Oxidative Dehydrogenation of Propane in a Perovskite Membrane Reactor with Multi-Step Oxygen Insertion

Oliver Czuprat, Steffen Werth, and Jürgen Caro
Institute for Physical Chemistry and Electrochemistry, Leibniz Universität Hannover, Hannover 30167, Germany

Thomas Schiestel
Fraunhofer Institute for Interfacial Engineering and Biotechnology, Stuttgart 70569, Germany

DOI 10.1002/aic.12158

A membrane reactor incorporating a hollow fiber with successive parts of oxygen permeable and passivated surface segments has been developed and was used for the oxidative dehydrogenation (DH) of propane. This membrane geometry allows a controlled oxygen feeding into the reactor over its axial length. In the oxidative DH, the thermodynamic limitation of propane DH can be overcome. By using this novel hollow fiber membrane reactor with a Pt/Sn/K DH catalyst, oxygen separation and propene formation could be established even at temperatures as low as 625°C with long-term stability. Combining the hollow fiber membrane and the DH catalyst, the highest propene selectivity of 75% was observed at a propane conversion of 26% and 625°C whereas the best propene yield of 36% was obtained at 675°C (48% propene selectivity). The performance of this reactor is evaluated by applying various reaction conditions. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2390–2396, 2010
Keywords: membrane reactor, oxidative dehydrogenation, propane dehydrogenation, oxygen transporting membrane, perovskites

Introduction

The demand for olefins, especially propene, is expected to increase significantly in the near future. Propene was the first petrochemical raw material to be employed on an industrial scale and is important for the production of polymers, mainly for the production of polypropylene, but also in the production of cumene, acrylonitrile, and acrylic acid/acrolein or propylene oxide.[1] In 2002, approximately 61% of propene production was via steam cracking and 34% was obtained by catalytic cracking. To cover the continuously increasing demand for propene, it was also necessary to generate about another 3% by catalytic dehydrogenation (DH).[2] An increase in the share of the catalytic DH of propane in the overall production of propene can be expected.

A number of technologies are available commercially for the DH of propane to propene: these include Oleflex developed by UOP (Des Plaines, IL); Catofin developed by Air Products and Chemicals (Allentown, PA); and Uhde's STAR developed by Phillips Petroleum (Bartlesville,[3] OK). These processes differ in their modes of operation, the DH catalyst, and the methods of catalyst regeneration.[1] The Uhde STAR process achieves a propene yield of 35.6% per pass at a propane selectivity of 89%. The temperature range inside the reactor which is operated discontinuously (7 h operation, 1 h regeneration) is between 570 and 590°C at 5 bar.[2]

One concept to overcome the thermodynamic limitation of propane conversion is the oxidative DH of hydrocarbons (ODH), where alkane and oxygen are co-fed and give rise to the olefin and water. The Gibbs free energy of the formation of water (–228.7 kJ mol^{-1} at room temperature) compensates

---

Correspondence concerning this article should be addressed to O. Czuprat at oliver.czuprat@pci.uni-hannover.de.

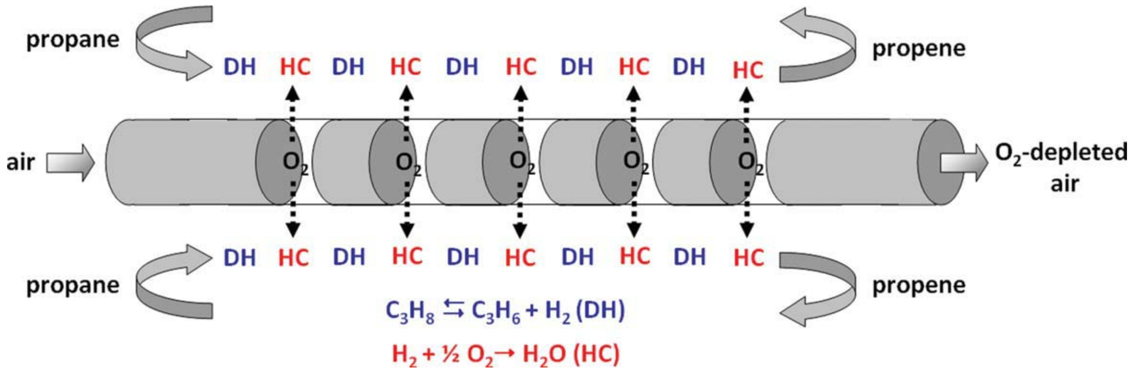

Figure 1. Scheme of the membrane reactor for the stepwise oxidative dehydrogenation of propane with a sequence of dehydrogenation (DH) and hydrogen combustion (HC).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

the Gibbs free energy of the endothermic DH of propane ($+124.3$ kJ mol^{-1}). Pioneering work was done by Imai and Jan on the DH of low alkanes.[4]

The main problem encountered in propane ODH is the presence of the consecutive reaction of olefin combustion, e.g., deep oxidation into carbon dioxide and water as well as partial oxidations or thermal cracking at higher reaction temperature that rapidly decreases the propylene yield when the conversion of the alkane is increased. The best yields reported in the co-feed method are lower than 30% with propane conversions lower than 40% which is still insufficient for technical applications. The best performance (24% propene yield) has been obtained with non-reducible alkali earth metal oxides at 650°C whereas the addition of lithium increased selectivity from 40% to 70% at low conversion.[5]

One way to retain a high selectivity at high conversions is a repeated DH and hydrogen combustion in a reactor. In this case, the initial catalytic alkane DH occurs in a first reaction zone. The product is then fed to a second reaction zone in which the major part of the produced hydrogen is burnt with oxygen. A repeated nonoxidative conventional DH of the remaining alkane occurs in a subsequent reaction zone, and then a repeated addition of oxygen burns off the hydrogen and so on. Comprehensive investigations of this concept were carried out, e.g., by Grasselli et al. using a solid oxygen carrier.[6]

The use of membranes is an interesting alternative to solid oxygen carriers in order to dose oxygen at a reduced average concentration to the reaction zone avoiding local hot spots and increasing selectivity. Additionally, high temperature oxygen-permselective membranes feed activated oxygen species leading to a different catalytic behavior than under conventional hydrocarbon/oxygen co-fed operations. Wang et al.[7] investigated the oxidative DH of propane (ODP) in a dense tubular $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane reactor. The propene selectivity was 4% at 23% conversion compared to 15% propene selectivity achieved under identical conditions in the fixed-bed reactor.

In contrast, the geometry of a hollow-fiber membrane offers a significantly higher ratio of membrane surface area per reactor volume and provides continuously active lattice oxygen. Recently, Wu et al.[8] reported the use of an asymmetric alumina hollow fiber with an outer Pd/Ag catalytic layer as an extractor membrane for hydrogen in the catalytic DH of propane. An initial propane conversion of 42% was achieved, but serious coke deposition on the catalytic surface led to a decrease in activity soon. Systems using dense perovskite hollow fiber membranes have been presented by our group, e.g., for the direct decomposition of nitrous oxide to nitrogen by in situ oxygen removal,[9] the simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane[10] and recently the multi-step oxidative DH of ethane (ODE).[11,12]

In this publication, we present the use of a dense mixed oxygen ion and electron conducting perovskite hollow fiber membrane of the composition $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ, $x + y + z = 1$) for the ODP with and without employing a DH catalyst. To the best of our knowledge, it is the first time that the ODP has been investigated with a perovskite hollow fiber membrane. It is an advantage of our BCFZ hollow fiber that it shows sufficient oxygen flux and stability at temperatures $\ll$800°C.[12] Additionally, steam is fed on the hydrocarbon side of the membrane in order to lower the partial pressure of propane as well as reducing coke deposition.

Most probably, two mechanisms occur simultaneously. As presented for the ODE, in our concept the DH of propane

$$C_3H_8 \leftrightarrows C_3H_6 + H_2 \tag{1}$$

occurs in a first reaction zone without addition of oxygen followed by the selective combustion (SC) of hydrogen

$$H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O \tag{2}$$

with oxygen delivered through the membrane (Figure 1).

Parallel, a direct oxy-DH of the propane or of the abstracted hydrogen at the perovskite surface following a Mars and van Krevelen mechanism takes place. To be supportive of this sequence of reactions, the membrane is divided into passivated and nonpassivated segments for oxygen permeation. This stepwise reaction can retain high selectivities and conversions beyond the thermodynamic equilibrium can be obtained. Furthermore, no regeneration of the reactor is required since no coke deposition could be observed.

In the following, different reactor set-ups with and without DH catalyst and oxygen supply via the hollow fiber membrane at different reaction conditions will be compared.

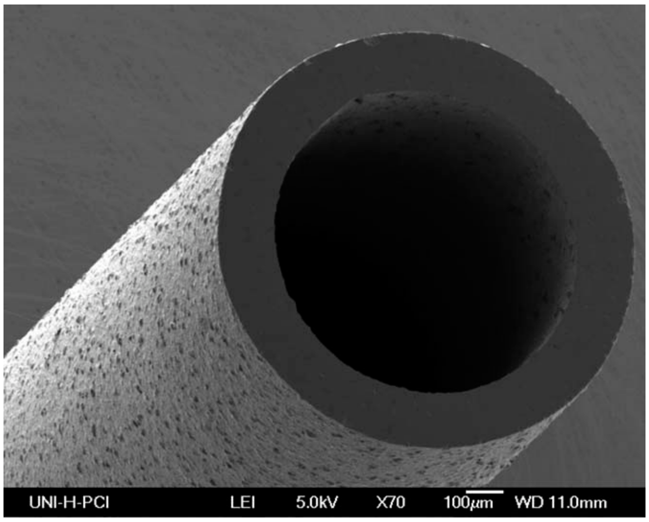

Figure 2. $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ, $x + y + z = 1$) hollow fiber membrane obtained by spinning at the Fraunhofer Institute for Interfacial and Biotechnology Stuttgart.[13]

Experimental

Preparation of the hollow fibers

The fabrication of the hollow fiber membrane of the composition $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ, $x + y + z = 1$, Figure 2) is described elsewhere.[13] The fibers with an outer diameter of ~1.1 mm and a wall thickness of ~0.14 mm were coated with gold paste (C 5754 B, Heraeus) and sintered at 950°C for 5 h to obtain five permeation zones (each 2-cm long) alternating with passivated areas (each 2-cm long, Figure 3). This procedure was repeated three times to ensure a leak-proof gold layer.

Studies in the hollow fiber membrane reactor

For the ODP, propane (99.5%) diluted with steam and helium (99.996%) was fed to the shell side of the membrane, while synthetic (C_xH_y-free) air or oxygen (99.9996%) diluted with helium was fed to the core side. All gas flows were controlled by mass flow controllers (Bronkhorst Hi-Tech). The gases at the exit of the reactor were analyzed by a gas chromatograph (Agilent Technologies, HP 6890) equipped with a Carboxen 1000 column (Supelco). Concentrations of C_3H_8, C_3H_6, C_2H_6, C_2H_4, CH_4, CO, CO_2, H_2, N_2, and O_2 were determined by calibration against standard gases. The absolute flow of the effluents was determined by using neon (99.995%) as an internal standard. All data points collected in this work were taken at steady-state conditions which were obtained after 1-3 hours. For experiments using the DH catalyst (PDH-964, BASF), the BCFZ hollow fiber was inserted into a porous alumina tube (outer diameter ~2.2 mm, wall thickness of ~0.4 mm) to avoid direct contact with the catalyst. The latter was milled in a mortar; a sieve fraction between 10 and 500 μm was sieved out and a portion of 0.25 g was dispersed between the inner porous alumina tube and the outer dense alumina tube (Figure 3).

Results and Discussion

Conventional thermal dehydrogenation without and with oxygen supply via BCFZ hollow fiber membrane

Figure 4 shows as a reference case the propane conversion, product selectivities as well as propene yields in our

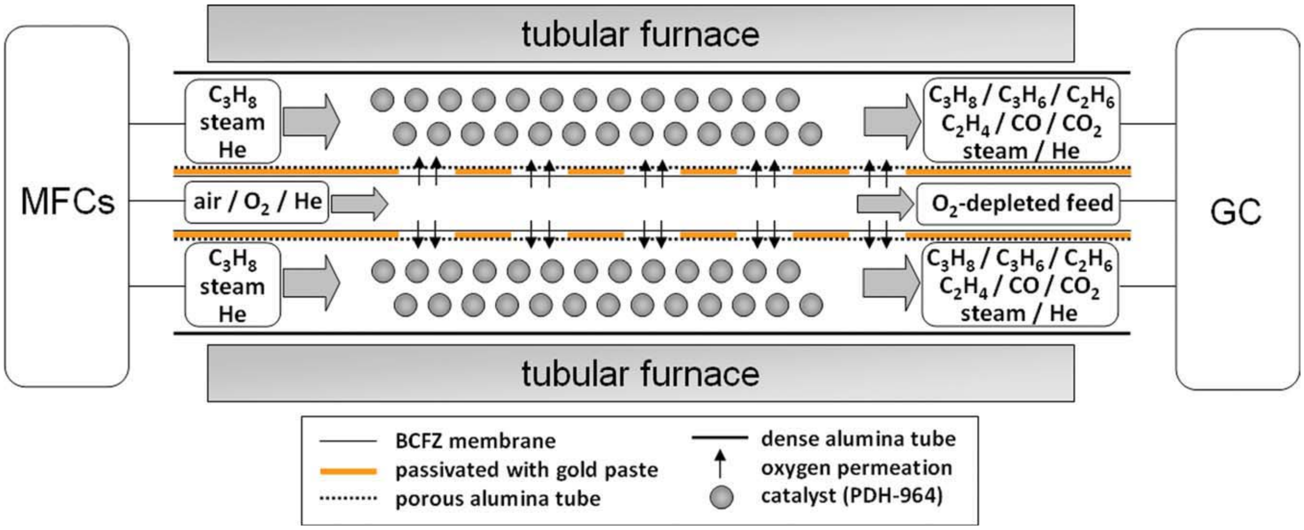

Figure 3. Schematic drawing of the reactor set-up and an incorporated multi-step BCFZ hollow fiber with five active zones for ODP.

At both ends 6 cm of the 30-cm long fiber were coated with gold. The inner 18 cm of the fiber were alternately passivated over 2 cm with and without gold thus forming five active zones for oxygen permeation, each 2-cm long. The active surface area for the multi-step oxygen permeating BCFZ hollow fiber is 2.2 cm^2 with a total oxygen permeable length of 10 cm. The dehydrogenation catalyst was dispersed between the outer dense alumina tube and the fiber, which was inserted into a porous alumina tube. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

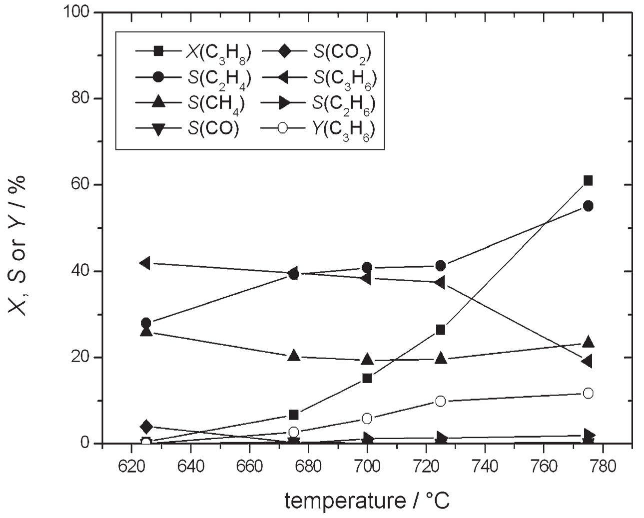

Figure 4. Reactor performance for the conventional thermal propane dehydrogenation (without oxygen addition and no catalyst).

Propane conversion and product selectivities as a function of the temperature (5 mL_N min^{-1} propane, 10 mL_N min^{-1} steam, and 35 mL_N min^{-1} helium).

reactor without oxygen supply and without any catalyst as a function of the temperature. A higher temperature leads to an increase in propane conversion, but also to a drop in propene selectivity due to augmented cracking of hydrocarbons to ethene and methane. As the increase in propane conversion at the same time is higher than the decrease in propene selectivity, the propene yield rises with higher temperature.

According to a homogeneous gas phase reaction or wall reactions, the propene yield at 625°C is around 0.3%, whereas at 725°C already a 10% yield is obtained. The overall olefin selectivity ranges from ca. 50% to 80%.

By supplying oxygen separated from air via the BCFZ hollow fiber membrane into the reactor using no DH catalyst, the propane conversion and propene yield could be enhanced significantly over the entire observed temperature range at a slightly lowered propene selectivity (Figure 5) compared to the pure thermal DH in the empty reactor (Figure 4). For example, at 675°C using the membrane reactor the obtained propene yield is almost four times higher than without oxygen supply. The higher the oven temperature, the higher the oxygen flux through the membrane according to the Wagner equation. Accordingly, more hydrogen can be burnt off, shifting the equilibrium towards the desired product.

For achieving good selectivities in our reactor, the kinetic compatibility between the reaction rates of the hydrogen forming DH step and the amount of permeated oxygen is essential.

The latter can be influenced by either (i) the ratio of active membrane surface to passivated membrane surface, by (ii) varying the temperature or (iii) the oxygen partial pressure on the core side of the membrane. As we can see in Figure 6, by decreasing the oxygen concentration on the core side of the membrane—and therefore lowering the propane conversion—the propene selectivity could be increased, especially in the range of oxygen concentrations below 20%.

For an industrial application of our membrane reactor, higher concentrations of propane/steam in the feed are more economic and desirable than those presented in the experiments so far. At a total propane and steam concentration of 10% in the feed, a propane conversion of approximately 60% at 21% propene selectivity is observed (Figure 7). By increasing the hydrocarbon/steam concentration, the propane conversion decreases continuously down to 10% for an undiluted feed. Above a total propane and steam concentration of 50% in the feed, the propene selectivity remains constant at 30% which seems to be the intrinsic selectivity of the reactor at these specific reaction conditions.

Conventional catalytic dehydrogenation without and with oxygen supply via BCFZ hollow fiber membrane

Using a DH catalyst in a fixed bed without oxygen supply through a BCFZ hollow fiber membrane, the propane conversion is enhanced over the total temperature range (Figure 8) compared to the blank reactor (Figure 4). Except the highest investigated temperature of 775°C, also the propene selectivity is higher than without using the catalyst.

By feeding oxygen via the hollow fiber membrane into the catalytic reactor, the propane conversion could be increased in the whole observed temperature range between 625°C and 775°C (Figure 9). For the membrane reactor an improved propene yield with a maximum at 725°C is found which equals an increase of around 50% in propene yield of the catalytic DH without oxygen supply (Figure 8).

As shown for the reactor containing only the hollow fiber membrane (Figure 6), the amount of permeated oxygen can be influenced by varying the oxygen partial pressure on the

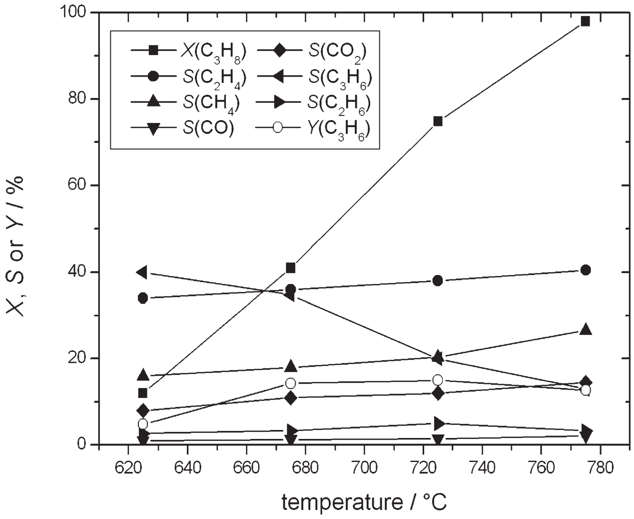

Figure 5. Temperature dependency of propane conversion, product selectivities, and propene yield of the membrane reactor with oxygen supply through the BCFZ hollow fiber and no dehydrogenation catalyst (shell: 5 mL_N min^{-1} propane, 10 mL_N min^{-1} steam, 35 mL_N min^{-1} helium; core: 50 mL_N min^{-1} air; 5 × 0.44 cm^2 effective membrane surface).

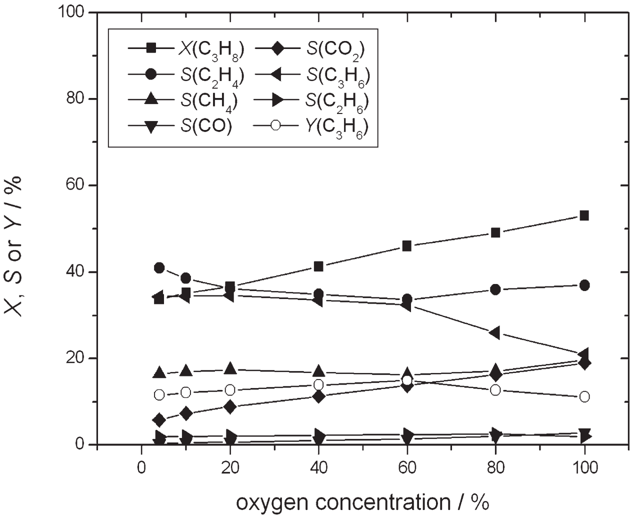

Figure 6. Effect of the oxygen partial pressure on the core side of the BCFZ hollow fiber membrane.

Propane conversion, product selectivities and propene yield as a function of the oxygen concentration at a total pressure of 1 bar at T = 675°C (shell: 5 mL$_N$ min^{-1} propane, 10 mL$_N$ min^{-1} steam, 35 mL$_N$ min^{-1} helium; core: F_{total} = 50 mL$_N$ min^{-1} oxygen diluted with helium; 5 × 0.44 cm^2 effective membrane surface).

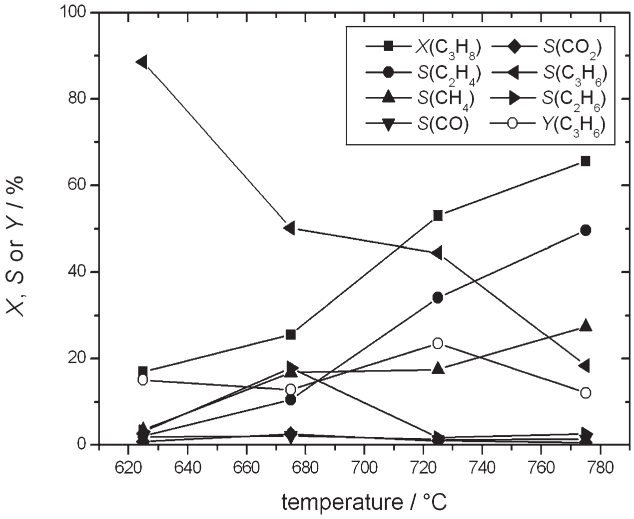

Figure 8. Reactor performance for the conventional catalytic propane dehydrogenation (without oxygen addition).

Propane conversion, product selectivities and propene yield as a function of temperature (5 mL$_N$ min^{-1} propane, 10 mL$_N$ min^{-1} steam, 35 mL$_N$ min^{-1} helium; 0.25 g of catalyst PDH-964; WHSV = 2.4/h).

feed side of the membrane (Figure 10). For example, when increasing the oxygen feed concentration from 10% to 20% while leaving the conditions on the permeate side untouched, the propane conversion can be increased from 51% to 75% while lowering the propene selectivity only from 52% to 46%.

Figure 11 shows the propane conversion and product selectivities as a function of the percentage of (propane + steam) in helium as feed on the shell side of the hollow fiber membrane. By decreasing this concentration to 10%, the

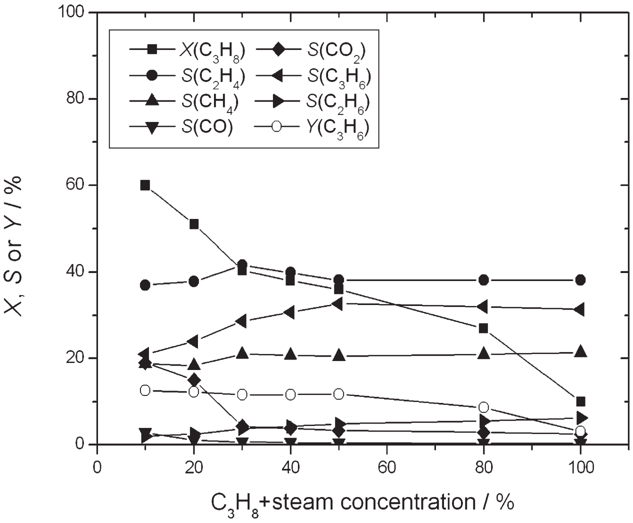

Figure 7. Effect of propane/steam concentration on propane conversion and product selectivities and propene yield in the BCFZ hollow fiber membrane reactor (shell: F_{total} = 50 mL$_N$ min^{-1}, steam to carbon = 2:3 diluted with helium; core: 50 mL$_N$ min^{-1} air; 5 × 0.44 cm^2 effective membrane surface; T = 675°C).

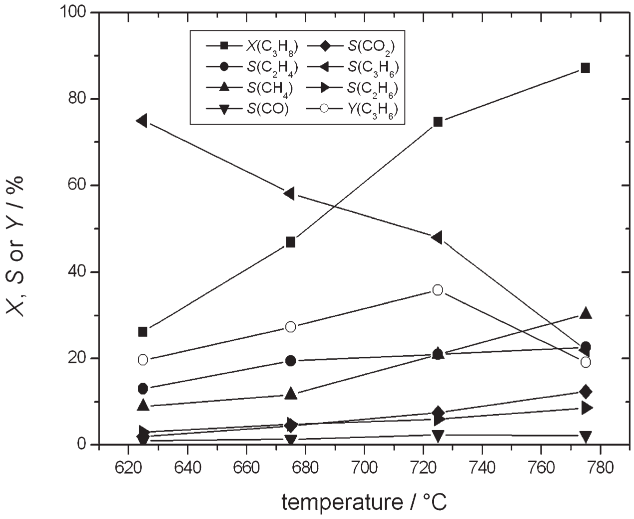

Figure 9. Impact of oxygen supply via a BCFZ hollow fiber membrane on the catalytic propane dehydrogenation.

Propane conversion, product selectivities and propene yield as a function of temperature (shell: 5 mL$_N$ min^{-1} propane, 10 mL$_N$ min^{-1} steam, 35 mL$_N$ min^{-1} helium; core: 50 mL$_N$ min^{-1} air; 5 × 0.44 cm^2 effective membrane surface; 0.25 g of catalyst PDH-964; WHSV = 2.4/h).

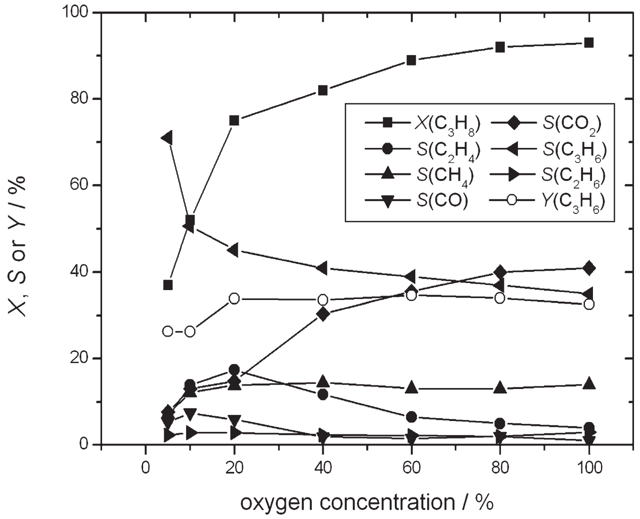

Figure 10. Interplay of oxygen partial pressure on the core side on propane conversion, product selectivities and propene yield (shell: 5 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ propane, 10 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ steam, 35 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ helium; core: F_{total} = 50 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ oxygen diluted with helium; 5 × 0.44 $\mathrm{cm^2}$ effective membrane surface; 0.25 g of catalyst PDH-964; *WHSV* = 2.4/h; *T* = 675°C).

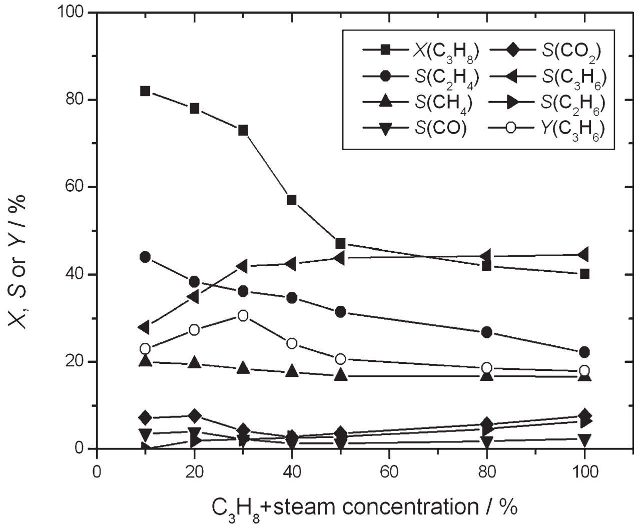

Figure 11. Effect of (propane + steam) concentration in helium on propane conversion and product selectivities in the membrane reactor with oxygen supply via the BCFZ hollow fiber and dehydrogenation catalyst (shell: F_{total} = 50 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$, steam to carbon = 2:3 diluted with helium; core: 50 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ air; 5 × 0.44 $\mathrm{cm^2}$ effective membrane surface; 0.25 g of catalyst PDH-964; WHSV = 2.4/h; *T* = 675°C).

Table 1. Propane Conversion, Propene Selectivity and Propene Yield Using 20% Oxygen Concentration in the Gas Feed on the Core Side of the Membrane (ID 2 and 4) and a Pt/Sn/K Dehydrogenation Catalyst (ID 3 and 4) Compared to the Blank Reactor with No Oxygen Supply and No Dehydrogenation Catalyst (ID 1) (shell: 5 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ propane, 10 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ steam, 35 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$ helium; core: F_{total} = 50 $\mathrm{mL_N}$ $\mathrm{min^{-1}}$, 20% oxygen; 0.25 g of catalyst PDH-964; WHSV = 2.4/h; *T* = 675°C)

ID	Catalyst	Fiber	$X(C_3H_8)$/%	$S(C_3H_6)$/%	$Y(C_3H_6)$/%	Figures
1	–	–	6	40	2	4
2	–	x	41	35	14	5
3	x	–	26	50	13	8
4	x	x	74	45	34	10

propane conversion increases above 80% while the propene selectivity—as expected—drops to 28%. Most notably, if we feed only a mixture of propane and steam (no helium as a dilutant), the reactor gives rise to a propane conversion of 40% at 45% propene selectivity.

Table 1 gives an overview about the effects of the DH catalyst and the oxygen permeating BCFZ hollow fiber membrane on the propane conversion as well as propene selectivity and yield. The pure thermal DH in an empty reactor without catalyst and hollow fiber gives only 2% propene yield (Figure 4) at 675°C. By supplying oxygen via the hollow fiber membrane at the same temperature the propane conversion is enhanced significantly from 6% to 41% whilst the selectivity towards propene only drops from 40% down to 35% (Figure 5).

The use of only the DH catalyst leads to a comparable propene yield of 13% (at a lower propane conversion and higher propene selectivity). Combining the catalyst with the BCFZ hollow fiber membrane gives rise to an increase of around 2.5 times the propene yield versus only the catalyst or only the fiber inside the reactor (Table 1).

Combining the catalyst with our hollow fiber, at a conversion of 93% at 675°C a propene selectivity of 35% is

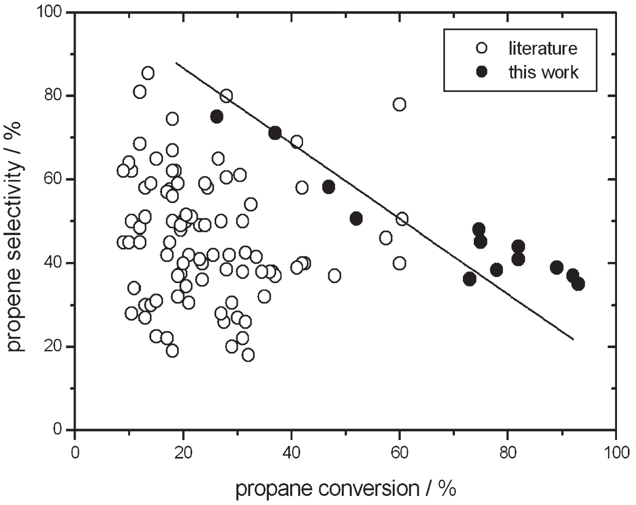

Figure 12. Propene selectivity as a function of propane conversion.

The data for various catalytic systems reported in the literature between 2000 and 2006 and giving alkane conversion higher than 10% were taken from.[5]

obtained (39% total olefin selectivity; Figure 10). The highest propene selectivity of 75% is observed at a propane conversion of 26% and 625°C (88% total olefin selectivity; Figure 9) whereas the best propene yield of 36% is achieved at 725°C (69% total olefin selectivity; Figure 9).

The oxygen permeable membrane supplies oxygen in successive stages into the reactor (i) burning off selectively the hydrogen from thermal DH and (ii) parallel the direct oxidation of propane/hydrogen by lattice oxygen of the perovskite takes place. Ongoing TAP experiments will provide a deeper insight into the molecular mechanisms. The membrane not only separates the hydrocarbon feed from oxygen but also avoids the need of an oxygen separation plant.

Our membrane reactor using a DH catalyst can compete with the best catalysts used in the co-feed mode of the ODP (Figure 12).

Conclusions

A membrane reactor for the oxidative DH of short chain hydrocarbons combining the conventional catalytic DH with the SC of the abstracted hydrogen is presented.

To attain kinetic compatibility between the rates of DH and oxygen supply via the $BaCo_xFe_yZr_zO_{3-\delta}$ perovskite hollow fiber membrane, certain parts of the hollow fiber have been passivated for oxygen transport by a gold coating.

Under our experimental conditions, the propene yield in the catalytic membrane reactor was twice the yield in the catalytic DH without oxygen supply.

The propene yield shows a maximum at 725°C and amount 36% (for 75% propane conversion and 48% propene selectivity). The total olefin yield ($C_2 + C_3$) amounts 69%.

Acknowledgments

The authors acknowledge the financial support of the project SynMem by the German Federal Ministry of Education and Research as well as BASF SE for providing the catalyst. Dr. Steffen Schirrmeister (Uhde GmbH) is thanked for the permit of publication.

Literature Cited

1. Eisele P, Killpack R. *Propene*. In: *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed. New York: John Wiley & Sons, Inc., 2001:1.
2. Caspary KJ, Gehrke H, Heinritz-Adrian M, Schwefer M. *Dehydrogenation of alkanes*. In: Ertl G, Knözinger H, Schüth F, Weitkamp J., editors *Handbook of Heterogeneous Catalysis*. Weinheim: Wiley-VCH, 2008:3206–3223.
3. TheUhde STAR Process, Oxydehydrogenation of Light Paraffins to Olefins. Uhde GmbH, 2009.
4. Imai T, Jan D-Y. European Patent 0 323 115, assigned to UOP, 1988.
5. Cavani F, Ballarini N, Cericola A. Oxidative dehydrogenation of ethane and propane: How far from commercial implementation? *Catal Today*. 2007;127:113–131.
6. Grasselli RK, Stern DL, Tsikoyiannis JG. Catalytic dehydrogenation (DH) of light paraffins combined with selective hydrogen combustion (SHC): I. DH → SHC → DH catalysts in series (co-fed process mode). *Appl. Catal. A*. 1999;189:1–8.
7. Wang H, Cong Y, Zhu X, Yang W. Oxidative dehydrogenation of propane in a dense tubular membrane reactor. *React Kinet Catal Lett*. 2003;79:351–356.
8. Wu Z, Hatim IMD, Kingsbury BFK, Gbenedio E, Li K. A novel inorganic hollow fiber membrane reactor for catalytic dehydrogenation of propane. *AIChE J*. 2003;49:3007–3017.
9. Jiang H, Wang H, Liang F, Werth S, Schiestel T, Caro J. Direct decomposition of nitrous oxide to nitrogen by in situ oxygen removal with a perovskite membrane. *Angew Chem Int Ed*. 2009;48:2983–2986.
10. Jiang H, Wang H, Werth S, Schiestel T, Caro J. Simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane in a hollow-fiber membrane reactor. *Angew Chem Int Ed*. 2008;47:9341–9344.
11. Czuprat O, Werth S, Schirrmeister S, Schiestel T, Caro J. Oxidative dehydrierung niederer Alkane in einem selektiven Membranreaktor mit gestufter Sauerstoffzugabe und in-situ-Wasserstoffoxidation. *Chem Ing Tech*. 2009;81:1591–1597.
12. Czuprat O, Werth S, Schirrmeister S, Schiestel T, Caro J. Olefin production by a multistep oxidative dehydrogenation in a perovskite hollow-fiber membrane reactor. *ChemCatChem*. 2009;1:401–405.
13. Schiestel T, Kilgus M, Peter S, Caspary KJ, Wang H, Caro J. Hollow fibre perovskite membranes for oxygen separation. *J Membr Sci*. 2005;258:1–4.

Manuscript received Oct. 7, 2009, and revision received Nov. 12, 2009.