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Comparison of different catalysts in the membrane-supported dehydrogenation of propane

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Dedicated to Prof. Jens Weitkamp on the occasion of his 60th birthday.

Abstract

Dehydrogenation of propane is studied in a high temperature packed bed catalytic membrane reactor with a hydrogen-selective silica membrane. The silica membrane is prepared by a two-step sol–gel process. The removal of hydrogen in the membrane reactor results in higher propane conversion and higher propene yields in comparison to an equivalent fixed-bed reactor. Unfortunately, as a result of the H_2 removal coking is favoured in the membrane reactor. Therefore, the higher propene yields are found only for the first 100–120 min time on stream. However, the lower selectivity of the membrane reactor due to coking is compensated to some extend by a reduced hydrogenolysis. Two commercial dehydrogenation catalysts of different activity were tested in the membrane reactor: Cr_2O_3/Al_2O_3 and Pt–Sn/Al_2O_3. The two catalysts show a different activity, coking, and regeneration behaviour in the membrane-supported propane dehydrogenation.

Keywords: Silica membrane; Propane dehydrogenation; Membrane reactor

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1. Introduction

In 2000 the two world-wide most important technical processes for the dehydrogenation of propane were the UOP Oleflex^{TM} and the Catofin^{TM} processes with propylene capacities of about 900,000 and 250,000,000 t Kg per year, respectively [1]. Whereas in the Catofin^{TM} process Cr_2O_3/Al_2O_3 is used as catalyst, in the UOP Oleflex^{TM} it is Pt–Sn/Al_2O_3. Both processes work at temperatures above 550 °C [2]. The relative high propane conversions in the Catofin^{TM} process between 48 and 65% per pass are achieved by applying reduced pressure of 0.3–0.5 bar. However, under these conditions severe coking is observed and the catalyst has to be regenerated in short-time intervals. The time for one cycle “reaction–regeneration” is relative short and lasts usually only 15–30 min [1]. In the case of the UOP Oleflex^{TM} process, the coking is reduced by the addition of hydrogen to the feed [2] which results in a cycle duration of about 7 h. Unfortunately, the addition of hydrogen reduces the propane conversion in the UOP Oleflex^{TM} process to about 40% for thermodynamic reasons.

The innovation potential of membrane reactors to support a catalytic reaction is described in some recent reviews [3–6]. For a large number of equilibrium-controlled dehydrogenations the conversion can be increased by the selective removal of H_2 through H_2-selective membranes. By using a H_2-selective membrane, it should be possible to reduce the temperature of a catalytic dehydrogenation. Another advantage of a membrane reactor can be the

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integration of reaction and separation in one apparatus. The three main demands on the membrane are [3]: (i) reasonable separation factors (>5), (ii) high hydrogen fluxes, and a (iii) long-time stability of the membrane material under technical conditions.

In principle two different H_2-selective membrane types can be used in a dehydrogenation membrane reactor: dense Pd/Ag alloy membranes and microporous metal oxide membranes. The dense Pd/Ag alloy membranes show the advantage that the permeated hydrogen is of sufficient purity for its further use without additional purification steps. However, the capital costs of Pd containing membranes are determined by the Pd price of about 17,000 € /kg which results in Pd costs of about 1200 € /m^2 on a smooth and of about 2000 € /m^2 on a rough support for a 6 μm thick Pd layer. Quite different statements are given on the stability of Pd/Ag alloy membranes in the presence of hydrocarbons [3,6–9].

Microporous metal oxide membranes can be divided into XRD amorphous and the crystalline zeolite membranes. Among the zeolite membranes mainly the MFI type membranes were used so far successfully for H_2 separation. Noble and co-workers [10] achieved a separation factor α for H_2/*iso*-butane mixtures of 12–15 with H_2-permeances of 0.032 m^3/m^2 hbar at 250 °C. Separation factors of 7–9 have been reported for a H_2/*iso*-butane mixture at 200 °C by Moulijn and co-workers [11]. In H_2/*iso*-butane separation experiments Dalmon and co-workers [12] obtained a separation factor $\alpha = 25$ at 450 °C with H_2-permeances of about 0.011 m^3/m^2 hbar. In another paper Dalmon and co-workers [13] found for high sweep to feed ratios H_2/*iso*-butane separation factors of 70 at 500 °C.

The prominent representative of the XRD amorphous metal oxide membranes are H_2-selective SiO_2 membranes which can be prepared by CVD [14–16] as well as by the sol–gel technique [17]. The sol–gel technique allows the preparation of SiO_2 membranes with permselectivities H_2/other components >1000 [18]. Spraying hot colloidal sols on hot supports at 160–180 °C represents a sophisticated coating technique which is characterised by a quick drying giving narrow pore systems [19]. Both sol–gel techniques using either hot or cold sols give highly H_2-selective membranes. Since these membranes were tested so far to $T < 300$ °C only, it remains open if these membranes are suitable for the propane dehydrogenation in a membrane reactor above 500 °C.

SiO_2 sol–gel membranes become high temperature stable if they are prepared by a two-step sol–gel process. In this technique, the hydrolysis of the starting Si-source (usually tetraethylorthosilicate, TEOS) and the condensation are decoupled and take place at different pH [20]. This two-step sol–gel process varying the pH is based on a concept developed by Brinker et al. [21,22].

Propane dehydrogenation in membrane reactors was tested using the above named H_2-selective SiO_2 sol–gel, SiO_2 CVD and Pd/Ag membranes [9,23–27]. In membrane reactors often a faster coking of the catalyst was observed in comparison with the classical fixed-bed reactor without H_2 removal. As a result, the propene selectivity in the membrane reactor was found to be lower than in the classical fixed-bed reactor. In a recent paper by Wolfrath et al. [28], the influence of the geometry of the catalyst arrangement on the propene selectivity was studied. By the use of the Pt–Sn/Al_2O_3 catalyst arranged in the shape of filaments, the propene selectivity could be increased from 88 to 93% but the propane conversion drops below the thermodynamic equilibrium after about 50 min.

In a former paper, we have reported on the influences of the membrane quality and reaction engineering parameters (sweep gas, WHSV) [20]. In this paper, we focus on the interplay of catalyst and membrane.

2. Experimental

2.1. Membrane preparation

Ceramic γ-alumina ultrafiltration membranes (pore size: 5–6 nm) on tubular supports of asymmetric structure (length 300 mm, inner/outer diameters approx. 7/10 mm, from the Hermsdorfer Institut für Technische Keramik, hitk, Hermsdorf, Germany) have been used as supports.

For gas separation experiments of H_2/C_3H_8 mixtures, the pores of the ultrafiltration membranes have to be narrowed to a size <0.43 nm (kinetic diameter of propane/propene). In this paper, we applied the sol–gel technique for this pore narrowing. It is known that the fluxes and selectivities of metal oxide membranes are strongly affected by the parameters of the sol–gel process. In particular, the degree of branching of the polymeric metal oxides turned out to be very important for the design of the pore sizes. Furthermore, it is known that lowly branched inorganic polymers lead to gel layers with a smaller mean pore size [29–32].

SiO_2 polymer sols were prepared by acid catalysed hydrolysis of tetraethoxysilane (TEOS) in alcoholic solution. The strongly acid starting sol ($pH < 1.0$) was diluted for dip-coating with pure ethanol or an ammonia/ethanol solution. These solutions with different pH were used for dip-coating to produce a silica layer on the γ-alumina ultrafiltration support. The polymeric SiO_2 sol was sucked into the vertically positioned tubes by means of reduced pressure. At the inner wall of the support tube the gel layer forms. After a defined contact time of a few seconds, Argon was slowly dosed and—following gravity—the sol flow out of the tube with a defined velocity. After drying at ambient temperature for 20 h, the membranes were calcined at 600 °C. Further details about the membrane preparation and characterisation are given in Ref. [20].

2.2. Catalytic dehydrogenation of propane

Propane was catalytically dehydrogenated on commercial Cr_2O_3/Al_2O_3[1] and Pt–Sn/Al_2O_3[2] catalysts at temperatures between 500 and 535 °C. More detailed information of the membrane reactor is given in Ref. [33] and Fig. 1.

The pelletized catalyst (3 g) was contained on the tube side of the membrane. The H_2 permeated through the SiO_2 membrane and was transported by the sweep gas N_2 into the GC. The sweep:feed ratio was between 5 and 6.7. The coked catalyst was regenerated at 450 °C with 3% oxygen in nitrogen over 14 h without removing the catalyst from the membrane tube.

As reference experiment to the packed bed catalytic membrane reactor (MR) the reaction was carried out in a classical fixed bed (CFB) with an inert quartz tube of the same dimension as the tubular membrane. According to the finite H_2-selectivity of the membrane, in the membrane-supported dehydrogenation a certain amount of the sweep gas nitrogen enters from the shell side to the tube side of the membrane containing the feed and the catalyst. This undesired dilution of the feed by an inert gas leads to a conversion enhancement due to lower partial pressures of all components. This effect was simulated in the reference experiment in the CFB by adding the corresponding amounts of nitrogen to the feed.

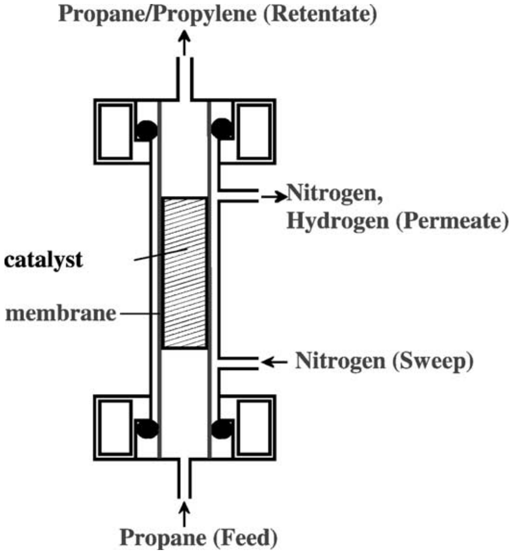

Fig. 1. Scheme of the membrane reactor.

3. Results

3.1. Membrane preparation

Fig. 2 shows a cross-section of the asymmetric tubular alumina membrane with the SiO_2 top layer. The γ-Al_2O_3 layer is completely covered by a very homogeneous nearly 100 nm thick SiO_2 gel layer. By applying a two-step sol–gel technique we could prepare H_2-selective SiO_2 membranes with H_2-permeances up to 25 m^3 (STP)/m^2 hbar and with permselectivities[3] H_2/C_3H_8 of up to 50 at 550 °C derived from single component permeances. For high feed and sweep flow conditions, all measured binary separation factors α H_2/C_3H_8 amount about 90% of the values of

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[1] Süd Chemie AG is thanked for providing this catalyst.

[2] Heraeus GmbH is thanked for supplying this catalyst.

[3] Following an IUPAC recommendation, the permselectivity is defined as the ratio of the single component permeances: terminology for membranes and membrane processes, IUPAC recommendations 1996, http://www.che.utexas.edu/nams/IUPAC/iupac.html.

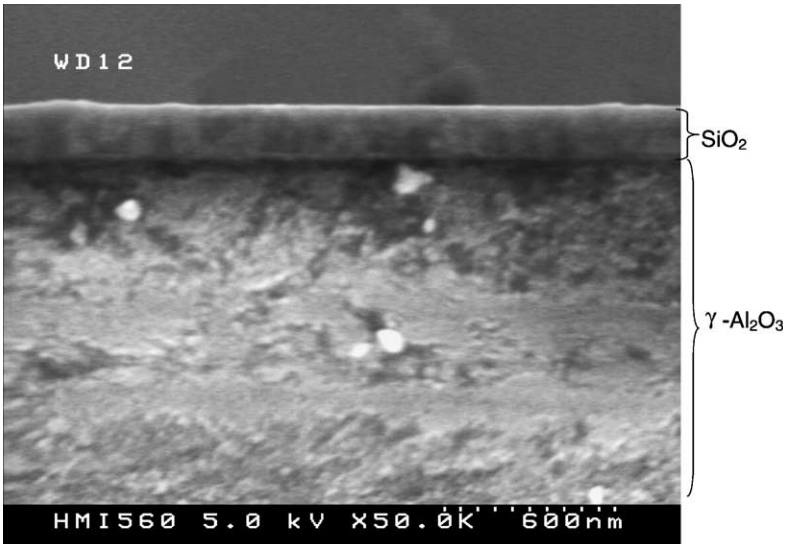

Fig. 2. Cross-section of the SiO_2 coated alumina support (membrane 2) with a 160 nm thick SiO_2 layer.

the permselectivities derived from the single component permeances.

The kinetic compatibility (see Table 1) of the interplay of catalyst and membrane required in our case either the use of (i) catalysts of higher activity or of (ii) membranes of lower permeance. According to a given geometry of the membrane (7 mm inner diameter, 30 cm length), the ratio of the membrane area (60 cm^2)/mass of catalyst (3 g) was $<20\,cm^2/g$. We have chosen the latter way (ii) and prepared membranes of lower permeance by a 3-fold SiO_2 sol–gel coating. As expected, the permeances decrease by the factor of 3–10 compared to the 2-fold coating. But surprisingly the permselectivities H_2/propane do not increase but decrease from 50 (2-fold coating) to about 20 (3-fold coating). We interpret this experimental finding by the overlap of fluxes through the regular membrane structure and through defect sites. Whereas the flow through the defect sites (pin holes, cracks) is not influenced by a further coating, mass transport through the regular SiO_2 membrane layer is reduced by an additional gel layer.

To fulfil the kinetic compatibility of the catalyst and the membrane, in this paper we have studied the following pairings of catalysts and membranes:

(a) The relative low active catalyst Cr_2O_3/Al_2O_3 was combined with a low flux SiO_2 sol–gel membrane

Table 1

Propene yield in the membrane reactor and mixture separation factor α as a function of the feed flow and WHSV, respectively, for the catalyst Cr_2O_3/Al_2O_3 and the SiO_2 sol–gel membrane with a H_2-permeance = 2.6 m^3 (STP)/m^2 hbar, C_3H_8-permeance = 0.11 m^3 (STP)/m^2 hbar using pure propane as feed, $T = 535\,^\circ C$, feed:sweep = 1:6.7

Feed flow (ml/min)	WHSV (h^{-1})	Propene yield (%) in MR	Binary mixture separation factor[a] α (H_2/C_3H_6)
10	0.37	28	6
20	0.73	26.8	14
30	1.1	26	19
40	1.47	22.2	22

[a] Following an IUPAC recommendation the separation factor α for the binary mixture hydrogen/other component was determined according to $\alpha = (x_{H_2,\mathrm{permeate}} : x_{\mathrm{component,permeate}})(x_{\mathrm{component,retentate}} : x_{H_2,\mathrm{retentate}})$. Terminology for membranes and membrane processes, IUPAC recommendations 1996, http://www.che.utexas.edu/nams/IUPAC/iupac.html.

with the single component flow characteristics: H_2-permeance = 2.6 m^3 (STP)/m^2 hbar, N_2-permeance = 0.2 m^3 (STP)/m^2 hbar and C_3H_8-permeance = 0.11 m^3 (STP)/m^2 hbar (membrane 1).

(b) The more active catalyst Pt–Sn/Al_2O_3 was combined with a high flux SiO_2 sol–gel membrane with the single component flow characteristics H_2-permeance = 10.0 m^3 (STP)/m^2 hbar, N_2-permeance = 0.82 m^3 (STP)/m^2 hbar and C_3H_8-permeance = 0.58 m^3 (STP)/m^2 hbar (membrane 2).

In these two arrangements, the ratio of membrane area to gram catalyst was constant and amounted 20 cm^2/g.

3.2. Kinetic compatibility of membrane and catalyst

Table 1 illustrates the problem of the kinetic compatibility of membrane and catalyst. The catalyst reaches only for low WHSV <0.5 h^{-1} the thermodynamic propane equilibrium conversion of about 26% which gives propene yields >28%. The highest propene yield was obtained at the lowest feed flow of 10 ml/min. In contrast, the membrane exhibits its highest separation factors only at short residence times, i.e. for high feed flow and high WHSV. The reason for this is a remarkable slip of propane from the feed to the permeate side of the membrane. Therefore, despite high separation factors low propane concentration are found in the permeate.

This problem was discussed by Harold et al. [34] for the cyclohexane dehydrogenation reaction at 477 K. When porous membranes are used, the cyclohexane conversion passes through a maximum at middle permeation/reaction rate ratios from 10 to 30. This is because at high permeation/reaction rate ratios the conversion is negatively impacted by reactant losses.

There exist several solutions to solve the problem that the catalyst needs low WHSV and the membrane needs high WHSV for optimum operation:

- Optimisation of the reactor geometry, by enlarging the diameter of the membrane tube to increase the ratio of the catalyst mass to membrane area (in our case <0.05 g/cm^2).
- Reduction of the permeance of the membrane by additional sol–gel coatings.
- Adding inert gas (N_2) to the feed allows to operate the MR at low WHSV (which is optimum for the catalyst) and to have high feed streams and short contact times (which is optimum for the separation performance of the membrane).
- Developing a catalyst of higher activity.

3.3. Catalytic dehydrogenation of propane in MR and CFB

It can be seen from Fig. 3 that the initial propene yield is in the MR higher compared to the CFB. This holds true for both the co- and counter-current flow modes of the MR. However, the H_2 removal in the MR is linked to an increased coking of the catalyst and

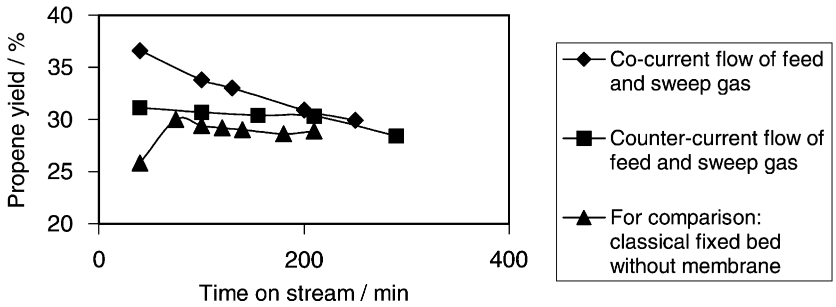

Fig. 3. Propene yield as a function of time on stream for two directions of the sweep gas relative to the feed stream in the membrane reactor (MR) and the classical fixed bed (CFB). Cr_2O_3/Al_2O_3, 535 °C, WHSV = 0.37 h^{-1}. Feed mixture of 10 ml/min propane + 20 ml/min N_2 (propane:nitrogen ratio of 1:2). In the MR 200 ml/min N_2 were used as sweep gas on the shell side. To simulate the undesired slip of the sweep gas from the shell to the tube side of the membrane, in the CFB experiments the feed was additionally diluted by 2 ml/min N_2 (propane:nitrogen ratio of 1:2.2).

after 200–300 min time on stream the performance of the MR and CFB become similar.

Fig. 3 shows that the propene yield in the MR is higher if feed and sweep gases stream in the co-current mode in comparison with the counter-current mode. If feed and sweep stream into the same direction (co-current) the H_2 partial pressure difference—and hence the driving force of permeation—is larger. In the co-current mode, the difference in the H_2 partial pressure between shell and tube side of the membrane is maximum at the reactor inlet. In the counter-current mode, the sweep gas enriched with hydrogen meets the alkane at the reactor inlet and H_2 back-diffusion from the shell to the tube side of the membrane can take place. It should be noted, when the permeation is high and the ratio sweep:feed is low, the co-current mode may result in a rapid equilibrium between the partial pressures in the permeate and retentate sides of the main permeating species. In the other part of the reactor, there is no more permeation of this species and only other components will permeate, leading to a decrease of the selectivity. In principle, this will not occur in the counter-current mode. In fact, the best sweep mode should depend on the ratio of the individual performances of both catalyst and membrane. In the following, only the co-current mode of the MR is studied. Figs. 4–6 show the corresponding propene selectivity and yield as well as propane conversion in the MR in comparison to the CFB.

3.4. *Catalytic dehydrogenation of propane applying the catalyst Cr_2O_3/Al_2O_3*

The propane conversion is in the MR by about 12% higher than in the CFB. However, the propene selectivity of the MR is about 10% lower than that of the CFB. Both findings are based on the removal of H_2. After 60 min time on stream, the propene yield is in the MR about 5% higher than in the CFB (see Fig. 4). However, this H_2 separation causes a faster coking of the catalyst which results in a reduced propane conversion. Therefore, in the MR the propene yield decreases with increasing time on stream faster than in the CFB.

3.5. *Catalytic dehydrogenation of propane applying the catalyst Pt–Sn/Al_2O_3*

By using the Pt–Sn/Al_2O_3 catalyst, we could find in the MR a propane conversion enhancement combined with an increased propene selectivity (see Fig. 5). The increase of the selectivity in the MR is due to the reduced hydrogenolysis of propane ($C_3H_8 + H_2 \leftrightarrow CH_4 + C_2H_6$) as a result of the H_2 removal. Whereas the methane content in the product stream was after 20 min time on stream >5 vol.% for the CFB, it was only <1 vol.% for the MR. This propene selectivity enhancement results together with a propane conversion increase of +4% in a propene yield of 22% in the MR

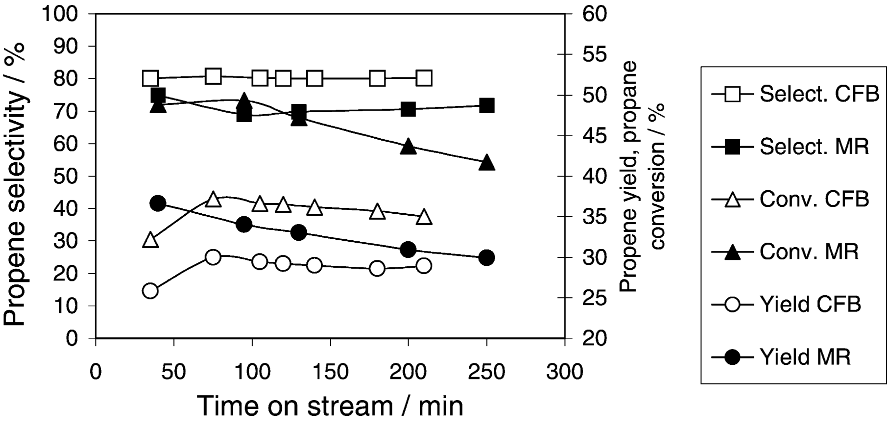

Fig. 4. Propene yield and selectivity as well as propane conversion in the membrane reactor (MR) and classical fixed bed (CFB). Cr_2O_3/Al_2O_3, WHSV = $0.37\,h^{-1}$, 535 °C. Feed mixture of 10 ml/min propane + 20 ml/min N_2 (propane:nitrogen ratio of 1:2). In the MR 200 ml/min N_2 were used as sweep gas on the shell side. To simulate the undesired slip of the sweep gas from the shell to the tube side of the membrane, in the CFB experiments the feed was additionally diluted by 2 ml/min N_2 (propane:nitrogen ratio of 1:2.2).

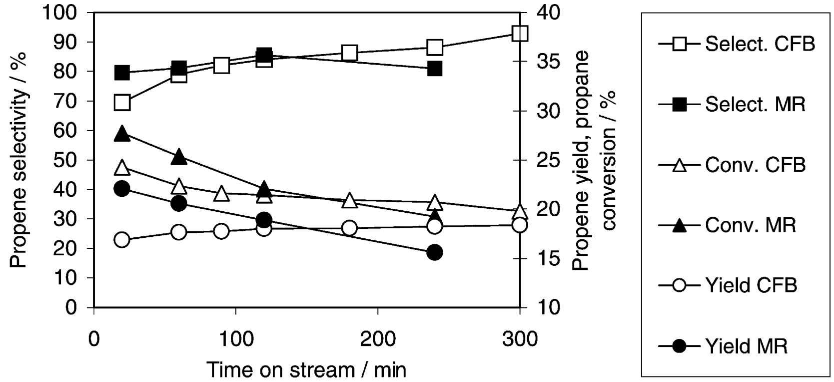

Fig. 5. Propene yield and selectivity as well as propane conversion in the membrane reactor (MR) and classical fixed bed (CFB). Pt–Sn/Al_2O_3, WHSV = 1.1 h^{-1}, 500 °C. Feed mixture of 30 ml/min propane + 20 ml/min N_2 (propane:nitrogen ratio of 3:2). In the MR 200 ml/min N_2 were used as sweep gas on the shell side. To simulate the undesired slip of the sweep gas from the shell to the tube side of the membrane, in the CFB experiments the feed was additionally diluted by 10 ml/min N_2 (propane:nitrogen ratio of 1:1).

in comparison with 17% in the CFB. In the CFB, the propene yield slightly increases with increasing time on stream according to the increasing propene selectivities. In the MR, the propene selectivity increases with time on stream as well over the first 100 min. However, this slight selectivity increase is overcompensated by the activity loss due to coking. So after 150 min time on stream the propene yields in MR and CFB are similar.

If the WHSV is increased from 1.1 to 2.2 h^{-1} the propene selectivity was found after 20 min to be higher in the CFB (92%) than in the MR (85%). There are different origins for the selectivity losses in the MR and CFB. In the MR coking reduces the selectivity, in the CFB hydrogenolysis into ethane/ethene and methane decreases the selectivity. Consequently, there is after 40 min no further increase of the propene yield in the MR (20%) compared to the CFB (16.7%). After 90 min time on stream the propene yield in the CFB exceeds that of the MR.

4. Discussion

The membrane reactors were operated under kinetic compatibility, i.e. the amount of H_2 generated by the

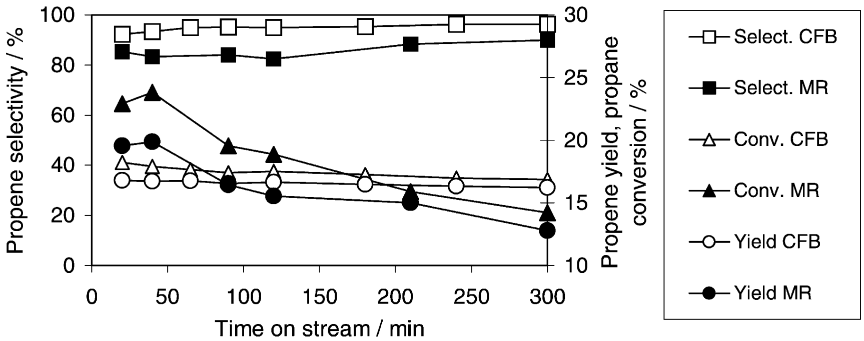

Fig. 6. Propene yield and selectivity as well as propane conversion in the membrane reactor (MR) and classical fixed bed (CFB). Pt–Sn/Al_2O_3, WHSV = 2.2 h^{-1}, 500 °C. Feed mixture of 60 ml/min propane + 20 ml/min N_2 (propane:nitrogen ratio of 3:1). In the MR 400 ml/min N_2 were used as sweep gas on the shell side. To simulate the undesired slip of the sweep gas from the shell to the tube side of the membrane, in the CFB experiments the feed was additionally diluted by 10 ml/min N_2 (propane:nitrogen ratio of 2:1).

catalyst per time has to permeate through the membrane. Comparing the MR and CFB reactors, an increase of the yield by about 5% is found for the MR. This relative low yield increase is comparable to the results of Dittmeyer et al. [6] on Pd/Ag membranes.

The two catalysts under study show following characteristics in the membrane-supported propene dehydrogenation:

Cr_2O_3/Al_2O_3:

- According to a relative low activity, this catalyst reaches the thermodynamic equilibrium conversion at 535 °C only for WHSV $<0.5\,h^{-1}$ (see Table 1). The kinetic compatibility of membrane and catalyst becomes problematic since a low WHSV results in a low contact time and a propane slip through the membrane is observed. Dilution of the feed with an inert gas—which can be easily recovered like steam—can solve the problem.
- The coked catalyst can be easily regenerated by oxidative treatment (3% O_2 in N_2 at 450 °C at 14 h).
- Membrane-supported dehydrogenation gives after 60 min time on stream at 535 °C a propene yield of 34% compared to 29% in the CFB (see Fig. 4). The propane conversions are 37% in the CFB and 49% in the MR (feed composition propane:inert gas = 1:2). However, the propene selectivity was found to be in the MR lower (70%) than in the CFB (80%).

Pt–Sn/Al_2O_3:

- The relative high activity of this catalyst allows WHSV up to $2.2\,h^{-1}$ at 500 °C which ensures a kinetic compatibility of catalyst and membrane.
- The main side reaction in the CFB is the hydrogenolysis. Up to 5 vol.% methane were found in the product stream of the CFB.
- In the MR, the hydrogenolysis is suppressed at medium WHSV ($1.1\,h^{-1}$) and the propene selectivity is in the MR (80%) higher than in the CFB (70%). The propene yield is 17% in the CFB and 22% in the MR (feed composition propane:inert gas = 1:1).
- At a technically interesting WHSV of $2.2\,h^{-1}$, the propene yield in the MR was found to be after 40 min time on stream substantially higher (21%) compared to the CFB (16%). According to a more pronounced coking in the MR, the propene yield drops and after 90 min operation time MR and CFB show a similar propene yield of 16% (see Fig. 6).
- If the reaction temperature is ≤500 °C the catalyst can be regenerated by a treatment in 2% O_2 in N_2 over 6 h at 500 °C. However, if the reaction temperature ≥535 °C, irreversible catalyst damage was observed under our reaction conditions applied and regeneration failed.

5. Conclusions

Comparing the membrane-supported dehydrogenation of propane at 535 °C in a membrane reactor and a classical fixed bed, in the average an increase of the propene yield by +5% is found for a medium WHSV of $1.1\,h^{-1}$.

For the two catalysts Cr_2O_3/Al_2O_3 and Pt–Sn/Al_2O_3 under study, a faster coking was observed in the membrane reactor. In the case of the Pt–Sn/Al_2O_3, the hydrogenolysis of propane into methane and C_2-species is reduced in the membrane reactor. The latter effects compensates to some extent the selectivity drop in the membrane reactor due to strong coking.

Membrane-supported catalysis needs a special catalyst development. The catalyst is expected to be coking resistant at extended residence times and highly selective. Modifications of the catalyst to suppress side reactions could result in an activity loss. The catalyst development should be based, therefore, on the catalyst Pt–Sn/Al_2O_3 rather than on Cr_2O_3/Al_2O_3 since the Pt catalyst shows a higher activity. Even catalysts which show under conventional conditions in the classical fixed bed extended hydrogenolysis can be involved in the development of catalysts for a membrane-supported dehydrogenation.

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