Oxidative coupling of methane in a BCFZ perovskite hollow fiber membrane reactor

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A membrane reactor incorporating a hollow fiber was used for the oxidative coupling of methane (OCM). The perovskite membrane of the composition $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$ (BCFZ, $x+y+z = 1$) allows a controlled oxygen feeding into the reactor over its axial length. By using this novel hollow fiber membrane reactor with a 2 wt% Mn/5 wt% Na$_2$WO$_4$ on SiO$_2$ catalyst as a packed bed around the fiber, oxygen separation from air and C$_2$ formation could be established at 800 °C with long-term stability. The highest C$_2$ selectivity of approximately 75% was observed at methane conversion of 6% with a C$_2$H$_4$ to C$_2$H$_6$ ratio of 2:1. The highest C$_2$H$_4$ to C$_2$H$_6$ ratio of 4:1 and maximum C$_2$ yield of 17% was obtained at 50% C$_2$ selectivity.

1. Introduction

Since methane is the main constituent of natural gas which will exceed the reserves of crude oil in the future, a strong economic interest exists in developing processes that transform methane to higher valued products. At present, methane is converted industrially to syngas via steam reforming$^1$ and to hydrocyanic acid by the Andrussov reaction.$^2$ The oxidative coupling of methane (OCM) to ethane and ethene is an attractive alternative for the existing processes based on crude oil and benefits from avoidance of sequential steps required to indirect routes involving CH$_4$ reforming and Fischer-Tropsch synthesis.$^3$ Most of the research on the highly exothermic catalytic OCM reaction started in the early 1980s with the pioneering works of Keller and Bhasin.$^4$

The mayor difficulty to be overcome in CH$_4$ conversion is the scission of the first C-H bond (ca. 435 kJ mol$^{-1}$). For this reason, the direct pyrolitic route to H$_2$ and C$_2$H$_4$ will be disfavoured thermodynamically and requires high temperatures, consequently resulting in poor selectivity.

The OCM reaction usually occurs via a heterogeneous-homogeneous mechanism, i.e. the reaction involves the catalytic formation of methyl groups, which desorb as free radicals (CH$_3$)$^5$ that ultimately react via predominantly homogeneous pathways.$^6$ It is generally agreed that dissociated oxygen as lattice
oxygen $O_2^-$ is supposed to be the active oxygen species, which presumably activates methane to generate CH$_3$ radicals. But there still exists noticeable disagreement or controversy concerning the active components or sites of the Na$_2$WO$_4$-Mn/SiO$_2$ catalyst. Li and coworkers related the excellent performance to WO$_4$ tetrahedral structures containing W=O and W-O-Si bonds$^{7,8}$. This model was further developed with the emphasis on the combination of tetrahedral WO$_4$ and octahedral MnO$_6$ sites, respectively, responsible for the activation of methane and the oxygen lattice transport.$^9$ In contrast, Lunsford et al. proposed that Na-O-Mn species attributed to the activation of methane and tungsten ions apparently improved the catalyst stability.$^{10}$ Recently, it was claimed that both Na-O-Mn and Na-O-W species act as active sites for the OCM reaction.$^{11}$

The ethane formed undergoes further transformations to ethene and carbon oxides. Both hydrocarbons can be consecutively oxidized to CO$_x$. Combustion of C$_2$ hydrocarbons becomes the main route to CO$_x$ with increasing methane conversion, since ethane and ethene have a higher reactivity compared to methane. Therefore, the contribution of direct methane oxidation to CO$_x$ decreases. All these pathways account for the inherently limited yield of OCM process of 28 % on a basis of fundamental kinetics.$^{12}$

Palermo et al.$^{13}$ pointed out that Na plays a dual role: (i) crystallization of amorphous silica to the crystalline form and (ii) stabilization and dispersion of surface WO$_x$ species with WO$_4$ as a possible candidate.$^{14}$

According to DFT calculations by Chen et al.$^{15}$, the tetrahedral [WO$_4$] site with a single bridge oxygen is the most probable active center responsible for methane activation.

The surface methyl radical generation reaction is temperature-dependent and dramatically slower than the temperature-independent radical coupling reaction in the gas phase.$^{16}$ Based on these observations it can be inferred that, in the absence of combustion, the C$_2$ production rate is limited by the generation rate of free methyl radicals and can be increased by increasing the temperature, since at low temperatures, active sites are less active. At low temperatures, most of the oxygen ions do not generate methyl radicals but recombine to gaseous oxygen and cause combustion, resulting in low selectivities.
C₂ products are favored by high CH₃ radical concentrations because their recombination is a bimolecular event.

On the other hand, high concentrations of oxygen are disadvantageous to high C₂ selectivities. Low oxygen concentrations are, however, unfavourable for high degrees of methane conversion and high C₂ yields. An alternative to staged oxygen delivery is the use of membrane reactors. Dosing the oxygen through a perovskite membrane shows several advantages: (i) due to the distributed feeding of oxygen over the whole reactor (or at least over the length of the oxygen permeable zone of the membrane) the oxygen partial pressure is low and homogeneous which thereby supports the partial oxidation and not the total oxidation, thus increasing the selectivity, (ii) in the sense of process intensification, two operation units become combined: the oxygen separator and the chemical reactor for the OCM reaction thus increasing the space-time-yield by 50%. It is estimated that about 30% of the costs in the C₂ synthesis stem from cryogenic air distillation according to Linde. Air separation using oxygen transport membranes operating at process temperature of the chemical reaction makes the use of methane as feedstock economically and ecologically attractive by energy saving resulting in reduction of CO₂ emission.

This method of contacting the reactants can also increase selectivity and yield to the desired products in reacting systems where several reactions take place since the kinetic order of oxygen for the desired reactions is lower than for the other reactions (usually deep oxidation reactions).

All models and experimental results of the OCM reaction have in common incomplete conversion of methane due to a high stoichiometric excess of methane with respect to oxygen; thereby the formation of side products, CO and CO₂, is partly suppressed.

Non-porous oxygen-ion-conducting perovskite oxides have potential as OCM catalytic membrane reactors using air as an economical oxygen source.¹⁷ At the membrane surface of the reactive side of the
membrane reactor, oxygen ions ($O_2^{2-}$) are competitively consumed by two reactions – methane activation

$$2 \text{CH}_4 + O_2^{2-} \rightarrow 2 \text{CH}_3 \cdot + \text{H}_2\text{O} \quad (I)$$

and recombination of oxygen ions according to

$$2 O_2^{2-} \rightarrow \text{O}_2 + 4e^{-} \quad (II)$$

Kao et al. showed that the use of a mixed-conducting ceramic membrane of the composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_3$ for oxygen insertion to the reaction zone could increase the $\text{C}_2$ selectivity compared to the fixed bed reactor (FBR).$^{19}$ Wang et al. packed an active OCM catalyst in a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ membrane tube and obtained a $\text{C}_2$ yield which is similar to that in a FBR, though a higher ratio of $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ was observed in the membrane tube reactor.$^{20}$ The selectivities in these materials appear to be limited by high oxygen ion recombination rates that compete for oxygen with the desired coupling reaction.

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,$^{21}$ the simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane$^{22}$ and recently the multi-step oxidative dehydrogenation of ethane (ODE)$^{23}$ and propane (ODP).$^{24}$

In this publication we present the use of a dense mixed oxygen ion and electron conducting (MIEC) perovskite hollow fiber membrane of the composition $\text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta}$ ($\text{BCFZ}$, $x+y+z=1$) for the oxidative coupling of methane employing 2 wt% Mn/5wt% $\text{Na}_2\text{WO}_4$ on $\text{SiO}_2$ as an OCM catalyst. To the best of our knowledge, it is the first time that a perovskite hollow fiber membrane reactor of the composition above is used for the oxidative coupling of methane.

2. Experimental Section
2.1. Preparation of the hollow fibers

The hollow fiber membranes of the composition \( \text{BaCo}_x\text{Fe}_y\text{Zr}_z\text{O}_{3-\delta} \) (BCFZ, \( x+y+z=1 \), Figure 1) were manufactured by phase inversion spinning followed by sintering as described elsewhere. In order to obtain the isothermal condition, two ends of the fibers with an outer diameter of \( \sim 1.1 \) mm and a wall thickness of \( \sim 0.14 \) mm were coated with gold paste (C 5754 B, Heraeus) and sintered at 950 °C for 5 hours to obtain a 3 cm long permeation zone in the middle of the furnace. This procedure was repeated three times to ensure a leak-proof gold layer not permeable to oxygen.

![Figure 1: BaCo\(_x\)Fe\(_y\)Zr\(_z\)O\(_{3-\delta}\) (BCFZ, \( x+y+z=1 \)) hollow fiber membrane obtained by spinning at the Fraunhofer Institute for Interfacial Engineering and Biotechnology.](image)

2.2. Preparation of the catalyst
Appropriate amounts of Mn(NO$_3$)$_2$·4 H$_2$O (Sigma-Aldrich) and Na$_2$WO$_4$·2 H$_2$O (Sigma Aldrich) were dissolved in deionized water and contacted with SiO$_2$ (Davisil, Grade 636, Sigma-Aldrich) under stirring at 130 °C for 5 h. Finally, the impregnated silica gel was treated for 8 h at 800 °C. In order to characterize the obtained catalyst before and after reaction, XRD were conducted with monochromated Cu K$_{\alpha1}$ radiation in the range of 10-70° 2θ at room temperature (Philips X’Pert-PW1710). Figure 2 shows the XRD patterns for the 2 wt% Mn/5 wt% Na$_2$WO$_4$ on SiO$_2$ catalyst. The fresh as well as the spent catalyst (on stream for 100 h) possess the reflections for the three SiO$_2$ modifications quartz, cristobalite and tridymite, whereas the first appears to increase during reaction. The amount of active Na$_2$WO$_4$ decreases slightly while being on stream under reaction conditions as can be inferred from the characteristic peaks at 2θ = 17.1 and 32.5°.
Figure 2. Powder XRD pattern of fresh and spent (on stream for 100 h) 2 wt% Mn/5 wt% Na$_2$WO$_4$ on SiO$_2$ catalyst.

SEM was carried out on a JEOL JSM-6700F field-emission instrument using a secondary electron detector (SE) at an accelerating voltage of 2 kV. EDX spectra were obtained at an accelerating voltage of 15 kV using a light-element detector (INCA 300, Oxford Instruments).

The elemental distribution by EDXS shown in Figure 3 qualitatively confirms also the loss of manganese species on the catalyst’s surface after being on stream for 100 h as well as an agglomeration of the catalyst particles.

Figure 3. SEM micrographs and corresponding elemental distribution for manganese by EDXS of the fresh and spent catalyst (on stream for 100 h), respectively.

2.3. Studies in the hollow fiber membrane reactor
For the OCM, pure methane (99.5%) - or diluted with steam and helium (99.996%) where specified - was fed to the shell side of the membrane, while synthetic (C\textsubscript{x}H\textsubscript{y}-free) air was fed to the core side. All gas flows were controlled by mass flow controllers (Bronkhorst High-Tech). The gases at the exit of the reactor were analyzed by a gas chromatograph (Agilent Technologies, HP6890N) equipped with a Carboxen 1000 column (Supelco). Concentrations of C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4}, CO, CO\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2} and O\textsubscript{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 OCM catalyst (2 wt% Mn/5 wt% Na\textsubscript{2}WO\textsubscript{4} on SiO\textsubscript{2}), 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 catalyst 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 4).

![Figure 4](image-url)

**Figure 4.** Schematic drawing of the reactor set-up and an incorporated BCFZ hollow fiber for OCM. At both ends the 30 long fiber was coated with gold to obtain a 3 cm long isothermal oxygen permeation
zone. The active surface area for the oxygen permeating BCFZ hollow fiber is 0.78 cm$^2$. The OCM catalyst was dispersed between the outer dense alumina tube and the fiber, which was inserted into a porous alumina tube.

3. Results and discussion

3.1. Intrinsic catalytic activity of the BCFZ perovskite for the OCM

First, we studied the OCM in a packed bed reactor. Figure 5 shows methane conversion as well as product selectivities as a function of the co-fed oxygen flow rate evaluating the intrinsic catalytic activity of BCFZ powder for the oxidative coupling of methane. A higher flow rate of co-fed oxygen increases methane conversion and the CO$\text{2}$ to CO ratio whereas the C$_2$ selectivity has a maximum at a methane to oxygen ratio of 25:1. Therefore, no substantial catalytic performance towards the oxidative coupling of methane can be assigned to the pure BCFZ perovskite.
Figure 5. Evaluation of the intrinsic catalytic activity of BCFZ powder in a fixed bed reactor showing methane conversion and product selectivities as a function of the co-fed oxygen flow rate (25 mL$_N$ min$^{-1}$ methane, 0-10 mL$_N$ min$^{-1}$ oxygen).

3.2. Effect of air dilution on core side

Introducing the BCFZ hollow fiber membrane and the 2 wt% Mn/5 wt% Na$_2$WO$_4$ on SiO$_2$ catalyst as a fixed packed bed around the fiber as shown in Figure 4, the methane conversion as well as C$_2$ selectivities are increased dramatically (see Figure 6). Lowering the oxygen concentration on the core side increases the C$_2$ selectivity, where ethane selectivity increases more compared to the ethene selectivity. A higher oxygen concentration on the core side of the membrane leading to a higher oxygen
transport through the membrane favors hydrocarbon oxidation. The ethene to ethane ratio varies between 2.3 and 3.5. At a higher concentration of oxygen it is more likely that the ethane formed during the OCM reaction undergoes further transformations, e.g. oxidative dehydrogenation.

Figure 6. Effect of the oxygen concentration obtained by air dilution on the core side while feeding pure methane at 25 mL$_N$ min$^{-1}$ on the shell side of the membrane. Methane conversion, product selectivities and C$_2$ yield as a function of the oxygen concentration on the core side of the membrane at 1 bar and $T = 800 ^\circ$C (shell: 25 mL$_N$ min$^{-1}$ methane; core: $F_{\text{total}} = 50$ mL$_N$ min$^{-1}$ air diluted with helium; 0.78 cm$^2$ effective membrane surface; 0.25 g of catalyst; $WHSV = 4.32$ h$^{-1}$).
3.3. Effect of total methane flow rate

By applying lower total flow rates of methane on the shell side than shown in Figure 6, its conversion can be increased (see Figure 7) due to a longer residence time of methane inside the reactor. A longer residence time, on the other hand, leads to an increased hydrocarbon oxidation and therefore to a drop in C2 selectivity. Especially, ethene and ethane are the precursors for COx due to their higher reactivity compared to methane.

![Figure 7](image-url)

**Figure 7.** Higher C2 selectivity due to air dilution on the core side of the membrane while feeding methane at 15 mL\textsubscript{N} min\textsuperscript{-1} on shell side. Methane conversion, product selectivities and C2 yield as a...
function of the oxygen concentration on the core side of the membrane at 1 bar and \( T = 800 \, ^\circ\text{C} \) (shell: 15 mL\(_N\) min\(^{-1}\) methane; core: \( F_{\text{total}} = 50 \, \text{mL}_N \, \text{min}^{-1} \) air diluted with helium; 0.78 cm\(^2\) effective membrane surface; 0.25 g of catalyst; \( WHSV = 2.59 \, \text{h}^{-1} \)).

It can be seen from the results shown in Figures 6 and 7 that a shorter contact time is helpful for the increase of the C\(_2\) selectivity by preventing hydrocarbon deep oxidation. On the other hand, a shorter contact time decreases the rate of reaction probability on the catalyst surface. Additionally, the gas can not get the optimum temperature for a high conversion due to the short residence time inside the heated reactor.

3.4. Dilution of methane

A dilutant is often used to control the excess heat of the reaction of OCM. In our experiments, helium and steam were selected as diluents. Diluting methane with an inert gas, e.g. helium, increases the methane conversion at a constant residence time inside the reactor (Figure 8) as expected, since the ratio of oxygen to methane is increased. A higher amount of oxygen can lead to an increased transformation of methane, but also to a higher degree of oxidation to CO\(_x\) since the rate constant for CO\(_x\) formation from C\(_2\)H\(_4\) oxidation is up to six times greater than that from the direct oxidation of CH\(_4\).\(^{26}\) The ethene selectivity at 100% methane concentration drops to approximately 35% when feeding 20% methane in helium.
Figure 8. Dilution of methane leading to its higher conversion at a constant total flow rate of 25 mL$_N$ min$^{-1}$ on the shell side of the membrane while feeding pure air on the core side. Methane conversion, product selectivities and C$_2$ yield as a function of the oxygen concentration on the core side at 1 bar and $T = 800 \, ^\circ$C (shell: $F_{\text{total}} = 25$ mL$_N$ min$^{-1}$ methane diluted with helium; core: 50 mL$_N$ min$^{-1}$ air; 0.78 cm$^2$ effective membrane surface; 0.25 g of catalyst; WHSV = 0.86-4.32 h$^{-1}$).

At a total flow rate of 50 mL$_N$ min$^{-1}$ on the shell side, the ethene selectivity can be maintained at a constant level above 50% even at low methane concentrations in the feed (results not shown). The shorter retention time within the reactor suppresses the hydrocarbon oxidation up to a certain extent. Summarizing, the methane concentration of the feed should be as high as possible for a high C$_2$ selectivity.
Using steam instead of helium as a dilutant can suppress CO$_2$ formation and maintain high ethene selectivities especially at low methane concentrations (see Figure 9) in comparison to results shown in Figure 8. The results indicate that steam not only has a dilution effect, but also suppresses the deep oxidation. Most importantly, the steam can distribute the temperature more evenly along the catalyst bed during the reaction. Consequently, the gas-phase reaction is suppressed and more C$_2$ product is preserved in the outlet.

**Figure 9.** Steam as dilutant for methane allowing high ethene selectivities at higher degrees of dilution at a constant total flow rate of 25 mL$_N$ min$^{-1}$ on the shell side of the membrane while feeding pure air on core side. Methane conversion, product selectivities and C$_2$ yield as a function of the oxygen concentration on the core side of the membrane at 1 bar and $T = 800$ °C (shell: $F_{\text{total}} = 50$ mL$_N$ min$^{-1}$).
methane diluted with steam; core: 50 mLN min⁻¹ air; 0.78 cm² effective membrane surface; 0.25 g of catalyst; $WHSV = 0.86-4.32$ h⁻¹).

Takanabe and Iglesia reported that the utilization of steam as dilutant introduces OH· radicals that result in improved C₂ selectivities and yields. One of the reasons discussed is that the presence of OH· radicals avoids strong adsorption of C₂H₄ on surfaces that favour its oxidation.²⁷

3.5. Effect of diluting air at lowered methane concentration

Figure 10 and 11 illustrate the effect of diluting the air on core side of the hollow fiber membrane while feeding diluted methane at two different flow rates. This set-up gave rise to the maximum C₂ yield of 17% and C₂ selectivity of 74% observed in this work.
Figure 10. Improved C\textsubscript{2} selectivities and C\textsubscript{2} yields by feeding diluted oxygen on core side while feeding 10\% methane on shell side of the hollow fiber membrane at a total flow rate of 25 mL\textsubscript{N} min\textsuperscript{-1}. Methane conversion, product selectivities and C\textsubscript{2} yield as a function of the oxygen concentration on the core side of the membrane at 1 bar and $T=800$ °C ($shell$: 5 mL\textsubscript{N} min\textsuperscript{-1} methane, 20 mL\textsubscript{N} min\textsuperscript{-1} helium; $core$: $F_{total} = 50$ mL\textsubscript{N} min\textsuperscript{-1} air diluted with helium; 0.78 cm\textsuperscript{2} effective membrane surface; 0.25 g of catalyst; $WHSV = 0.86$ h\textsuperscript{-1}).
Figure 11. Effect of reducing the oxygen partial pressure by air dilution with helium on core side while feeding 10 \% methane at a total flow rate of 50 mL\textsubscript{N} min\textsuperscript{-1} on shell side of the hollow fiber membrane. Methane conversion, product selectivities and C\textsubscript{2} yield as a function of the oxygen concentration on the core side of the membrane at 1 bar and \( T = 800 \degree C \) (shell: 10 mL\textsubscript{N} min\textsuperscript{-1} methane, 40 mL\textsubscript{N} min\textsuperscript{-1} helium; core: \( F_{\text{total}} = 50 \) mL\textsubscript{N} min\textsuperscript{-1} air diluted with helium; 0.78 cm\textsuperscript{2} effective membrane surface; 0.25 g of catalyst; \( WHSV = 1.72 \text{ h}^{-1})\).

Generally speaking, a higher methane conversion due to a higher amount of oxygen supplied across the membrane to the hydrocarbon side, increases the ethylene to ethane ratio. This can be explained by the fact that catalysts used for the OCM reaction are – for a certain extent - also good for the oxidative dehydrogenation of ethane to ethylene.\textsuperscript{28} At a higher concentration of oxygen it is more likely that the
ethane formed undergoes further transformations, e.g. oxidative dehydrogenation on the catalyst’s surface.

Figure 12. Controlling the ethylene to ethane ratio by the degree of methane conversion.
Figure 13. Performance of the hollow fiber membrane reactor for the OCM using a 2 wt% Mn/5 wt% Na₂WO₄ on SiO₂ catalyst. C₂ selectivity as a function of methane conversion (> 5%).

All processes for the oxidative coupling of methane suffer from the high costs for low-temperature separations of C₂ products from the reactor effluent containing a high concentration of unconverted methane besides the various side products. A process concept for converting natural gas into ethene and hydrogen or hydrocarbon liquids has been described recently by Hall²⁹, being licensed by SynFuels International. This technology, which has been explored in an industrial pilot plant, is claimed to be economically viable depending on the methane price entering the overall cost scheme; thus, it can be considered attractive for remote gas or in situations where the gas is just flared off. For a 1.4 MSCMD
(million standard cubic meters per day) plant US$25 per barrel of liquid product has been estimated assuming remote gas at US$0.018 m$^{-3}$, 10-year straight line amortization, 25% fixed costs and US$1.3 per barrel operating costs. As claimed in a patent$^{30}$, the economy of methane-to-ethene processing can be improved when both the catalytic OCM reaction and the separation of ethene from the reactor-effluent components (methane, ethane, carbon oxides) are performed at elevated pressure. Elevated pressures reduce not only the size of the various process units due to an increase of the reaction rates but they improve also the efficiency of the separation process. For separating the ethene an aqueous silver-nitrate solution was used as a complexing absorbent.

When arranged in bundles, with hollow fibre geometry a high membrane area per reactor/permeator volume can be achieved. Economic goals, e.g. membrane area per m$^3$ permeator of the order of 5000 m$^2$ at a price of well below 1000 €/m$^2$ can be met by the perovskite hollow fibres. Furthermore, thin walled hollow fibres show a better mechanical stability than disk-shaped membranes of the same wall thickness. The successful development of perovskite hollow fibre is considered a remarkable step towards their industrial application, e.g. for the oxidative coupling of methane.

Based on our results, the oxygen necessary for a methanol-plant with a capacity of 2000 tons/day based on partial oxidation of methane could be delivered by 4600 km fibres. Such fibres would need a relatively small volume of 3–4 m$^3$ depending on the packing density. When comparing this volume to a classical air separation unit, the enhancement in space–time–yield (in terms of oxygen per plant size) is obvious.

4. Conclusions

A membrane reactor with oxygen supply via a BaCo$_x$Fe$_y$Zr$_z$O$_{3-\delta}$ (BCFZ, $x+y+z=1$) perovskite hollow fiber for the oxidative coupling of methane is presented for the first time in the literature. Having a dense membrane that separates hydrocarbon and oxygen feed, reduces the risks of explosive mixtures as
well as saves costs since no oxygen plant is required. Furthermore, it allows a precise control of the oxygen insertion thus increasing C$_2$ selectivity. Using a 2 wt% Mn/5 wt% Na$_2$WO$_4$ on SiO$_2$ catalyst, C$_2$ formation could be studied at 800 °C with long-term stability and a maximum ethene to ethane ratio of 4:1. The highest C$_2$ selectivity of approximately 75% was observed at a methane conversion of 6%, whereas the highest C$_2$H$_4$ to C$_2$H$_6$ ratio of 4:1 and maximum C$_2$ yield of 17% was obtained at 50% C$_2$ selectivity (see Figure 10). For industrial implementation of such a system, one could use a multitude of hollow fiber bundles in a catalytic fixed bed and operate in cross flow to avoid the need for gold sealing. Furthermore, it can be inferred from the presented results that the gaseous oxygen produced accelerates the non-catalytic gas phase methane combustion leading to a decrease of the C$_2$ selectivity. The C$_2$ selectivity and yield might be improved by packing an active OCM catalyst on the membrane surface. According to the present results, also more steam should be added to the reactants in further experiments to prevent hydrocarbon from deep oxidation in the gas-phase due to the better removal of excess heat from the catalyst bed.

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Literature Cited


