Dehydrogenation of propane with selective hydrogen combustion:
A mechanistic study by transient analysis of products

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Abstract

By transient analysis of products (TAP) studies, the mechanism of the propane dehydrogenation on a Pt-Sn catalyst in a perovskite hollow fiber membrane reactor could be enlightened and optimum operation conditions for the catalytic membrane reactor could be identified. The interactions of H\textsubscript{2} and C\textsubscript{3}H\textsubscript{8} with the membrane and the catalyst in absence and presence of gas-phase oxygen with a submillisecond time resolution using \textsuperscript{18}O as isotopic traces were investigated. If the product mixture of the propane dehydrogenation comes into contact with the surface of the perovskite BaCo\textsubscript{x}Fe\textsubscript{y}Zr\textsubscript{z}O\textsubscript{3−δ} (BCFZ, x+y+z = 1) hollow fiber membrane, from this mixture the hydrogen is selectively combusted by lattice oxygen species of the perovskite. Under the steady state kinetic compatibility of hydrogen formation by propane dehydrogenation on the Pt-Sn catalyst and its combustion by perovskite lattice oxygen species, no non-selective molecular oxygen is released from the perovskite into the gas phase.
1 Introduction

Oxidative dehydrogenation of light alkanes to the respective olefins, e.g. propane to propene, is considered as a promising alternative to the catalytic non-oxidative dehydrogenation, since there is no equilibrium constraint of the conversion. However, the oxidative dehydrogenation in conventional reactors operating with oxygen and alkane co-feeding is not suitable for an industrial application due to poor olefin selectivity at high alkane conversions. Grasselli et al. [1,2] suggested a concept to overcome the thermodynamic limitation of the non-oxidative dehydrogenation of propane to propene by selective hydrogen combustion. According to this concept, propane is dehydrogenated over a Pt-Sn-containing catalyst followed by selective hydrogen combustion and again catalytic propane dehydrogenation. Sb$_2$O$_4$, In$_2$O$_3$, WO$_3$ and Bi$_2$O$_3$ supported on SiO$_2$ revealed the best activity for the hydrogen oxidation. The dehydrogenation and combustion can be performed in either separated reactors containing the respective catalysts or in one reactor loaded with a mixture of these catalysts. For the former process scheme, additional steps for separation of O$_2$ from N$_2$ or C$_3$H$_6$/C$_3$H$_8$ from N$_2$ are required, if pure oxygen or air is used for the selective hydrogen combustion, respectively. When using the one-reactor concept, the catalysts must be periodically regenerated. These both drawbacks can be avoided by applying dense perovskite ceramic membranes exhibiting high oxygen ionic and electronic conductivity for olefin synthesis [3,4]. Such membranes of the composition of BaCo$_x$Fe$_y$Zr$_z$O$_{3−δ}$ (BCFZ, $x+y+z=1$) are produced by the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB) in Stuttgart in hollow fibre geometry [5]. The group at the Leibniz Universität Hannover has intensively applied reactors made of these membranes for various reactions such as the direct decomposition of nitrous oxide [6] and nitric oxide [7] to nitrogen and oxygen in combination with syngas production from methane, the simultaneous production of hydrogen by thermal

The number of potential applications of these mixed ionic electronic conducting (MIEC) membranes continuously grows, but mechanistic studies of the ongoing catalytic reactions are rare. This fundamental knowledge is highly essential for developing new effective catalytic materials or for improving the existing ones as well as for the optimization of reactor operation. Recently, we demonstrated that the temporal analysis of products (TAP) reactor provided useful mechanistic insights for optimising ethane dehydrogenation to ethylene and methane oxidation to syngas in an oxygen-conducting perovskite BaCo$_x$Fe$_y$Zr$_z$O$_{3+δ}$ (BCFZ) membrane reactor [11]. In the present study, we extended this approach for analysing mechanistic aspects of previously investigated propane dehydrogenation with selective hydrogen combustion in the above membrane reactor containing a commercial Pt-Sn dehydrogenation catalyst [3]. The aim of this study was to identify reaction pathways responsible for the dehydrogenation and combustion. To this end, we investigated interactions of H$_2$ and C$_3$H$_8$ with the membrane and the catalyst in absence and presence of gas-phase oxygen with a submillisecond time resolution using $^{18}$O as isotopic traces.

2 Experimental

2.1 Membrane reactor for the multi-step dehydrogenation with selective hydrogen combustion

Figure 1 shows a scheme of the BCFZ perovskite membrane reactor for the multi-step dehydrogenation of propane with simultaneous hydrogen combustion. More details can be found in [3]. The fabrication of the perovskite hollow fiber membrane is described elsewhere [5]. 5 mL$_N$ min$^{-1}$ propane, 10 mL$_N$ min$^{-1}$ steam and 35 mL$_N$ min$^{-1}$ helium were fed on the shell side of the hollow fiber at 1 bar, while 50 mL$_N$ min$^{-1}$ synthetic air was applied on the core side at 1 bar. The total amount of Pt-Sn catalyst inside the reactor which was heated to 675 ºC was 0.25 g (WHSV = 2.4 h$^{-1}$).
2.2 *Transient experiments*

Transient experiments were performed in the TAP-2 reactor, a transient pulse technique operating in vacuum with sub-millisecond time resolution [12,13]. The crushed BCFZ perovskite membrane (70 mg, sieve fraction of 200-500 µm) or the Pt-Sn dehydrogenation catalyst (40 mg, sieve fraction of 200-500 µm) were packed within the isothermal zone of the quartz micro-reactor (40 mm length and 6 mm i.d.) between two layers of quartz particles of the same sieve fraction. Before transient experiments, the perovskite was pre-treated at ambient pressure in an oxygen flow of 20 ml min⁻¹ at 675 °C for 30 min. After the treatment, the perovskite was exposed to vacuum (10⁻⁵ Pa). A strong loss of oxygen observed upon perovskite exposure to vacuum conditions was recovered by¹⁶O₂ pulsing performed previous to the following transient experiments over the perovskite. Pulse experiments over the Pt-Sn catalyst were performed without any pretreatment.

In order to prove if lattice oxygen of the perovskite or adsorbed oxygen species participate in H₂ and C₃H₈ oxidation, single H₂/Xe = 1/1 or C₃H₈/Xe = 1/1 as well as simultaneous ¹⁸O₂/Ar = 1/1 and H₂/Xe = 1/1 (C₃H₈/Xe = 1/1) pulse experiments were performed at 675°C. The ability of the Pt-Sn catalyst to activate H₂ and C₃H₈ as well as to oxidize these components was probed by single H₂/Xe = 1/1 or C₃H₈/Xe = 1/1 and simultaneous ¹⁸O₂/Ar = 1/1 and H₂/Xe = 1/1 (C₃H₈/Xe = 1/1) pulse experiments at 675°C. In addition, multi-pulse experiments with H₂ were carried out at 675°C. In these experiments, a H₂/Xe = 1/1 mixture was repeatedly pulsed (in total ca. 200 pulses) over the perovskite and the catalyst.

In the performed experiments, ¹⁸O₂ (95-98%), ¹⁶O₂(5.0), H₂(5.0), C₃H₈ (3.5), Ar (5.0) and Xe (4.0) were used without further purification. Isotopically labelled oxygen was supplied by ISOCOM GmbH. Transient responses of feed molecules and reaction products were recorded at the reactor outlet using a quadrupole mass spectrometer (HAL RD 301 Hiden Analytical) at the following atomic mass units (AMUs): 36 (¹⁸O₂), 34 (¹⁸O¹⁶O), 32 (¹⁶O₂), 20 (Ar, H₂¹⁸O), 19 (H₂¹⁸O), 18 (¹⁸O₂, H₂¹⁶O), 17 (H₂¹⁶O), 2 (H₂), 40 (Ar), and 132 (Xe). For the H₂ multi-
pulse experiments, the responses repeated 50 times at the each AMU were treated without averaging. Otherwise, pulses repeated 10 times for each AMU were averaged to improve the signal to noise ratio. The concentration of feed components and reaction products was determined from the respective AMUs using standard fragmentation patterns and sensitivity factors.

3 Results and Discussion

The catalytic performance of the BCFZ hollow fibre membrane reactor for propane dehydrogenation in the presence and absence of oxygen flow through the membrane and with and without a Pt-Sn dehydrogenation catalyst has been previously reported [3]. The most relevant results are summarized in Table 1. These data are the basis of present mechanistic analysis. The perovskite showed low propane conversion and propene yield in the absence of the dehydrogenation catalyst and oxygen (ID 1 in Table 1). The yield was increased by a factor of 7 when oxygen was supplied through the membrane (ID 2 in Table 1). The increase is due to a growth in the propane conversion indicating the importance of oxygen for the propane dehydrogenation. A similar effect on the propene yield was achieved in the presence of the dehydrogenation Pt-Sn catalyst but in the absence of oxygen (ID 3 in Table 1). In this case, the propene selectivity increased, too. The performance of the membrane reactor was further improved, when propane was dehydrogenated in the presence of the Pt-Sn catalyst and oxygen supplied through the membrane (ID 4 in Table 1). It is important to highlight that the propene selectivity was very close to that in the test 3 but the propane conversion was approximately 3 times higher. This synergetic effect of the catalyst and oxygen was suggested to be due to selective hydrogen oxidation favouring non-oxidative propane dehydrogenation [3]. In order to deeper understand mechanistic origins governing the activity and selectivity of such reactor operation, we investigated C₃H₈ transformations and H₂ oxidation over the
perovskite and the Pt-Sn catalyst by transient analysis of products. The results obtained are presented and discussed below.

The interaction of \( \text{C}_3\text{H}_8 \) with the oxidized BCFZ perovskite and the as-received Pt-Sn catalyst was investigated at 675°C by means of single \( \text{C}_3\text{H}_8 \) (\( \text{C}_3\text{H}_8/\text{Xe} = 1/1 \)) pulse experiments. Typical transient responses of the observed carbon-containing products along with the response of the unreacted propane in the single \( \text{C}_3\text{H}_8 \) pulse experiments are plotted in Figure 2. It is clearly seen from this figure that the perovskite and the Pt-Sn catalyst differ in the reaction products. Moreover, the shapes of their transient responses are also dissimilar indicating that the mechanism and the kinetics of propane activation are different over the perovskite and the Pt-Sn catalyst. \( \text{C}_3\text{H}_6 \) and \( \text{CO}_2 \) were formed over the perovskite (Figure 2a). Since gas-phase \( \text{O}_2 \) was not present in the \( \text{C}_3\text{H}_8 \) pulse, these reaction products were formed by \( \text{C}_3\text{H}_8 \) oxidation with lattice oxygen of the perovskite. This is in agreement with our previous mechanistic study of ethane and methane oxidation over the same perovskite [11]. In contrast to the perovskite, no \( \text{CO}_2 \) but \( \text{H}_2 \) in addition to \( \text{C}_3\text{H}_6 \) was formed over the Pt-Sn catalyst (Figure 2b). With other words, the catalyst dehydrogenates propane to propene non-oxidatively. Moreover, the propane conversion was higher compared to that over the perovskite. The difference in the activity of these two materials agrees well with the results of steady-state experiments in the membrane reactor (ID 1 and 3 in Table 1).

In order to prove whether adsorbed oxygen species formed from gas-phase \( \text{O}_2 \) participate in the alkane activation, \( ^{18}\text{O}_2 \) (\( ^{18}\text{O}_2/\text{Ar} = 1/1 \)) and \( \text{C}_3\text{H}_8 \) (\( \text{C}_3\text{H}_8/\text{Xe} = 1/1 \)) were simultaneously pulsed as co-feed over the oxidized perovskite containing \( ^{16}\text{O} \) lattice oxygen. No carbon oxides \( \text{CO}_x \) containing \( ^{18}\text{O} \) were observed (not shown here). Therefore, we concluded that only lattice oxygen from the perovskite takes part in the formation of \( \text{CO}_2 \) under the transient conditions applied. When \( ^{18}\text{O}_2 \) and \( \text{C}_3\text{H}_8 \) were pulsed over the Pt-Sn catalyst, \( \text{C}^{18}\text{O} \) was observed as a reaction product (Figure 3). This means that adsorbed oxygen species activate the C-C bond in \( \text{C}_3\text{H}_8/\text{C}_3\text{H}_6 \) yielding \( \text{CO} \). These species catalyze also propane cracking to
ethylene (Figure 3). Taking the results of the transient experiments into account, a slightly lower propene selectivity in the membrane reactor in the presence of the Pt-Sn catalyst and oxygen flow through the membrane (ID 4 in Table 1) compared to the performance in the absence of the oxygen flow (ID 3 in Table 1) can be due to $\ce{C3H8/C3H6}$ conversion to $\ce{C2H4}$ and CO. Gas-phase $\ce{O2}$ in that case can be provided by the recombinative desorption of oxygen species diffused through the perovskite membrane.

Another important question to be answered was if the perovskite and the Pt-Sn catalyst are able to oxidize $\ce{H2}$ in absence and presence of gas-phase $\ce{O2}$. To this end, single $\ce{H2}$ ($\ce{H2/Xe} = 1/1$) as well as simultaneous $^{18}\ce{O2}$ ($^{18}\ce{O2}/\ce{Ar} = 1/1$) and $\ce{H2}$ ($\ce{H2/Xe} = 1/1$) pulse experiments were performed. The oxidized perovskite showed high activity towards $\ce{H2}$ oxidation in the absence of gas-phase $\ce{O2}$, i.e. lattice oxygen participates in this reaction. Based on the results of $\ce{C3H8}$ pulse experiments in Figure 2, it is concluded that $\ce{C3H8}$ and $\ce{H2}$ compete for the same active catalyst sites, i.e. lattice oxygen. As in the case of $\ce{C3H8}$ conversion, adsorbed oxygen formed from gas-phase $^{18}\ce{O2}$ does not participate in $\ce{H2}$ oxidation (the results are not shown for brevity). However, the perovskite shows different activity for the oxidation of $\ce{C3H8}$ and $\ce{H2}$. Typical transient responses of $\ce{H2}$ at the reactor outlet are presented in Figure 4. One can see that the outlet concentration of $\ce{H2}$ increases with increasing number in the $\ce{H2}$ pulses. Correspondently, the $\ce{H2}$ conversion decreases. This decrease can be explained by continuous consumption of lattice oxygen of the perovskite for $\ce{H2}$ oxidation. In other words, the more hydrogen is pulsed over the perovskite, the more lattice oxygen is removed from the lattice thus yielding to a decrease in the hydrogen combustion and an increasing hydrogen response signal. Such behaviour was not observed for $\ce{C3H8}$ oxidation. Moreover, the conversion of $\ce{H2}$ was higher than that of $\ce{C3H8}$.

In order to complete the mechanistic picture of propane dehydrogenation in the BCFZ perovskite membrane reactor for the multi-step dehydrogenation of propane with simultaneous hydrogen combustion, we analyzed the interaction of $\ce{H2}$ with the Pt-Sn catalyst
in absence and presence of gas-phase O\(_2\). Figure 5 compares the transient responses of H\(_2\) obtained upon H\(_2\) pulsing over the Pt-Sn catalyst and the perovskite. The very narrow shape of the H\(_2\) transient over the perovskite is due to irreversible H\(_2\) oxidation by lattice oxygen species. Contrarily, H\(_2\) interacts reversibly and probably dissociatively with the catalyst as concluded from the broad H\(_2\) response in Figure 5. Moreover, since the shapes of the H\(_2\) transients obtained in single H\(_2\) and simultaneous \(^{18}\)O\(_2\)-H\(_2\) pulse experiments are very similar, the presence of gas-phase O\(_2\) does not significantly influence the interaction of H\(_2\) with this catalyst. It should be also stressed that only tiny amounts of H\(_2\)\(^{18}\)O were detected in the latter experiments, i.e. the Pt-Sn catalyst is not active for H\(_2\) oxidation even in the presence of gas-phase O\(_2\).

4 Conclusion

The results of present transient and previous steady-state membrane reactor studies enabled us to develop the following mechanistic concept of propane dehydrogenation with selective hydrogen combustion in the BCFZ perovskite membrane reactor containing a commercial Pt-Sn dehydrogenation catalyst. Lattice oxygen species of the perovskite are highly active for combustion of H\(_2\), which is formed over the Pt-Sn catalyst via non-oxidative propane dehydrogenation. The H\(_2\) oxidation fulfills a double role: i) increasing non-oxidative propane conversion to propene and ii) increasing the reduction degree of the BCFZ perovskite. As demonstrated in our previous mechanistic analysis of ethane and methane conversion in the perovskite membrane reactor [11], high reduction degree of the membrane is favorable for selective conversions. That is to say, lattice oxygen species of the perovskite are responsible for selective propene and non-selective CO\(_x\) formation from propane.

If the rates of H\(_2\) and C\(_3\)H\(_8\) oxidation over the perovskite are slower than the diffusion rate of oxygen ions through the BCFZ membrane, gas-phase O\(_2\) can be formed on the shell side of
the membrane. Our transient analysis demonstrated that the Pt-Sn catalyst starts to convert propane to ethylene and carbon monoxide in the presence of gas-phase oxygen. As a result, the performance of the reactor will downgrade. Therefore, in order to selectively convert propane to propene in the reactor, the kinetic compatibility between the reaction rates of hydrogen production and its combustion over the perovskite is essential. The amount of oxygen permeated through the membrane can be tuned by varying oxygen partial pressure on the feed side of the membrane.

Acknowledgements

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References


Table 1  Propane conversion, propene selectivity and propene yield using synthetic air with 20% oxygen as feed on the core side of the BCFZ hollow fiber membrane (ID 2 and 4) with and without a Pt-Sn dehydrogenation catalyst. For comparison experiments in a fixed bed reactor (ID 3) and in the blank reactor without oxygen supply and dehydrogenation catalyst (ID 1). Experimental conditions: *shell side of the hollow fiber:* 5 mL$_N$ min$^{-1}$ propane, 10 mL$_N$ min$^{-1}$ steam, 35 mL$_N$ min$^{-1}$ helium; *core side:* $F_{\text{total}}$ = 50 mL$_N$ min$^{-1}$, 20% oxygen; 0.25 g of Pt-Sn catalyst; WHSV = 2.4 h$^{-1}$; $T$ = 675 °C.

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Figure captions

Figure 1  Scheme of the hollow fibre membrane reactor for the multi-step catalytic dehydrogenation of propane with selective hydrogen combustion.

Figure 2  Transient responses recorded after C₃H₈ (C₃H₈/Xe = 1/1) pulsing over (a) oxidized BCFZ perovskite and (b) as received Pt-Sn catalyst at 675°C.

Figure 3  Transient responses recorded after simultaneous pulsing of C₃H₈ (C₃H₈/Xe = 1/1) and ¹⁸O₂ (¹⁸O₂/Ar = 1/1) over as received Pt-Sn catalyst at 675°C.

Figure 4  Individual H₂ transient responses recorded after H₂ (H₂/Xe = 1/1) multi-pulsing over oxidized BCFZ perovskite at 675°C.

Figure 5  Averaged H₂ transient responses recorded after H₂ (H₂/Xe = 1/1) pulsing and simultaneous pulsing of H₂ (H₂/Xe = 1/1) and ¹⁸O₂ (¹⁸O₂/Ar = 1/1) over oxidized BCFZ perovskite and as received Pt-Sn catalyst at 675 °C.
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