the propane feed stream ≤ 16.5 μmol/s. This is because at high propane feed, the hydrogen cannot be removed fast enough through the membrane and conversion is again limited by the thermodynamic equilibrium. In this study, the comparison is made between the performance of the CVI-silica membrane and a Pd/Ag membrane when used as the H_2 selective membrane. The performance of the Pd/Ag membrane is far superior to the performance of the SiO_2 membrane. H_2 fluxes of more than 0.1 mol/m^{2}s were measured and the H_2/Ar permselectivity exceeds 4500. When it is run under comparable conditions, the performance of the Pd/Ag membrane reactor is much better. The increase in propane conversion persists at values of the propane feed stream that are about six times higher (105 μmol/s).

Since the H_2 is selectively removed from the reaction mixture, it is not available for any competitive side reactions. The production of methane, which limits the propene selectivity of the reaction in a conventional plug-flow reactor, is much less in a catalytic membrane reactor. This means that the selectivity in the membrane reactor is higher than in the plug-flow reactor when they are run under similar conditions. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Pd/Ag membrane; Membrane reactor; Propane dehydrogenation

1. Introduction

The direct dehydrogenation of alkanes to alkenes can be found in 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 economical reasons, two main fundamental problems are responsible for the lack of commercial application of direct dehydrogenation of propane. First, the dehydrogenation reaction (Eq. (1)) is endothermic.

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \qquad (1)$$

For this dehydrogenation reaction, with a $\Delta H^0_{733\,\mathrm{K}}$ of ca. 130 kJ/mol, the equilibrium conversion (ξ_{eq}) at atmospheric pressure is limited to ~18% at 500°C and ~50% at 600°C.

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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 (<1 h 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. Many studies on dehydrogenation reactions of alkanes can be found in literature, dealing with the reaction mechanisms [2–3] and with the rate of reaction [4–5]. All concerned 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 non-selective gas-phase reactions.

In recent years, a completely different approach is being considered: the catalytic membrane reactor. In this concept, one of the products (H_2) is removed from the reaction mixture using a gas separative membrane. By selectively removing the hydrogen, the equilibrium composition of the reaction mixture is changed and the production of propene increases. Sometimes this effect is incorrectly called '*cheating the equilibrium*'. In reality, the fact is used that the thermodynamic equilibrium constant does not change if the temperature is kept constant.

In a previous study [1], the direct dehydrogenation of propane to propene in a packed-bed-catalytic membrane reactor was described using a chemical vapour deposition (CVI)-silica membrane [13]. The catalytic membrane reactor experiments (at 500°C) proved that the concept really works and that the propane conversion could be improved to a value which is more than twice as high than the thermodynamic equilibrium (~18%). However, the increase was only significant at low weight hour space velocity (WHSV = mass [g] of C_3H_8 feed gas per hour per gram of catalyst).

For the experiments that are described in this paper, a commercial Pd/Ag membrane (from Johnson Matthey) is used. The performance of this membrane is superior to the CVI-silica membrane; both what the permeation and the separation characteristics are concerned. The catalytic membrane reactor experiments are performed under similar conditions. The results of the experiments will be discussed and compared to the results that were obtained with the CVI-silica membrane. The dehydrogenation reaction was also studied in a conventional plug-flow reactor using the same catalyst. The effect of removing H_2 from the reaction mixture on the C_3H_8 conversion, the C_3H_6 yield and the selectivity will also be mentioned in this paper.

2. Experiments

2.1. The membrane

Different kinds of gas separative membranes can be used to separate H_2 from a gas mixture. Palladium [6] or a palladium/silver alloy, porous glass [7], mesoporous alumina [8–9] and different types of silica [10–12] are the materials that are commonly used for these H_2 selective membranes. The use of Pd membranes in (catalytic) membrane reactors was pioneered by Gryaznov and his co-workers in Russia [14].

Recently, Johnson Matthey developed a thin film Pd/Ag membrane on an alumina support, which is commercially available. One of these membranes is used for these experiments. The tubular Al_2O_3 membrane is 200 mm long and has an outer diameter of 25 mm. On the outside of the tube, the H_2 selective Pd/Ag top layer is deposited by chemical plating [15–16] (on a ~10-μm thick γ-Al_2O_3 intermediate layer). The thickness of the gas selective Pd/Ag thin film is ca. 7.5 μm and the silver content of the alloy is 20–25%. The CVI-silica membrane that was used in the previous study was ~250 mm long and had an inner and outer diameter of, respectively, ~7 and ~10 mm (Table 1). Both membranes were mounted in a stainless-steal module using graphite seals at both ends. The membrane characteristics are determined by single gas permeation and binary gas separation measurements in a '*Velterop membrane test apparatus* (MTA) [1].

Table 1
Differences in membrane reactor configuration

Membrane	Pd/Ag	CVI-SiO_2
Dimensions		
Inner diameter (mm)	21	7
Outer diameter (mm)	25	10
Length (mm)	200	250
Surface area (10^{-4} m^2)	140	60
Amount of catalyst (g)	21	7.5

2.1.1. Flux (Φ) and permselectivity (α_0)

The gas flux (Φ) and permselectivity (α_0) are determined by single gas, flow controlled permeation measurements. For these measurements, the pressures at the feed side (p_h) and at the shell side (p_l) are measured for a fixed feed gas flow at a constant temperature. The permeation (F_0 [mol/m^2 Pa s]) is defined as the gas flux through the membrane ($\Phi = f/S =$ flow per unit of surface area [mol/m^2 s]) divided by the pressure difference (Δp), which acts as the driving force. The H_2 transport mechanism through a dense Pd/Ag membrane is quite different from the transport mechanism through a microporous silica membrane.

The H_2 flux through noble metals (like the Pd/Ag membrane) is a special case of a solution/diffusion mechanism [17–18,20]. The H_2 molecules are adsorbed and catalytically dissociated on the metal surface and can subsequently diffuse through the metal matrix. On the other side of the membrane, the recombination and desorption takes place. The rate of diffusion can be described in terms of Fick's first law:

$$\Phi_{H_2} = \frac{F}{\ell}(p_h^n - p_l^n) = F_0(p_h^n - p_l^n) \qquad (2)$$

The permeation (F_0) is the permeability (F) per unit of diffusion length (ℓ is the thickness of the Pd/Ag top layer). Assuming that the diffusion of hydrogen through the bulk of the palladium membrane is rate limiting compared to the H_2 dissociation at the membrane surface, $n = 1/2$ (Sievert's law) because the concentration of dissolved hydrogen is proportional to the square root of the hydrogen pressure. This means that the hydrogen is transported through the metal as atomic species [21]. Several experiments have shown that the H_2 flux through a Pd membrane can better be described with an exponent $0.3 < n < 0.8$ [19]. In principal, other gases should not be able to diffuse through the dense metal membrane. This implies that the H_2 separation factor should be infinite (∞).

Traditionally, the diffusion through the microporous silica membrane [1] is described by the Knudsen/Poiseulle law:

$$F_0 = \frac{\Phi}{\Delta p} = F_{0,\mathrm{K}} + F_{0,\mathrm{P}} = K_0 + B_0\bar{p} \qquad (3)$$

where mean pressure $\bar{p} = 1/2\ (p_h + p_l)$ [Pa].

The permeation of pure Knudsen membranes ($B_0 = 0$) is independent of pressure and proportional to the inverse square root of the molecular mass ($K_0 \propto 1/\sqrt{M}$). Knudsen membranes can therefore separate gasses with a different molecular mass. The Knudsen separation factor is then defined as:

$$\alpha_{\mathrm{KN}}\left(\frac{A}{B}\right) = \sqrt{\frac{M_B}{M_A}} \qquad (4)$$

Both the transport mechanism of H_2 diffusion through dense noble metal membranes (Eq. (2)) and the gas transport through microporous membranes (Eq. (3)) can be described by the Fick's first law. Because H_2 is transported through the metal membrane as atomic species and not as a molecule, the flux (Φ) is proportional to the square root of the pressure ($n = 1/2$). In microporous membranes, no dissociation takes place and the gasses are transported as molecules. The flux (Φ) is therefore directly proportional to the pressure difference (Δp) ($n = 1$). In both cases, the proportionality factor is the permeation (F_0). The permselectivity (α_0) is the ratio of the permeation values of two gasses measured at the same temperature:

$$\alpha_0\left(\frac{A}{B}\right) = \left[\frac{F_0(A)}{F_0(B)}\right]_{T=C^{\mathrm{te}}} \qquad (5)$$

2.1.2. Binary gas separation (α)

The binary gas separation measurements are performed in the MTA using a mixture of H_2 and Ar as a feed gas. At the shell side, a sweep gas (N_2) is used. The pressure difference (Δp) can be set by individually controlling the pressures at the feed side (p_h) and at the shell side (p_l). The compositions of the permeate and retentate are determined by a gas chromatograph (GC) which is equipped with a hot wire detector (HWD). The separation factor (α) can be calculated from the molar ratios (X) of the two gasses in the permeate and the feed:

$$\alpha\left(\frac{\mathrm{H_2}}{\mathrm{Ar}}\right) = \left[\frac{X_{\mathrm{H_2}}}{X_{\mathrm{Ar}}}\right]_{\mathrm{perm}} \div \left[\frac{X_{\mathrm{H_2}}}{X_{\mathrm{Ar}}}\right]_{\mathrm{feed}} \qquad (6)$$

2.2. The catalytic membrane reactor

In order to be able to compare the results of using different H_2 selective membranes in the catalytic membrane reactor experiments, the same chromia/alumina (Cr_2O_3/γ-Al_2O_3) catalysts is used as in the experiments with the SiO_2 membrane [1]. The catalyst does not contain any promoter elements and the specific surface area (BET) is between 80 and 90 m^2/g. The membrane reactor tube is filled with ~21 g of catalyst with a grain size between 200 and 500 μm. For these experiments, the reactor is run at 500°C and at atmospheric pressure at both sides of the membrane ($p_h = p_l = 0.1$ MPa); the same conditions that were used in the previous study [1]. The only differences between the two sets of experiments are the dimensions of the membranes and the amount of catalyst that is used in the catalytic membrane reactors (Table 1).

The driving force for the H_2 transport through the membrane is created by using an inert (N_2) sweep gas in a co-current mode. Undiluted propane (C_3H_8) is used as the feed gas.

The compositions of the permeate and the retentate are measured with a gas chromatograph. The conversion (ξ) can be calculated from the difference in propane concentration between the retentate and the feed:

$$\xi_{C_3H_8} = \frac{\lfloor X_{C_3H_8} \rfloor_{\text{feed}} - \lfloor X_{C_3H_8} \rfloor_{\text{ret.}}}{[X_{C_3H_8}]_{\text{feed}}} \times 100\% \qquad (7)$$

At 500°C and 0.1 MPa the conversion is limited by the thermodynamic equilibrium to a value of ca. 18%. For the yield (Y) and the selectivity (σ) of the reaction, only the propene production in the retentate is considered. The products that diffuse through the membrane to the shell side are not taken into account in these calculations and are considered as waste which are not recovered.

$$Y_{C_3H_6} = \lfloor X_{C_3H_6} \rfloor_{\text{ret.}} \times 100\% \qquad (8)$$

$$\sigma_{C_3H_6} = \frac{Y_{C_3H_6}}{\xi_{C_3H_8}} \times 100\% \qquad (9)$$

Unless stated otherwise, molar propene yield and selectivity are used in this paper instead of carbon yield and carbon selectivity.

3. Results and discussion

3.1. The Membrane

3.1.1. Flux (Φ) and permselectivity (α_0)

The gas flux was measured at constant temperature (400 and 500°C) using vacuum at the shell side of the membrane ($p_l < 10^{-3}$ MPa). At the feed side, the pressure (p_h) was varied between 0.05 and 0.6 MPa. The most significant results of the single gas permeation measurements (gas flux and permselectivity) are given in Table 2. Because of the different H_2 transport mech-

Table 2
Results of the single gas permeation measurements[a]

Membrane, *M*	Gas flux, Φ (10^{-3} mol/m^2 s)							
	Pd/Ag ($A^b = 140 \times 10^{-4}$ m^2)				SiO_2 ($A^b = 60 \times 10^{-4}$ m^2)			
	H_2 2.02	He 4.00	N_2 28.01	Ar 39.95	H_2 2.02	He 4.00	N_2 28.01	C_3H_8 44.10
400°C, $p_h = 0.1$ MPa	74.3	0.05 (8)	0.02 (9)	0.02 (0)	3.13	17.3	0.20	0.22
$p_h = 0.3$ MPa	145	0.14 (4)	0.06 (3)	0.04 (5)	9.93	52.2	0.79	0.88
500°C, $p_h = 0.1$ MPa	86.7	0.05 (6)	0.02 (6)	0.01 (8)	13.9	51.0	0.19	0.15
$p_h = 0.3$ MPa	170	0.14 (0)	0.05 (6)	0.03 (9)	42.9	156	0.68	0.64
Knudsen (α_{KN})	Permselectivity, α_0							
	H_2/He 1.41	H_2/N_2 3.72	H_2/Ar 4.45	He/Ar 3.16	H_2/He 1.41	H_2/N_2 3.72	H_2/C_3H_8 4.67	He/C_3H_8 3.32
400°C, $p_h = 0.1$ MPa	1275	2550	3640	2.90	0.18	15.7	14.2	78.6
$p_h = 0.3$ MPa	1010	2305	3190	3.20	0.19	12.7	11.4	60
500°C, $p_h = 0.1$ MPa	1555	3280	4915	3.11	0.27	73.2	92.7	34.0
$p_h = 0.3$ MPa	1210	3030	4410	3.59	0.28	62.2	68.1	247

[a] Gas flux (Φ) and permselectivity (α_0) of the Pd/Ag and the SiO_2 membranes: $p_l < 10^{-3}$ MPa (vacuum).
[b] Effective surface area.

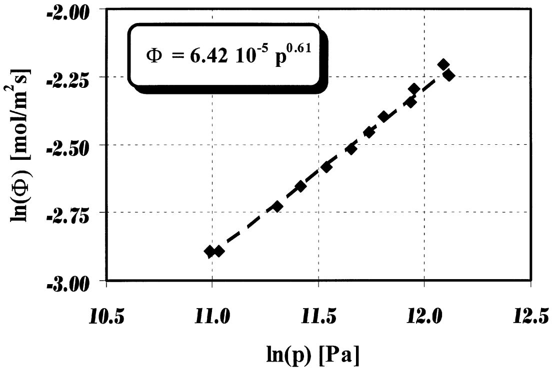

Fig. 1. H_2 flux vs. pressure measured at 400°C.

anisms through the different membranes, it is difficult to compare the permeation values. Therefore, the gas fluxes are given in Table 2 instead of the permeation values.

The pressure dependence of the H_2 flux for the Pd/Ag membrane (n in Eq. (2)) was found to be to the power 0.61 (Fig. 1), which is a relatively good match to the theoretical value of 0.5. The H_2 diffusion through the metal membrane is activated by temperature and can be described by an Arrhenius equation. The activation energy (E_a) is $\approx$11–12 kJ/mol. This is a little lower than the H_2 activation energy that was found for the SiO_2 membrane, but the H_2 permeation of the silica membrane at 400°C is 15–25 times lower than through the Pd/Ag membrane. At 500°C, the performance of the silica membrane is much better. The H_2 flux is only about five times lower than for the metal membrane.

Although no gasses other than H_2 should be able to diffuse through the dense Pd/Ag membrane, in reality there is still a very small flux of other gasses that can permeate from the feed side to the shell side of the module. These other gasses can permeate through very small defects in the Pd/Ag top layer and/or through very small leaks at or in the graphite seals. Because of these small leaks, the hydrogen permselectivity is limited ($<\infty$). Despite these parasitic gas fluxes, the gas separation characteristics of the Pd/Ag membrane are much better than the characteristics of the silica membrane when measured under the same conditions. Because palladium is a well-known catalyst for dehydrogenation reactions of alkanes, it is not possible to measure the propane permeation at high temperature.

For the Pd/Ag membrane, a Knudsen-like transport mechanism seems to be controlling the diffusion of all gasses except H_2. This indicates that there are probably some microporous defects in the Pd/Ag top layer of the membrane.

The transport mechanism for the microporous silica membrane is not fully clear. Only at high temperature ($\gtrsim$450°C) a Knudsen like dependence of the permeation on the molecular mass is observed for the heavier gasses (CH_4, C_3H_8, CO_2 and N_2). There is still, however, a small pressure dependence. The permeation of these gasses decreases with increasing temperature, but does not follow the Knudsen/Poiseulle law (Eq. (3)). Helium and hydrogen are activated by temperature with $E_a = 17$–20 kJ/mol for both gasses. Contrary to the Knudsen transport mechanism, the He flux ($M = 4.00$) through the CVI-silica membrane is actually higher than the H_2 flux ($M = 2.02$). This could be due to a possible interaction of the hydrogen with the silica material. It is not very likely that the small difference in kinetic diameter between the two gasses ($d_{\mathrm{kin}}(\mathrm{He}) = 0.260$ nm, $d_{\mathrm{kin}}(H_2) = 0.289$ nm) is responsible for the higher He flux.

3.1.2. Binary gas separation (α)

The H_2/Ar separation measurements were performed at atmospheric pressure ($p_h = p_l = 0.1$ MPa) and at 400 and 500°C. The experiments were done using $H_2 \div \mathrm{Ar}$ mixtures that contained 50 and 90% H_2. The total feed flow for these experiments were kept constant at 100 sccm (‘standard cubic centimetres per minute’: cm^3/min STP). At the shell side, a constant flow of N_2 was used. The results of the binary gas separation measurements as a function of the sweep gas flow is shown in Fig. 2.

Despite the low driving force for permeation, the Pd/Ag membrane performs very well. The real separation factor (α) is dependent on the sweep stream flow. When a high sweep stream is used, the H_2 that is permeating through the membrane is removed from the membrane surface very effectively. This is essential to keep the H_2 partial pressure over the membrane as high as possible, which results in a better H_2 transport. With these high sweep streams, the real separation factor approaches the ideal permselectivity. These results are consistent with similar experiments relating to observations with the CVI-silica membrane [1].

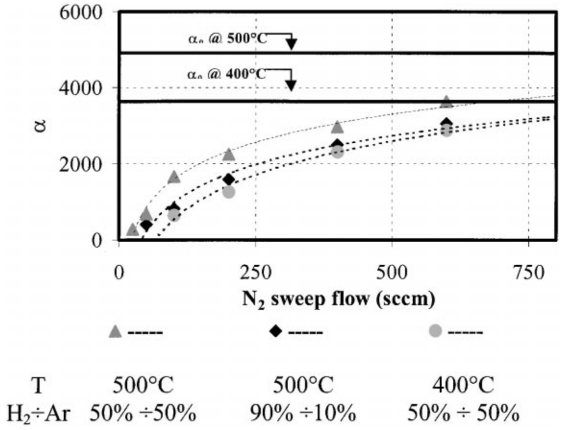

Fig. 2. H_2/Ar separation factor (α) vs. N_2 sweep stream flow at 400 and 500°C for $H_2 \div Ar = 50 \div 50\%$ and $90 \div 10\%$.

3.2. The catalytic membrane reactor

At 500°C, the deactivation of the catalyst is relatively slow. The propane conversion (ξ) is stable for at least 7 h; then ξ gradually decreases (to half of its original value in ca. 30 h) due to coke formation on the catalyst. The catalyst can easily be regenerated by burning of the coke over night (at 500°C) in a 4% O_2 in N_2 mixture. After the catalyst is oxidised it needs to be reactivated in pure H_2 (100 sccm) for ca. 1 h.

The most important results of the membrane reactor experiments are shown in Fig. 3: (●) for the Pd/Ag membrane reactor and (■) for the experiments that were done previously with the SiO_2 membrane [1]. These experiments were done at 500°C and at atmospheric pressure at both sides of the membrane ($p_h = p_l = 0.1$ MPa). By using a N_2 sweep gas (in a co-current mode), a partial pressure difference is created which acts as the driving force for the H_2 permeation through the membrane. The feed for these experiments was undiluted propane (C_3H_8).

In a first series of experiments, a constant flow of N_2 (1000 sccm) was used as the sweep gas and the C_3H_8 feed flow was varied (closed symbols in Fig. 3). Changing the flow of the feed stream means that the weight hour space velocity (WHSV) changes because the amount of catalyst in the reactor is constant. It is clear that the performance of the Pd/Ag membrane reactor (●) is better than what was found for the SiO_2 reactor (■). The general behaviour is the same for both reactors: by selectively removing one of the products (H_2) from the reaction mixture the propene yield ($Y(C_3H_6)$) can be improved to values higher than the thermodynamic equilibrium composition. The increase in C_3H_6 yield is only noticed for low values of the WHSV: $\lesssim 0.8\,h^{-1}$ in this case of the Pd/Ag membrane reactor. For the CVI-silica membrane reactor this '*critical WHSV value*' is $\lesssim 0.35\,h^{-1}$ which is 2.3 times lower (Fig. 3a). However, 2.8 times more catalyst is present in the Pd/Ag reactor (Table 1). This means that the propane feed stream, at which the conversion becomes higher than the theoretical equilibrium value ('*critical value for*

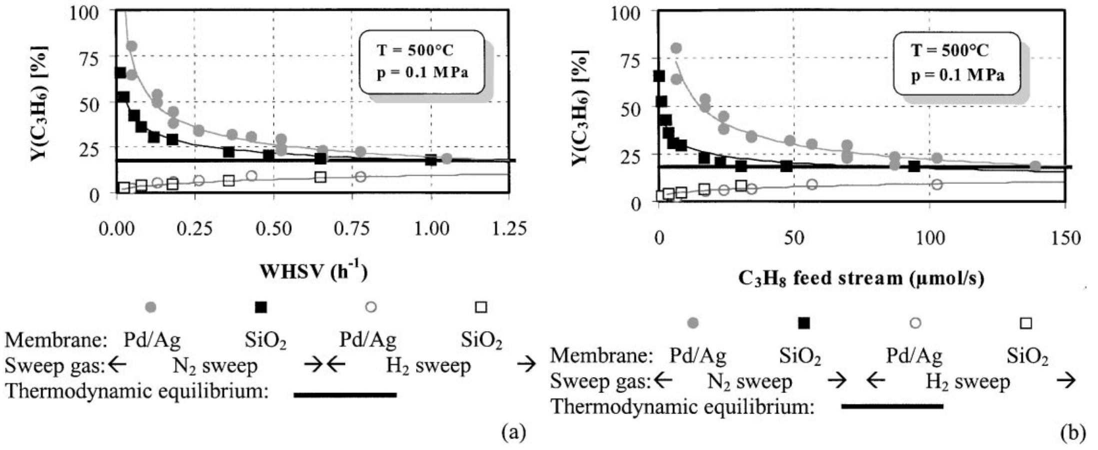

Fig. 3. Propene yield ($Y(C_3H_6)$) vs. WHSV (a) and vs. propane feed stream (b) at 500°C and $p = 0.1$ MPa. ((●) Pd/Ag membrane, (■) SiO_2 membrane; open symbols: H_2 sweep, closed symbols: N_2 sweep).

the propane feed stream') is ∼105 μmol/s for Pd/Ag which is ca. 6.4 times higher than what is found for SiO_2 (∼16.5 μmol/s) (Fig. 3b).

It is unknown, and very difficult to determine the amount of catalyst, which is effectively participating in the dehydrogenation reaction. Experiments that were done in a conventional '*plug-flow reactor*' (with dimensions that are comparable to the SiO_2 membrane reactor) with the same Cr_2O_3/Al_2O_3 catalyst, indicated that the reaction is very fast under the process conditions that are used. The experimental propane conversion is very close to the theoretical thermodynamic equilibrium value, even when a limited amount of catalyst (<5 g) is used. If the activity of the catalyst is indeed this high, only a small amount of catalyst is really participating in the reaction. Therefore, it is reasonable to assume that the performance of the two reactors should be done as function of the C_3H_8 feed stream (Fig. 3b) instead of using the WHSV (Fig. 3a).

If the propane feed stream is higher than the critical value, the equilibrium composition is found. This means that the reaction rate, under these reaction conditions, is high enough to reach equilibrium and that the conversion is limited by the thermodynamics of the reaction. It also means that the hydrogen permeation rate through the membrane is too low (compared to the reaction rate) to effectively remove enough H_2 fast enough from the reaction mixture to make a difference. In our previous study [1], the idea was already put forward that a higher H_2 permeation rate would give a higher '*critical feed stream value*'. The H_2 flux through the Pd/Ag membrane is ca. 6.2 times higher than the H_2 flux through the CVI-silica membrane (at 500°C and 0.1 MPa) (Table 2). This is almost identical to the 6.4 times higher '*critical feed stream value*' that is found for the Pd/Ag membrane reactor compared to the SiO_2 membrane reactor.

The performance of the Pd/Ag membrane reactor is even better if the feed streams are compared at which the propene yield is two times the thermodynamic equilibrium value. For the Pd/Ag membrane reactor, this propene yield of 36% is reached with a C_3H_8 feed stream of ∼35.3 μmol/s; about eight times higher than the value in the case of the silica membrane reactor (∼4.38 μmol C_3H_8/s). The reason why the difference in membrane reactor performance is even higher in this case is due to the higher selectivity of the Pd/Ag membrane. Because of the relatively low H_2/C_3H_8 and H_2/C_3H_6 separation factors of the SiO_2 membrane, some propane and propene also diffuse through the membrane from the feed side to the shell side of the reactor. For the calculations of the propene yield that are represented in Fig. 3, only the retentate gas mixture is considered and that the products in the permeate are not taken into account. Furthermore, also some of the propane diffuses to the shell side of the SiO_2 membrane reactor and will not be able to participate in the reaction. The separation factor for the Pd/Ag membrane reactor is at least 75 times higher than for the silica membrane and the diffusion of propane and/or propene from the feed to the shell side almost negligible. This means that, in the case of the SiO_2 membrane, some of the propene diffuses into the permeate stream and is considered as waste, while in the case of the Pd/Ag membrane, almost all the propene remains in the retentate and contributes to the yield that is represented in Fig. 3. This extra contribution to the propene yield in the case of the Pd/Ag membrane reactor explains the larger difference in performance between the two membrane reactors.

At very low values of the feed stream, the difference in performance between the two membrane reactors is getting smaller. This can also be contributed to the difference in membrane selectivity. In the case of the silica membrane, the N_2 sweep gas is diffusing from the shell side into the feed side of the membrane reactor. Because of this back diffusion of the sweep gas, the reaction mixture is diluted by N_2. By diluting the reaction mixture, the theoretical yield (according to Le Chatelier's law) is higher than the thermodynamic C_3H_6 yield for the pure gas (∼18%). Although this dilution effect cannot be responsible for the increase in conversion that is observed [1], it can explain why the difference in performance between the Pd/Ag and the SiO_2 membrane reactors is becoming smaller at very low values of the feed stream. While the reaction mixture is diluted by the sweep gas in the case of the silica membrane, the N_2 back diffusion through the Pd/Ag membrane is negligible.

When, instead of nitrogen, hydrogen is used as a sweep gas, the effect of the membrane reactor is bypassed; it is even reversed (open symbols in Fig. 3; (○) Pd/Ag and (□) SiO_2 membrane reactors). Because of the H_2 partial pressure difference over the membrane, part of the H_2 will diffuse from the shell side into the reaction mixture. According to Le Chatelier's principle, the conversion has to go down. In this mode of operation both reactors behave exactly alike as would be expected. This proves that Le Chatelier's principle is followed and that the principle of the membrane reactor is nothing more than using the equilibrium constant.

The C_3H_6 molar selectivity is for all the measurements that were done in the Pd/Ag membrane reactor very high (at least between 85 and 95%). When a low propane feed stream is used, the residence time of the gas mixture in the reactor is long. Because the catalyst is not 100% specific, the selectivity will be a little bit lower. The decrease in selectivity is however not drastic. The selectivity of a membrane reactor (both for the Pd/Ag and the SiO_2 membranes) is in any case higher than what is found using a conventional plug-flow reactor (under the same operating conditions). The main by-products are methane (CH_4), ethane (C_2H_6) and ethene (C_2H_4), which result from the catalytic cracking reactions. By selectively removing H_2 from the reaction mixture, much less of these byproducts are produced and the selectivity is improved. Further experiments in a conventional continuous plug-flow reactor are being carried out to confirm this.

4. Summary and conclusions

From the experiments, it is clear that the concept of the catalytic membrane reactor works if the right process parameters are used. These parameters depend on the quality of the gas separative membrane and that of the catalyst. The relationships between the reaction rate, the flow rate of the feed gas and the H_2 permeation rate are very important in optimising the conditions for the direct dehydrogenation process.

In this paper, the performance of a commercial Pd/Ag membrane (Johnson Matthey) was compared to the performance of a CVI-silica membrane (Media and Process Technology) which was used in previous experiments [1]. For the propane dehydrogenation experiments, the same commercial $Cr_2O_3/\gamma\text{-}Al_2O_3$ catalyst was used (grain size = 200–500 μm and BET specific surface area = 80–90 m^2/g).

The performance of the Pd/Ag membrane is in all respects superior to the performance of the CVI-silica membrane. The pure H_2 flux is (at 500°C and with $\Delta p = 0.1$ MPa) ca. 6.2 times higher: ∼87 mmol/m^2s for Pd/Ag versus ∼14 mmol/m^2s for SiO_2. The difference in permselectivity is even more pronounced. $\alpha(H_2/N_2)$ is ca. 3300 for the Pd/Ag membrane, which is ∼45 times higher than for the SiO_2 membrane ($\alpha(H_2/N_2) \approx 73$).

The general behaviour of the propane dehydrogenation experiments is the same for both catalytic membrane reactors. It confirms that the concept of the catalytic membrane reactor does indeed work. The propene yield can be much higher than what is predicted by the thermodynamic equilibrium. The increase in C_3H_6 yield is only noticed when the feed stream is lower than a critical value. This '*critical feed stream value*' (CFSV) for the Pd/Ag membrane reactor (∼105 μmol/s) is ca. 6.4 times higher than for the CVI-silica membrane reactor (∼16.5 μmol/s). If the propane feed stream is higher than the CFSV the reaction is limited by the thermodynamic equilibrium. This means that, under these process conditions, the reaction rate is still high enough to reach equilibrium, but that the H_2 permeation rate through the membrane is too low (compared to the reaction rate) to effectively remove enough H_2 fast enough from the reaction mixture. Because the H_2 flux through the Pd/Ag membrane is ca. 6.2 times higher than in the case of the SiO_2 membrane, the CFSV will also be higher (∼6.4 times) in the case of the Pd/Ag membrane reactor.

The difference in performance between the two types of membrane reactors becomes larger with decreasing values of the feed stream. The propene yield is two times higher than the equilibrium value for a propane feed of ∼35.3 μmol/s in the case of the Pd/Ag membrane reactor; about eight times higher than the value in the case of the silica membrane reactor (∼4.38 μmol C_3H_8/s). Because of the high H_2 selectivity of the Pd/Ag membrane, almost no propane and propene diffuses through the membrane into the shell side of the reactor and almost all of the propene that is produced will contribute to the value that is represented in Fig. 3. Because of the lower selectivity of the silica membrane reactor, some of the propene will diffuse through the membrane to the permeate side. This propene concentration is not taken into account in the value of the propene yield that is represented in Fig. 3. In these calculations, it is regarded as waste that is not recovered. This can explain the larger difference in performance between the two types of membrane reactors.

At very low values of the feed stream, the difference in performance between the two membrane reactors becomes smaller again. This can also be explained by the difference in selectivity between the two membranes. At very low values of the feed stream, some N_2 sweep gas diffuses from the shell side into the feed side of the SiO_2 membrane reactor and the reaction mixture is diluted. By diluting the reaction mixture, the theoretical yield (according to Le Chatelier's principle) is higher than the thermodynamic C_3H_6 yield for the pure gas. For the Pd/Ag membrane reactor, the back diffusion of the sweep gas is almost negligible. This means that, at very low feed stream values, there will be an extra contribution to the propene yield due to the dilution effect in the case of the SiO_2 membrane reactor which explains the difference in performance between the two types of membrane reactors becomes smaller again.

The results of these measurements prove that the concept of the catalytic membrane reactor does indeed work if the right process conditions are chosen. The key to the membrane reactor concept is thermodynamics. A high H_2 permeation rate makes it possible to work with a high propane feed stream, which means that the propene production rate will also be higher. It is of course also important to have a high membrane selectivity to minimise the loss of feed and/or products because of diffusion into the permeate gas stream. A high membrane selectivity also inhibits the dilution of the reaction mixture by the sweep gas, which assures a higher purity of the product.

5. List of symbols

B_0	Poiseulle factor
E_a	activation energy
F_0	gas permeation
$F_{0,K}$	Knudsen contribution to the gas permeation
$F_{0,P}$	Poiseulle contribution to the gas permeation
K_0	Knudsen factor
M	molecular mass of the gas
p_h	pressure at the feed side
p_l	pressure at the shell side
Δp	pressure difference over the membrane ($p_h - p_l$)
$\bar{p}$	mean pressure ($1/2(p_h + p_l)$)
sccm	standard cubic centimetres per minute: (cm^3/min STP)
WHSV	weight hour space velocity (mass [g] of feed gas per hour per gram of catalyst)
X_i	molar ratio of component i
Y	yield of the reaction

Greek symbols

α_0	permselectivity
α_{KN}	Knudsen separation factor
Φ	gas flux through the membrane
σ	selectivity of the reaction
ξ	conversion of the reaction

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