Highly Durable C₂ Hydrocarbon Production via the Oxidative Coupling of Methane Using a BaFe₀.₉Zr₀.₁O₃₋δ Mixed Ionic and Electronic Conducting Membrane and La₂O₃ Catalyst

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ABSTRACT: The oxidative coupling of methane (OCM) is an attractive technology for the production of ethane (C₂H₆) and ethylene (C₂H₄); and significant performance and efficiency gains as well as reduced carbon dioxide (CO₂) emissions are expected when OCM takes place within mixed ionic and electronic conducting (MIEC) ceramic membrane reactors (CMRs). So far, research on OCM in CMRs has been limited to unstable and incompatible materials investigated under short-term measurements that hinder upscaled and commercial application. To this end, this work demonstrates long-term stable OCM performance enabled by a BaFe₀.₉Zr₀.₁O₃₋δ (BFZ91) perovskite utilized as the oxygen-ion MIEC membrane and lanthanum oxide (La₂O₃) used as the OCM catalyst. Experimental measurements conducted in the temperature (T) range of 750–900 °C and at inlet methane (CH₄) mole fractions (X(CH₄)) of 0–30% revealed a highly stable performance during 23 days of continuous operation, which was further confirmed by material characterization. Under the aforementioned operating conditions, BFZ91 offers a high oxygen (O₂) permeation flux (J(O₂)) between 0.5–1.5 (μmol/cm²/s); CH₄ conversion (C(CH₄)) reached ~35% while the selectivities to C₂H₆ (S(C₂H₆)) and C₂H₄ (S(C₂H₄)) were as high as ~50% and ~40%, respectively, showing a strong dependency on the operating conditions. Yields of C₂H₆ (Y(C₂H₆)) and C₂H₄ (Y(C₂H₄)) in the range of 1–5% and 1–7%, respectively, were measured, with more C₂H₄ being produced at higher T. In the absence of La₂O₃, C(CH₄) and C₂ (C₂H₆ and C₂H₄) yields are lower confirming that BFZ91 does not promote CH₄ oxidation, reforming, or coupling on its surface at high rates. The OCM performance of BFZ91 with La₂O₃ was also found to be stable under partial O₂ consumption and pure CH₄ conditions. Furthermore, a detailed analysis of the mixture composition allowed the identification of the primary reactions in the OCM chemistry. Our results reveal that within our reactor, CH₄ full oxidation to CO₂ and steam (H₂O) happens simultaneously with CH₄ oxidation to C₂H₆ and H₂O (both on the La₂O₃ catalyst), but the production of the valuable C₂H₄ is primarily taking place through the C₂H₆ non-oxidative dehydrogenation in the gas phase; this reaction was not found to proceed on the La₂O₃ catalyst. Besides the promise of the investigated materials toward commercialization, the methods to study the OCM chemistry and the membrane catalyst coupling presented here are expected to promote further advances in the field of OCM.

KEYWORDS: oxidative coupling of methane, ceramic membrane reactors, BaFe₀.₉Zr₀.₁O₃₋δ mixed ionic–electronic conductor, La₂O₃ catalyst, OCM chemistry, long-term OCM measurements

1. INTRODUCTION
C₂H₆ is one of the most important commodity chemicals worldwide with a 2018 global production of ~185 million metric tons (MMT).¹ During 2019, the production of C₂H₆ in the United States (US) was the highest among other chemicals and plastics reaching ~32 MMT.² Its high demand is related primarily to its use as a building block in the production of polymers, such as polyethylene and polyvinyl chloride.³ Other uses of C₂H₆ include the synthesis of intermediate chemical compounds and its utilization as a plant hormone in agriculture.³ Given its high demand, projections reveal that the global C₂H₆ production could rise to ~260 MMT by 2023 and in the long term to ~290 MMT by 2030.¹ The price of C₂H₆ is relatively high and can exhibit significant fluctuations during a calendar year. For example, the C₂H₆ contract price in the US during 2019 ranged between $530–650 per metric ton driven by...
monthly changes in the C₂H₄ demand and production and by variations in the feedstock price.⁵

C₂H₄ is primarily produced by steam cracking of naphtha or ethane⁶ but other feedstocks such as propane, butane, and gas oil are also used.⁷ Naphtha is the main feedstock in Europe and Asia while ethane crackers are mostly used in North America and the Middle East.⁸ Steam-cracking reactions are highly endothermic and take place at temperatures between 750−950 °C.⁹ From an energy consumption and yield point of view, when using C₂H₄ as the feedstock, the process requires ~12.5−21 GJ per ton of produced C₂H₄ and C₂H₆ yields are as high as ~80%.⁹,⁷ For naphtha, the process becomes more energy intensive and requires ~14−22 GJ per ton of produced C₂H₄, while the C₂H₆ yields drop significantly to ~30% because of the formation of various byproducts such as methane, propylene, butane, and other fuel oils.⁷,⁹ For naphtha, one also has to account for variations in its composition which affect the final product yield.⁷ Besides the high energy requirements and the corresponding CO₂ emissions, cracking reactions are thermodynamically limited because of species accumulation in the reactor (e.g., H₂ formation from C₂H₆ pyrolysis). Moreover, C₂H₆ and naphtha crackers suffer from severe carbon deposition, a safety hazard that requires periodic shutdown.¹⁰ Finally, the purification of C₂H₄ is another challenge with a significant energy penalty given that it is based on high-pressure cryogenic distillation taking place at temperatures of −160 °C.¹⁰

An alternative to the production of C₂H₄ is the oxidative coupling of methane (OCM). The process was first suggested by Keller and Bhasin,¹¹ and it involves co-feeding CH₄ and O₂ in a single stream, which react in the presence of a catalyst at T = 650−900 °C to produce C₂ as follows:

\[
2\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{H}_2\text{O}
\]

\[
\Delta H_{298K}^\circ \approx -176.9 \text{ kJ/mol C}_2\text{H}_6
\]

\[
2\text{CH}_4 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}
\]

\[
\Delta H_{298K}^\circ \approx -281.8 \text{ kJ/mol C}_2\text{H}_4
\]

OCM has several advantages when compared to steam cracking including: ¹² (1) reduced energy consumption because of the reaction exothermicity resulting in fewer CO₂ emissions; (2) the feedstock is natural gas (composed primarily of CH₄), which is currently cheap ($2.3−3/GJ) and widely produced in the US from shale reserves with future production increase from gas hydrate exploitation; (3) lower cost, due to the direct conversion of CH₄ to C₂ without the need for intermediate steps that require the use of syngas; and (4) formation of H₂O in the products because of the CH₄ reaction with O₂ removes equilibrium limitations and reduces downstream separation costs. However, OCM has four important challenges: (1) the process is kinetically controlled because at equilibrium, CH₄ partial or full oxidation takes place;¹³ (2) the produced C₂ species can pyrolyze at the OCM operating T and this creates the need to reduce the T and the residence time at the expense of catalyst performance and CH₄ conversion, respectively; (3) the process requires a selective and long-term stable catalyst to drive the reaction at relatively low T; and (4) CH₄ oxidation forms byproducts, such as carbon monoxide (CO), CO₂, and so forth, that reduce the C₂ selectivity and yield.

Co-feeding CH₄ and O₂ in a single-stream reactor relies on a fixed-bed catalyst to drive OCM. However, this conventional OCM technology has three major limitations: (1) it needs pure O₂ whose production is based on cryogenic air separation, and hence, creates a significant energy penalty;¹⁴ (2) while the OCM stoichiometric CH₄/O₂ ratio for C₂H₄ production is 2 (reaction 2), in practice, ratios of 5−10 are required to avoid deep oxidation of CH₄ and hence, most of it remains unconverted or forms undesired species; and (3) the reaction exothermicity (reactions 1 and 2) combined with nonuniform conversion along the catalyst bed results to large T gradients, which is a safety risk and could lead to local catalyst deactivation along the reactor, thus reducing the C₂ yields further.

Despite intense research to design selective OCM catalysts,¹²,¹⁵ only one commercial reactor has been reported to date but its C₂ yield is currently unknown.¹⁶ Early techno-economic analyses proposed that economic viability of the conventional OCM process requires a single-pass C₂H₄ yield higher than 25%.¹²,¹⁷,¹⁸ However, more recent investigations focusing on C₂H₄ production in Europe propose that the fuel-to-chemicals efficiency of naphtha crackers can be achieved from conventional OCM only if single-pass C₂H₄ yields around 45−50% can be obtained.¹⁹,²⁰ Similar studies show that besides efficiency, the C₂H₄ price from plants employing the conventional OCM technology can compete with naphtha crackers only if OCM yields higher than 30% can be achieved.²¹ This is because of the large capital cost of units required to separate C₂ from the gaseous stream, and the recombination of syngas (produced from secondary reactions) back to CH₄. Operating expenses related to the cost of natural gas and electricity significantly affect the C₂H₄ production price.²¹ To decrease the cost of the separation units, and hence, the C₂H₄ price, it has been suggested that the target yields should be achieved with high C₂ selectivity catalysts compared to high CH₄ conversion catalysts.²¹

An alternative technology for OCM that has the potential to improve upon the conventional OCM relies on oxygen-ion conducting ceramic membrane reactors (CMRs). A recent techno-economic analysis suggested that the price of C₂H₄ produced from membrane-based OCM plants could potentially compete with naphtha crackers if C₂H₄ yields higher than 30% can be achieved.²² Note, however, that estimating the price of a membrane reactor has its own challenges given that the large-scale deployment of these reactors has so far been limited. The same study also confirms that significant CO₂ emission reduction can be attained with CMRs.²² OCM in CMRs enables process intensification given that pure O₂ can be separated from an O₂ containing gaseous stream and be converted to added-value chemicals in the same reactor, hence reducing the reactor size and cost. In addition, given that increased CH₄/O₂ ratios generally allow for higher C₂ selectivity, it has been demonstrated that CMRs offer higher C₂ selectivity compared to the conventional OCM.²³,²⁴,²⁵ Moreover, the gradual introduction of O₂ through the membrane allows for a better thermal management with decreased T gradients. Finally, OCM in CMRs takes place along the entire reactor length in contrast to conventional fixed-bed OCM reactors, where the C₂ production is confined at the initial stages of the catalyst followed by the pyrolysis of the desired species or by secondary undesired reactions that reduce the C₂ yield.²⁶ It is evident that in OCM with CMRs, the design of the reactor (its geometry, in particular) is another important variable that needs to be explored and optimized.

CMRs consist of two different gaseous streams separated by a ceramic oxide material.¹²,¹⁴,¹⁷,²⁷ Membrane materials commonly used in oxygen-ion CMRs exhibit mixed ionic and electronic
conductivity and hence allow the transport of  \( \mathrm{O}_2 \) (in the form of ions) from a high  \( \mathrm{O}_2 \) chemical potential (\( \mu_{\mathrm{O}_2} \)) stream to a low  \( \mu_{\mathrm{O}_3} \) stream without external polarization, that is, it is a purely thermochemical process driven by surface reactions on the gas–membrane interfaces coupled with the diffusion of charged species (oxygen vacancies, small polarons etc.) within the material. When air is introduced on one stream (the air side) and \( \mathrm{CH}_4 \) on the other (the \( \mathrm{CH}_4 \) side), \( \mathrm{O}_2 \) is converted to oxygen ions (\( \mathrm{O}^{2-} \)) on the air side surface, which are then incorporated into the material. \( \mathrm{O}^{2-} \) diffuse through the membrane to the \( \mathrm{CH}_4 \) side via an oxygen vacancy-mediated mechanism that also involves the transport of electrons and electron holes to preserve charge neutrality in the bulk of the material. At the \( \mathrm{CH}_4 \) side surface, \( \mathrm{CH}_4 \) may react either with  \( \mathrm{O}^{2-} \) directly on the surface or with desorbed \( \mathrm{O}_2 \) in the gas phase. In the presence of a catalyst, \( \mathrm{O}_3 \) and \( \mathrm{CH}_4 \) react on its surface to form \( \mathrm{C}_2^+ \) species and other products.

The success of OCM in CMRs requires a membrane-catalyst configuration that can operate with acceptable  \( J_{\mathrm{O}_2} \) and high \( C_2^+ \) yields under long times without the formation of undesired phases that could degrade the performance. The former, that is, the value of  \( J_{\mathrm{O}_2} \), is a challenge in CMRs because  \( J_{\mathrm{O}_2} \) can only be controlled indirectly by the operating conditions and the membrane properties. These establish a  \( \mu_{\mathrm{O}_2} \) gradient along the two membrane sides and do not allow for the direct control of \( \mathrm{O}_2 \) through the membrane. The latter, that is, undesired phases, can arise because of: (1) decomposition of the material on the OCM side due to operation under a low partial pressure of \( \mathrm{O}_2 \) (\( P_{\mathrm{O}_2} \)); (2) cation segregation from the bulk to the surface induced by elastic and electrostatic interactions; (3) reaction of the materials with gaseous species (e.g., formation of stable surface carbonate species because of  \( \mathrm{CO}_2 \) in the gaseous stream); and (4) reaction of the membrane with the OCM catalyst forming undesired phases.

Prior work on OCM using oxygen-ion conducting CMRs has focused on the development of membrane-catalyst materials with high  \( J_{\mathrm{O}_2} \) and increased \( C_2^+ \) selectivity and yield. Unfortunately, the trend in OCM is that high \( C_2^+ \) selectivity is accompanied by low \( \mathrm{CH}_4 \) conversion and vice versa, and this limits the maximum \( C_2^+ \) yield that can be obtained. For example, Igenegbai et al. investigated OCM using dense BaCe0.8Gd0.2O3-\( \delta \) (BCG) and nickel-doped Ba0.5Sr0.5Co0.8Fe0.2O3 (BYS) catalysts deposited on LSGM porous supports, respectively, acting as OCM catalysts. Stable operation with BCG (\( C_2^+ \) yields as a function of time when \( \mathrm{CH}_4 \) and air were co-fed in a single chamber reactor.) The addition of zirconium (Zr) in the B-site gave similar OCM performance compared to BCG and improved the resistance to decomposition; however, the decomposition was not eliminated completely showing that under long term, the material does not survive the OCM conditions. Volatile elements should also be avoided as they impact the long-term stability. For example, bismuth oxide (\( \mathrm{Bi}_2\mathrm{O}_3 \)) has a melting point equal to 817 °C; operation above this temperature results in the loss of bismuth because of evaporation.

Evaporation has also been observed for lithium at 800 °C. These membrane-catalyst instabilities clearly demonstrate that research on OCM in CMRs should focus both on material performance and stability, which should be demonstrated under the long-term operation.

To meet the aforementioned performance and long-term stability criteria, the present work investigates OCM using a BFZ91 ceramic membrane coupled with \( \mathrm{La}_2\mathrm{O}_3 \) powder. BFZ91 has been shown to deliver a high \( J_{\mathrm{O}_2} \) and to be stable structurally and in the presence of different hydrocarbon environments, while \( \mathrm{La}_2\mathrm{O}_3 \) is one of the most active and stable OCM catalysts among the various doped and undoped rare earth oxides. Both BFZ91 and \( \mathrm{La}_2\mathrm{O}_3 \) were characterized prior to the OCM measurements, and trends related to their properties are investigated and discussed. In the absence of \( \mathrm{La}_2\mathrm{O}_3 \), the BFZ91 membrane is relatively inactive toward the catalytic \( \mathrm{CH}_4 \) decomposition or oxidation, and hence, it serves as a means to separate \( \mathrm{O}_2 \) from air without converting much \( \mathrm{CH}_4 \) to the (un)desired products. In the presence of \( \mathrm{La}_2\mathrm{O}_3 \), long-term
measurements conducted in a button-cell reactor demonstrate that the BFZ91-La2O3 combination is highly stable for 23 days in the stream, during which the temperature and inlet CH4 mole fraction were varied between \( T = 750–900 \, ^\circ \text{C} \) and \( X_{\text{in,CH4}} = 0 – 30\% \), respectively. This is further confirmed by post-mortem material characterization showing the absence of secondary phases. To the best of our knowledge, this is the first time that materials with such a prolonged OCM lifetime are reported for the CMR technology. \( J_{\text{OCM}}, C_{\text{CH4}}, C_{\text{H2}} \) and \( C_{\text{C2H4}} \) selectivity, yield, and activity (i.e., molar production rate scaled to the catalyst mass) \((\dot{r})\) are used as performance metrics. Our results confirm that \( J_{\text{OCM}} \) is limited by both bulk diffusion and surface reactions at \( T = 750–800 \, ^\circ \text{C} \), higher fluxes are obtained at \( T = 850–900 \, ^\circ \text{C} \), during which surface reactions at the CH4 side are accelerated. The maximum \( Y_{\text{C2H4}} \) is \( \sim 10\% \) and it is obtained at \( T = 850 \, ^\circ \text{C} \) and \( X_{\text{in,CH4}} = 5\% \) during which \( J_{\text{OCM}} \approx 0.91 \, (\mu \text{mol/cm}^2/\text{s}) \) and \( S_{\text{C2H4}} \approx 39\% \). Experiments under partial O2 consumption and pure CH4 conditions also demonstrated a stable performance. For the latter, secondary phases were detected on the CH4 side because of the highly reducing conditions under pure CH4; however, our 3-day measurement showed no loss of performance as a function of time. Finally, the analysis of the gas-phase mixture composition near the membrane surface (approximately 1 mm for the OCM measurements, 0.1 g of La2O3 powder were deposited on the CH4 side of the BFZ91 membrane to create a fixed-bed type configuration, as shown in Supporting Information Figure S2.

Prior to any measurements, the reactor temperature was increased to 1025 \( \, ^\circ \text{C} \) with ambient air flowing in the air side (200 sccm) and pure argon (Ar) in the CH4 side (100 sccm) and was maintained at these conditions overnight. This heat treatment is required to soften the gold rings so that they can attach well on the alumina tubes and on the membrane, thus ensuring a gas-tight system with minimized leaks. For all the experiments reported herein, the nitrogen \((\text{N}_2)\) mole fraction at the exit of the CH4 side of the reactor was below 0.1%, demonstrating that air leaks are negligible and do not affect the measurements.

To estimate \( J_{\text{OCM}}, C_{\text{CH4}}, O_2 \) conversion \((C_{\text{O2}})\), \( C_2 \) selectivities, yields, and activities, measurements of species mole fractions at the inlet and outlet of the CH4 side are used as the input to a mole balance system of equations. All relevant equations are reported in the Supporting Information (Section 2). To understand the role of gas phase and surface reactions because of the presence of the BFZ91 membrane and La2O3 catalyst, measurements using an alumina microprobe with outer and inner diameters equal to 1.6 and 0.8 mm, respectively, were conducted near the membrane surface (approximately 1 mm away) and within the La2O3 bed. Silica was used as a desiccant material to remove any H2O from the mixture prior to introduction into the gas chromatograph (GC) for analysis. To estimate the mole fraction of H2O near the membrane surface (but still in the gas phase), a carbon to hydrogen atom balance between that location and the CH4 side inlet was used. Then, the GC measurements were corrected to estimate the true \((\text{i.e., on a wet basis})\) mole fraction of species within the reactor. The system of equations is reported in the Supporting Information (Section 3). Experimental uncertainties are included in all plots; to highlight this, data are plotted using open markers. All species mole fractions reported in this work are plotted on a wet basis, that is, accounting for H2O in the mixture.

2.2. Preparation of Dense BFZ91 Pellets for OCM Measurements. To prepare dense, disk-shaped BFZ91 pellets for OCM measurements, the calcined powder was mixed with 3 wt % polyvinyl butyral (acting as a binder) and ethanol and the mixture was homogenized in a mortar using a pestle. After ethanol evaporated, the powder-binder mixture was pressed uniaxially at 12 MPa in a cylindrical die to form the green body which was densified by sintering in ambient air at 1200 \( \, ^\circ \text{C} \) for 8 h using heating and cooling rates equal to 3 \( \, ^\circ \text{C}/\text{min} \). The sintered pellets had a final diameter of \( D \approx 16 \, \text{mm} \) and were then polished to the final thickness using silicon carbide sandpapers of different grit sizes until a smooth, mirror-like surface was obtained. The density of the final BFZ91 pellets was estimated using the Archimedes principle.

2.3. Button-Cell Reactor for OCM Measurements. Experimental measurements were obtained using a button-cell reactor shown in Supporting Information Figure S1. Additional information about the experimental setup is provided in the Supporting Information (Section 1) and in a previous work. For the OCM measurements, 0.1 g of La2O3 powder were mixed with 3 wt % polyvinyl butyral (acting as a binder) and ethanol and the mixture was homogenized in a mortar using a pestle. After ethanol evaporated, the powder-binder mixture was pressed uniaxially at 12 MPa in a cylindrical die to form the green body which was densified by sintering in ambient air at 1200 \( \, ^\circ \text{C} \) for 8 h using heating and cooling rates equal to 3 \( \, ^\circ \text{C}/\text{min} \). The sintered pellets had a final diameter of \( D \approx 16 \, \text{mm} \) and were then polished to the final thickness using silicon carbide sandpapers of different grit sizes until a smooth, mirror-like surface was obtained. The density of the final BFZ91 pellets was estimated using the Archimedes principle.
operating at voltage and current equal to 4.5 kV and 40 mA, respectively. The patterns were recorded in the 2θ range of 20–80° and were analyzed using the software HighScore Plus. The same software was also used for phase identification and Rietveld refinement. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were conducted using a Zeiss Merlin high-resolution scanning electron microscope. TGA measurements were conducted using a Q50 thermal analyzer from TA Instruments. Buoyancy corrections were included by repeating the TGA measurements at identical conditions using an empty sample pan. To estimate the surface area of the powder materials, the Brunauer–Emmett–Teller (BET) method was employed using an ASAP 2020 surface area analyzer from Micromeritics. To remove any moisture, the (BET) method was employed using a ASAP 2020 surface area analyzer from Micromeritics. To remove any moisture, the analyzer from Micromeritics. To remove any moisture, the analyzer from Micromeritics.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the As-Prepared BFZ91 Powder and Pellet

It is known that the BaFeO₃₋ₓ parent perovskite exhibits a hexagonal crystal structure at room temperature, but the structure changes to triclinic at 700 °C and then to cubic at 900 °C when exposed to air. High TₓO₃ is achieved at temperatures exceeding 750 °C, that is, when BaFeO₃₋ₓ obtains a triclinic or cubic phase. Given that phase transitions during heating and cooling could lead to mechanical failure of the dense membrane because of volume changes, phase stabilization is required by appropriate doping. The addition of 2–10% of Zr in the B-site of BaFeO₃₋ₓ can eliminate the aforementioned phase transition, giving rise to a cubic crystal structure at room temperature. When the Zr doping increases to 15%, secondary phases appear demonstrating that the solubility limit of Zr in BaFeO₃₋ₓ is less than 15%.

#### Supporting Information

Figure S3 shows the XRD patterns of the BFZ91 powder before and after calcination at high temperature; the latter is also shown in Figure 1a. The XRD pattern of the uncalkined powder (i.e., raw ash) is composed of several peaks that correspond to the intermediate phases of the solid solution. Calcination in ambient air at 950 °C for 4 h activates cation diffusion and leads to the formation of a phase pure perovskite oxide. The calcined BFZ91 powder exhibits a cubic crystal structure in the Pm₃m space group without any secondary phases. The diffraction pattern agrees with that of BaFe₀.₉₉Zr₀.₀₅O₂.₇₆ (ICDD 04-022-8935) and is in agreement with a previous work on Zr-doped BaFeO₃₋ₓ oxides. High-temperature XRD measurements for BFZ91 in ambient air have also shown that the cubic structure is preserved up to 950 °C. The surface area of the calcined BFZ91 powder was estimated at 4.0 ± 0.3 m²/g using BET.

Figure 1 compares the XRD pattern of the calcined BFZ91 powder (a,b) and that of the sintered BFZ91 pellet (c,d) prior to polishing. Subplots b and d zoom into the 2θ range of 29–33° to highlight the peak shift between the two patterns.

### Table 1. Crystal Structure, Space Group, Lattice Constants and Phase Identification for: (1) the Calcined BFZ91 Powder (950 °C for 4 h), (2) the As-Prepared Dense BFZ91 Pellet (1200 °C for 8 h), (3) the As-Received La₂O₃ Powder, and (4) the As-Received La₂O₃ Powder after Heat-Treatment in Ambient Air at 800 °C for 2 h

<table>
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<th>no.</th>
<th>material</th>
<th>phases</th>
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<th>space group</th>
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<th>phase %</th>
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<td>1</td>
<td>calcined BFZ91 powder</td>
<td>BaFe₀.₉₉Zr₀.₀₅O₂.₇₆</td>
<td>cubic</td>
<td>Pm₃m</td>
<td>a = b = c = 4.022</td>
<td>100.0</td>
</tr>
<tr>
<td>2</td>
<td>as-prepared BFZ91 pellet</td>
<td>BaFe₀.₉₅Zr₀.₀₅O₂.₆₃₅</td>
<td>cubic</td>
<td>Pm₃m</td>
<td>a = b = c = 4.079</td>
<td>100.0</td>
</tr>
<tr>
<td>3</td>
<td>as-received La₂O₃ powder</td>
<td>La₂O₃</td>
<td>hexagonal</td>
<td>P₃₃₁</td>
<td>a = b = c = 3.937</td>
<td>97.3</td>
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<tr>
<td>4</td>
<td>La₂O₃ powder</td>
<td>La₂O₃</td>
<td>hexagonal</td>
<td>P₃₃₁</td>
<td>a = b = c = 3.937</td>
<td>100.0</td>
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Figure 1. Comparison between the XRD pattern of the calcined BFZ91 powder (a,b) and that of the sintered BFZ91 pellet (c,d) prior to polishing.
increases because of sintering at 1200 °C. This is confirmed by the increase in the peak intensity and the decrease in the peak width as compared to the peaks of the calcined BFZ91 powder. The crystal structure of the BFZ91 pellet remains cubic (space group $Pm\overline{3}m$) and no secondary phases are detected. An interesting observation is that the peak positions of the sintered BFZ91 pellet shift to lower 2θ angles when compared to the peak positions of the calcined BFZ91 powder. This is highlighted in Figure 1 (subplots b and d), which zoom into the 2θ range of 29−33°. This peak shift toward lower 2θ angles implies a unit cell lattice expansion for the sintered BFZ91 pellet compared to the unit cell of the calcined BFZ91 powder. Rietveld refinement was used to estimate the lattice constant of each pattern, and the results are shown in Table 1, confirming the aforementioned lattice expansion of the BFZ91 pellet ($a = b = c = 4.079$ Å) compared to that of the BFZ91 powder ($a = b = c = 4.022$ Å).

Interestingly, the oxygen content of the BFZ91 powder and pellet estimated based on the Rietveld refinement is different (Table 1). Although iodometric titration is a more accurate method to evaluate the oxygen deficiency ($\delta$) of each material, the fact that less oxygen is estimated in the structure of the BFZ91 pellet suggests that the source of the lattice expansion of the BFZ91 pellet could be related to an irreversible loss of oxygen because of sintering at 1200 °C. This is consistent with the tendency of ceramic oxides to lose oxygen from their structure when the temperature is increased and as a function of $P_{O_2}$. To support our hypothesis, we conducted TGA measurements with: (1) the calcined BFZ91 powder (950 °C, 4 h), which will be denoted BFZ91-950, and (2) the BFZ91-950 powder recalcined at 1200 °C for 8 h, that is, using the same heat treatment employed during the sintering of a BFZ91 pellet; this powder will be denoted BFZ91-1200. For the TGA measurements, approximately 0.1 g of powder were first heated from room temperature to 150 °C for 2 h to ensure the investigated materials were dehydrated. Then, the temperature was decreased to 30 °C until mass equilibration. After this step, the TGA furnace was heated from 30 to 1000 °C using a heating rate equal to 20 °C/min followed by equilibration at 1000 °C for 3 h. Ambient air at 100 sccm was flowing continuously during the measurements. The results are shown in Figure 2 (the dehydration step is not plotted), which also includes the oxygen deficiency change ($\Delta \delta$) calculated using the following equation:

$$\Delta \delta = \frac{W_{BaFe_{0.95}Zr_{0.05}O_{3.6}} - W_{O_2}}{m_s}$$

In eq 3, $W_{BaFe_{0.95}Zr_{0.05}O_{3.6}}$ is the molar weight of the off-stoichiometric $BaFe_{0.95}Zr_{0.05}O_{3.6}$ material at room temperature (calculated using the stoichiometry defined in Table 1 for each sample), $\Delta m$ is the change in the sample’s mass during the TGA measurement, $m_s$ is the sample’s starting mass, and $W_{O_2}$ is the atomic weight of oxygen. Figure 2 indeed shows that the oxygen loss is different in the studied powders throughout the entire heating step with BFZ91-950 losing more oxygen compared to BFZ91-1200. As a result, $\Delta \delta$ is higher for BFZ91-950 compared to BFZ91-1200. Note that the calculated $\Delta \delta$ values, as shown in Figure 2, are in agreement with TGA measurements conducted in air for $BaFe_{0.98}Zr_{0.02}O_{2.56}$.

In that work, however, the lattice expansion observed here was not reported. Based on the XRD and TGA results, as shown in Figures 1 and 2, respectively, we suggest that the lattice expansion of the BFZ91 pellet is because of an irreversible increase in the content of oxygen vacancies induced by the sintering at high temperatures. We note here that although the XRD and TGA results shown in Figures 1 and 2, respectively, confirm a lattice expansion induced by sintering at higher temperatures, the lattice expansion is not related only with changes in the amount of oxygen in the structure but also because of changes in the amount of the iron (Fe) charged species within the material. To further elaborate on this, we postulate the following point defect chemistry model for BFZ91 written using the Kröger–Vink notation:

$$\text{BFZ91}$$

Figure 2. TGA measurements in ambient air (100 sccm) between $T = 30$−1000 °C for BFZ91-950 (red dashed line) and BFZ91-1200 (blue solid line). (a) Weight percentage during the heating step, (b) weight percentage during equilibration at 1000 °C for 3 h, (c) $\Delta \delta$ during the heating step, and (d) $\Delta \delta$ during equilibration at 1000 °C for 3 h.
The kinetics of reactions 4 and 5 account for the Fe disproportionation. A similar point defect model has been proposed for other materials. In reactions 4 and 5, $V_{O^\bullet\bullet}$ denotes an oxygen vacancy, $O_{O^\bullet}$ is an oxygen ion ($O^{2-}$) incorporated into an $O^{2-}$ lattice site while $Fe_{o^\bullet\bullet}$, $Fe_{o^\bullet}$, and $Fe_{o^\bullet}$ correspond to $Fe^{4+}$, $Fe^{3+}$, and $Fe^{2+}$ incorporated into the $Fe^{2+}$ lattice site, respectively. $Fe_{o^\bullet\bullet}$, $Fe_{o^\bullet}$, and $Fe_{o^\bullet}$ participate in the electron transfer required to ionize $O_2$ prior to incorporation into the material. Depending on the BFZ91 defect chemistry and thermodynamics, $O_2$ incorporation may also happen because of the following reaction, which is the combination of reactions 4 and 5:

$$\frac{1}{2}O_2(g) + V_{O^\bullet\bullet} + 2Fe_{o^\bullet} \rightleftharpoons O_{O^\bullet} + 2Fe_{o^\bullet}$$

(4)

$$2Fe_{o^\bullet} \rightleftharpoons Fe_{o^\bullet\bullet} + Fe_{o^\bullet}$$

(5)

Reaction 4 reflects the $O_2$ incorporation into the material while reaction 5 accounts for the Fe disproportionation. A similar point defect model has been proposed for other materials. In reactions 4 and 5, $V_{O^\bullet\bullet}$ denotes an oxygen vacancy, $O_{O^\bullet}$ is an oxygen ion ($O^{2-}$) incorporated into an $O^{2-}$ lattice site while $Fe_{o^\bullet\bullet}$, $Fe_{o^\bullet}$, and $Fe_{o^\bullet}$ correspond to $Fe^{4+}$, $Fe^{3+}$, and $Fe^{2+}$ incorporated into the $Fe^{2+}$ lattice site, respectively. $Fe_{o^\bullet\bullet}$, $Fe_{o^\bullet}$, and $Fe_{o^\bullet}$ participate in the electron transfer required to ionize $O_2$ prior to incorporation into the material. Depending on the BFZ91 defect chemistry and thermodynamics, $O_2$ incorporation may also happen because of the following reaction, which is the combination of reactions 4 and 5:

$$\frac{1}{2}O_2(g) + V_{O^\bullet\bullet} + 2Fe_{o^\bullet} \rightleftharpoons O_{O^\bullet} + 2Fe_{o^\bullet}$$

(6)

Although determining the exact defect chemistry and thermodynamics of BFZ91 is outside the scope of this investigation and will be addressed in our future work, the proposed point defect model allows for a deeper understanding of the observed chemical expansion phenomenon and its implications on the properties of the investigated materials. The mass loss, as shown in Figure 2, is because of oxygen release from the material leaving behind oxygen vacancies. According to reactions 4–6, this should be accompanied by a change in the concentration of the different Fe states ($Fe_{o^\bullet\bullet}$, $Fe_{o^\bullet}$, and $Fe_{o^\bullet}$) dictated by the thermodynamics of reactions 4–6, the ABO$_{3-δ}$ stoichiometry, and the conservation of charge neutrality in the bulk of the material. This means that BFZ91-950 and BFZ91-1200 have different amounts of oxygen vacancies in their structure as well as different concentrations of Fe states. Besides having an impact on the final unit cell volume (as the different Fe states are characterized by a different ionic radius), the different concentrations of the charged species are expected to affect the kinetics of reactions 4–6, and the diffusion of charged species within the material. As a result, this phenomenon becomes very important when calculating properties of materials (e.g., electronic and ionic conductivity, oxygen diffusivity) and various other properties (e.g., $T$ and $P_{O_2}$, etc.).

Figure 3. XRD patterns of: (a) as-received La$_2$O$_3$ powder and (b) as-received La$_2$O$_3$ powder after heat-treatment in ambient air at 800 °C for 2 h. Blue circles correspond to La(OH)$_3$ peaks (ICDD 04-016-2506). Note that the logarithmic y-axis is used to increase the visibility of the La(OH)$_3$ peaks.
La(OH)₃ decomposes to lanthanum hydroxide oxide (LaOOH) and then to La₂O₃ through the following two-step mechanism:72

\[
\text{La(OH)}_3 \rightarrow \text{LaOOH} + \text{H}_2\text{O} \tag{7}
\]

\[
2\text{LaOOH} \rightarrow \text{La}_2\text{O}_3 + \text{H}_2\text{O} \tag{8}
\]

Kinetically, the formation of LaOOH through reaction 7 happens at \( T \approx 330 \) °C while full dehydration to La₂O₃ via reaction 8 takes place at \( T \approx 490 \) °C.72 At \( T = 550 \) °C, XRD results show that pure La₂O₃ is obtained.72 However, the aforementioned decomposition mechanism changes in the presence of CO₂ given that lanthanum is a basic element, and hence, its oxides and hydroxides can easily form lanthanum dioxycarbonate (La₂O₂CO₃) or other carbonate species. The decomposition of La(OH)₃ in ambient air proceeds through the following mechanism:73,74

\[
2\text{La(OH)}_3 + \text{CO}_2 \rightarrow \text{La}_2\text{O}_2\text{CO}_3 + 3\text{H}_2\text{O} \tag{9}
\]

\[
\text{La}_2\text{O}_2\text{CO}_3 \rightarrow \text{La}_2\text{O}_3 + \text{CO}_2 \tag{10}
\]

Reaction 9 takes place between \( T = 200–600 \) °C, while reaction 10 happens at high rates in the interval \( T = 650–800 \) °C.73 XRD results reported in the literature confirm the presence of La₂O₂CO₃ at 500–700 °C during the process of La(OH)₃ decomposition in air.73,75 While pure La₂O₃ is observed at 800 °C.75 This is consistent with additional data showing that reaction 10 is triggered at \( T \approx 700–725 \) °C.76–78 To further confirm the aforementioned literature results, we have heat treated the as-received La₂O₃ powder in ambient air at 800 °C for 2 h. As shown in Figure 3b, XRD results obtained immediately after this heat treatment confirm that a pure phase La₂O₃ material can be obtained without any additional La(OH)₃ or La₂O₂CO₃ phases. To facilitate the discussion in the following sections, Figure 4 shows the stability of La(OH)₃ and La₂O₂CO₃ as a function of \( T \) and \( P_{\text{H}_2\text{O}} \) or \( P_{\text{CO}_2} \). Regarding the \( T \) at which decomposition to La₂O₃ occurs for a fixed partial pressure, the differences between the results in Figure 4 and the literature results presented earlier are because the former provide information from a purely thermodynamic point of view while the latter are based on TGA measurements for which the kinetics of the reactions are also considered.

Based on the aforementioned discussion, the following important conclusions are drawn. First, although the as-received La₂O₃ powder contains a small amount of La(OH)₃, the latter decomposes to pure La₂O₃ during the initial heating of the button-cell reactor in pure Ar from room temperature to 1025 °C (see Section 2.3 and Figure 4). After sealing is completed, the reactor temperature decreases to \( T = 750 \) °C while pure Ar is still flowing on the CH₄ side. OCM experiments begin at \( T = 750 \) °C or \( T = 850 \) °C, and hence, the starting OCM catalyst is expected to be pure La₂O₃ without any secondary phases. This is consistent with a previous work on undoped and Sr-doped La₂O₃, where pretreatment in pure N₂ at 800 °C was conducted prior to OCM experiments to remove such impurities.60 Second, although it is thermodynamically favorable for lanthanum hydroxides and carbonates to decompose at \( T > 725 \) °C, we stress that this happens in the presence of air or an inert gas. As shown in Figure 4, at a fixed \( T \), the partial pressure of H₂O and CO₂ can alter the tendency toward the formation of lanthanum hydroxides or carbonates. Under OCM conditions, the gaseous environment will include species such as CH₄, O₂, H₂O, CO₂, C₂ and so forth. Depending on their concentrations, new lanthanum-based phases may appear, which could have beneficial or deleterious effects on the C₂ production. For example, La₂O₂CO₃ rods have been shown to be active for OCM at low temperatures (420–500 °C) when prepared using a hydrothermal method but low OCM activity was observed for La₂O₂CO₃ plates synthesized via a precipitation method.76

The thermodynamics of the aforementioned lanthanum-containing species create another challenge regarding the characterization of the used La₂O₃ catalyst. After the end of the OCM measurements, cooling down the reactor from \( T \geq 750 \) °C to room temperature can happen in two ways: (1) by flowing pure Ar in the CH₄ side of the reactor and (2) by flowing CH₄–Ar mixtures. In the first scenario, if lanthanum hydroxides or carbonates form on La₂O₃ during OCM (because of exposure to a hydrocarbon environment), cooling down the reactor in pure Ar will lead to their decomposition, and hence, these phases

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**Figure 4.** Ellingham diagrams showing the stability of La(OH)₃ (left) and La₂O₂CO₃ (right) as a function of \( T \) and \( P_{\text{H}_2\text{O}} \) or \( P_{\text{CO}_2} \) (for absolute pressure of 1 atm). The light pink zone denotes the area of La(OH)₃ and La₂O₂CO₃ formation, while the light blue zone denotes the area of La₂O₃ formation. The red solid line denotes the standard-state Gibbs free energy change of the corresponding reaction \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \). The dashed lines correspond to the standard-state Gibbs free energy change as a function of \( T \) for a fixed partial pressure \( \Delta G^\circ = RT \ln P_{\text{H}_2\text{O}} \) or \( \Delta G^\circ = RT \ln P_{\text{CO}_2} \). Standard-state molar enthalpies of formation and standard-state molar entropies for each species were obtained from reference tables.77,79

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**Table 1.** Standard-state molar enthalpies of formation and standard-state molar entropies for each species...
may not be detected by common characterization methods such as XRD although they may still form under the OCM conditions reported in this work. If the second option is employed, then, as will be shown in the next section, species such as $\text{H}_2\text{O}$ or $\text{O}_2$ will still form through CH$_4$ full oxidation because of the finite $\text{O}_2$ permeation through the membrane. These will react with La$_2\text{O}_3$ at $T < 725 \degree\text{C}$ forming lanthanum hydroxides or carbonates. These phases may be detected by XRD, but they will correspond to phases formed during the cooling of the reactor rather than under the OCM conditions of our work. Cooling down the reactor by flowing an inert gas in the feed side (instead of air) could solve the aforementioned problem, but then, the presence of CH$_4$ in the stream will decompose the BFZ91 membrane. In our work, we have chosen to cool down the reactor using ambient air in the air side and 5% CH$_4$ (balanced with Ar) in the CH$_4$ side in order to preserve the structure of the BFZ91 membrane and reduce the impact of CH$_4$ and its gaseous products on the final La$_2\text{O}_3$ crystal structure.

As a final remark, note that the aforementioned challenge demonstrates once again the implications of properly characterizing OCM catalysts with ex situ techniques and highlights the importance of using in situ catalyst characterization methods. Similar conclusions have been drawn for La$_2\text{O}_3$ investigated ex situ using X-ray photoelectron spectroscopy after OCM measurements.

### 3.3. CH$_4$ Conversion Using BFZ91 in the Absence of a Catalyst

To determine the species produced by the reaction of CH$_4$ with O$_2$ that permeates through BFZ91 and to identify any catalytic reactions taking place on BFZ91, we begin our analysis with experiments conducted in the absence of a catalyst on the CH$_4$ side of BFZ91. These reference measurements are taken in the range $T = 800 - 900 \degree\text{C}$ and $X_{\text{CH}_4} = 0 - 30\%$.

Figure 5a shows that at $T = 800 \degree\text{C}$, $J_{O2} \approx 0.75 (\mu\text{mol/cm}^2/\text{s})$, and it is almost constant in the range $X_{\text{CH}_4} = 0 - 30\%$. However, at $T = 850 \degree\text{C}$ and $T = 900 \degree\text{C}$, $J_{O2}$ rises as more CH$_4$ is added into the stream. This dependency is related to the rate-limiting step of the O$_2$ permeation mechanism. It is known that in CMRs, $J_{O2}$ is limited by surface reactions on either gas–membrane interface or by bulk diffusion. In the presence of a fuel, its reaction with O$_2$ from the membrane can increase $J_{O2}$ if surface reactions on the fuel side are not rate limiting. This is because of a decrease in the fuel side $\mu_{\text{O}_2}$ leading to an overall increase in the $\mu_{\text{O}_2}$ gradient between the two membrane sides. Previous work has shown that BFZ91 exhibits thickness limitations, and hence, higher $J_{O2}$ can be achieved using thinner membranes.

The results in Figure 5a suggest that at $T = 800 \degree\text{C}$, the CH$_4$ side surface reaction is limiting $J_{O2}$ if surface reactions on the fuel side are not rate limiting. This is because of a decrease in the fuel side $\mu_{\text{O}_2}$ leading to an overall increase in the $\mu_{\text{O}_2}$ gradient between the two membrane sides.
Figure 6. Long-term OCM measurements of BFZ91 with La2O3 powder on the CH4 side. (a) JCH4 (black) as a function of time and (b) nCH4 (orange), nC2H4 (pink) and nC2H6 (green) as a function of time. Red dashed lines correspond to increases in the reactor temperature while blue dotted lines correspond to instants of XCH4 change. Measurements were conducted every 1 h. During the experiment, ambient air was flowing in the air side at Qair = 200 sccm while CH4−Ar mixtures with QCH4−Ar = 100 sccm were introduced in the CH4 side. The thickness of the membrane was 0.68 mm, while the thickness of the La2O3 catalyst layer was 1.5 mm.

compared to the nonreactive case. This effect is more pronounced at 850 and 900 °C.

As shown in Figure 5c,d, at T = 800 °C, CCH4 < 2% while CCO2 < 8%. At higher T and for the same XCH4, both CCH4 and CCO2 increase, consistent with enhanced reactivity at elevated T. However, for the same T, CCH4 decreases as more CH4 is added into the stream; CCO2 increases but does not reach 100%, a sign that under the conditions investigated herein, CH4 cannot fully convert all the available O2 into products in the presence of BFZ91. In addition, Figure Sb and Supporting Information Figure S4 show that for all cases, the CH4 side XCH4 and XCO2 are high, further confirming that CH4 does not react with O2 or gaseous O2 at considerable rates (especially at lower T) and that a low PCH4 environment cannot be established when using BFZ91 alone. According to Supporting Information Figure S4, some fraction of the fuel succeeds to react with lattice oxygen on the BFZ91 surface or with molecular O2 in the gas phase, as demonstrated by the nonzero mole fraction of C2H6, C2H4, H2O, CO2, H2, and CO. The production of these species, however, is low, as confirmed by the low yields shown in Figure 5e−h and in Supporting Information Figure S5. For comparison, the results of the same experiment in the presence of La2O3 (shown in Section 3.5) reveal negligible O2 near the CH4 side of the membrane, CCO2 ≈ 100% and higher C2 yields.

The aforementioned results lead us to the following important conclusions. First, it appears that the BFZ91 membrane does not have a strong catalytic activity toward the decomposition or oxidation of CH4. This is a notable property of the BFZ91 membrane, which is expected to increase the C2 yields by avoiding side reactions of CH4 producing species other than C2H6 and C2H4. Second, according to Figure 5e,g and Supporting Information Figure S5, some activity toward the production of C2 is observed. For example, SC2H6 is around 10%−30% while that of SC2H4 is around 10−30%. However, the corresponding yields are below 2%. Although a C2 yield of ~3% can be obtained at 900 °C, the use of an OCM-active catalyst is expected to promote C2 production at lower T. The same results confirm that overall, the role of the BFZ91 membrane is to avoid CH4−Ar mixtures with QCH4−Ar = 100 sccm were introduced in the CH4 side. The thickness of the membrane was 0.68 mm, while the thickness of the La2O3 catalyst layer was 1.5 mm.

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already conducted studies using CO₂ mole fractions of 50 and 75% in the stream. Although long-term studies were not reported, the obtained \( J_{\text{O}_2} \) was higher than LSCF membranes operating under the same conditions. Because the formation of BaCO₃ is favorable at high T and CO₂, we would expect that any irreversible membrane deactivation at such conditions would have been immediate and would have lowered \( J_{\text{O}_2} \) significantly. However, more detailed studies (outside the scope of this work) are required to understand the high resistance of BFZ91 against BaCO₃ formation.

### 3.4. Performance and Stability of BFZ91 and La₂O₃ under Long-Term OCM Measurements

To evaluate the OCM performance of BFZ91 with La₂O₃, we conducted long-term measurements between \( T = 750 \sim 900 \) °C and \( X_{\text{CH}_4}^{\text{in}} = 0 \sim 30\% \). During the experiment, the temperature was fixed and \( X_{\text{CH}_4}^{\text{in}} \) increased to a specified value. Measurements were obtained every 1 h until the performance reached steady state. Once steady state was achieved, \( X_{\text{CH}_4}^{\text{in}} \) increased again and the process was repeated. When the measurement at \( X_{\text{CH}_4}^{\text{in}} = 30\% \) was completed, CH₄ was removed progressively and the temperature of the reactor increased to the next interval by flowing pure Ar in the CH₄ side. According to Figure 4 and the discussion in Section 3.2, this means that thermodynamically, the starting catalyst at each temperature was pure La₂O₃. Measurements were repeated in the same sequence for all the temperatures investigated here. The long-term measurements lasted for approximately 23 days after which we decided to stop the experiment. Note that Figure 6 only shows the reactive measurements; no stability was measured for \( X_{\text{CH}_4}^{\text{in}} = 0\% \).

Figure 6 shows \( J_{\text{O}_2} \) and the activities of C₂H₆, C₂H₄, and C₂ (C₂H₂, C₃H₄, and acetylene (C₂H₂)) as a function of time,
Figure 9. Steady-state OCM measurements of BFZ91 with La$_2$O$_3$ as a function of $T$ and $X_{\text{CH}_4}^{\text{in}}$. (a) $J_{O_2}$, (b) $C_{\text{CH}_4}$, (c) $S_{\text{CH}_4}$, (d) $C_{\text{CH}_2}$, (e) $Y_{\text{CH}_4}$, (f) $Y_{\text{CH}_2}$, (g) $\tilde{n}_{\text{CH}_2}$, and (h) $\tilde{n}_{\text{CH}_4}$. Color marker-line equivalence: (1) $T = 750 \pm 3^\circ \text{C}$: red circles-dotted line, (2) $T = 800 \pm 3^\circ \text{C}$: blue squares-dashed line, (3) $T = 850 \pm 3^\circ \text{C}$: green diamonds-dashed dotted line, and (4) $T = 900 \pm 4^\circ \text{C}$: black triangles-solid line. Lines are guides to the eye. The thickness of the membrane was 0.68 mm, while the thickness of the La$_2$O$_3$ catalyst layer was 1.5 mm.

Figure 10. Steady-state OCM measurements of BFZ91 with La$_2$O$_3$ as a function of $T$ and $X_{\text{CH}_4}^{\text{in}}$. (a) $S_{\text{H}_2}$, (b) $Y_{\text{H}_2}$, (c) $S_{\text{CO}_2}$, (d) $Y_{\text{CO}_2}$, (e) $S_{\text{CO}}$, and (h) $Y_{\text{CO}}$. Color marker-line equivalence: (1) $T = 750 \pm 3^\circ \text{C}$: red circles-dotted line, (2) $T = 800 \pm 3^\circ \text{C}$: blue squares-dashed line, (3) $T = 850 \pm 3^\circ \text{C}$: green diamonds-dashed dotted line, and (4) $T = 900 \pm 4^\circ \text{C}$: black triangles-solid line. Lines are guides to the eye. The thickness of the membrane was 0.68 mm, while the thickness of the La$_2$O$_3$ catalyst layer was 1.5 mm.
which clearly demonstrate the high stability of BFZ91 and \( \text{La}_2\text{O}_3 \) towards \( \text{C}_2 \) production. During the entire 23-day experiment, \( \dot{J}_\text{O}_2 \) and \( n_{\text{CH}_4}^\text{out} \) were stable without any loss of performance. To the best of our knowledge, this is the first time that such long-term OCM measurements are demonstrated with stable membrane-catalyst materials that have been subjected to temperature and fuel cycling for long times. We note here that at 850 and 900 °C, \( \dot{J}_\text{O}_2 \) shows a gradual increase as a function of time for the same \( X_{\text{CH}_4}^\text{in} \) value, while the activities of the \( \text{C}_2 \) species remain constant. This gradual \( \dot{J}_\text{O}_2 \) increase results from the progressive increase of \( X_{\text{CO}_2}^\text{in} \) and \( X_{\text{H}_2\text{O}}^\text{out} \) as a function of time.

Figure 7 shows the XRD patterns of the unused and used BFZ91 and \( \text{La}_2\text{O}_3 \). According to Figure 7, no phase transformations or secondary phases were detected on the air and \( \text{CH}_4 \) side of the BFZ91 membrane after the end of the OCM measurements. The same is true for the used \( \text{La}_2\text{O}_3 \) powder. For \( \text{La}_2\text{O}_3 \), we have already discussed that we cannot draw a safe conclusion about the formation of stable lanthanum hydroxides and carbonates during OCM based on ex situ XRD; however, recent in operando Raman spectroscopy studies demonstrated the high stability of \( \text{La}_2\text{O}_3 \) under industrially relevant OCM conditions.\(^{62}\) Nevertheless, the fact that ex situ XRD reveals the absence of secondary phases on \( \text{La}_2\text{O}_3 \) is consistent with the Ellingham diagrams of Figure 4 and the mole fractions of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) formed near the membrane surface (Figures 11 and 12 discussed later in Section 3.6). Although the aforementioned results may confirm the high structural stability of the BFZ91 membrane in a hydrocarbon environment and its compatibility with \( \text{La}_2\text{O}_3 \), they do not account for the possible formation of amorphous phases on the membrane or the \( \text{La}_2\text{O}_3 \) catalyst. Such amorphous phases, if present, could degrade the performance under longer trials. Indeed, Schucker et al. have proposed that amorphous phases of \( \text{SrCO}_3 \), \( \text{SrO} \), and \( \text{SrO}_2 \) may exist on \( \text{Sr} \)-doped \( \text{La}_2\text{O}_3 \) under OCM conditions.\(^{62}\) In that work, the authors confirm that such amorphous phases cannot be detected by XRD or Raman spectroscopy. However, the study of Schucker et al. does not provide long-term measurements to verify a performance loss as a function of time that could be ascribed to the aforementioned phases.\(^{62}\) In our work, considering that our 23-day measurement is by itself a long-term trial allows us to conclude that amorphous phases, if present on the materials, do not degrade the OCM performance.

Figure 8 presents the microstructure of the BFZ91 pellet and \( \text{La}_2\text{O}_3 \) powder before and after the OCM measurements. The as-sintered BFZ91 pellet (Figure 8a) shows a large distribution of grain boundary sizes, which range between 0.5−5 μm. No signs of porosity are observed, which confirm the high relative density of the pellet estimated using the Archimedes principle. Figure 8b shows one of the sides of the BFZ91 pellet after polishing. A flat surface is observed with some lines that correspond to scratches from the polishing procedure. Some material expulsion is also noticed despite the fact that a high grit number sandpaper was used to ensure a polished finish. Figure 8c,d shows the air and \( \text{CH}_4 \) side of the BFZ91 pellet, respectively, after the end of the OCM measurements with \( \text{La}_2\text{O}_3 \). On both sides, surface terraces have become visible within some of the grains, which is probably related to the grain crystallographic orientation and the polishing process as no such terraces are observed in Figure 8a. Similar observations have been reported for other materials\(^{87,88}\) but the examination of this effect is outside the scope of this work. No particle-like structures are found on either side of the BFZ91 pellet, consistent with the XRD results of Figure 7. The microstructure of the BFZ91 pellet after the end of
the measurements without La$_2$O$_3$ is similar to the one shown in Figure 8c,d. Finally, Figure 8e,f presents the as-purchased and used La$_2$O$_3$ powder, respectively. The used powder shows significant sintering because of the high $T$ operation. As shown in Supporting Information Figure S7 comparing the La$_2$O$_3$ catalyst after the end of the OCM measurements and after calcination of a fresh catalyst at $T = 1025$ °C for 24 h, the sintering of the La$_2$O$_3$ powder observed, as shown in Figure 8f, is primarily related to the sealing procedure followed in this work and not because of operation in a reactive environment. This also confirms that the sintering of the La$_2$O$_3$ catalyst happened before the beginning of the OCM measurements. If this step could be avoided, then, the sintering of the La$_2$O$_3$ powder would be lower given that the maximum $T$ investigated in our work is 900 °C. Unfortunately, the amount of the La$_2$O$_3$ catalyst used in the OCM experiment is low and did not allow quantification of its surface area using BET.

Finally, based on the XRD and SEM results, as shown in Figures 7 and 8, no signs of carbon deposition are observed on the used materials. In addition, if carbon forms in the products, its surface area using BET.

3.5. Analysis of BFZ91 and La$_2$O$_3$ Steady-State OCM Measurements. At each $T$ and $X_{\text{CH}_4}^{\text{in}}$, as shown in Figure 6, detailed measurements were obtained after steady state was achieved to shed light into the performance and OCM chemistry. Figures 9-12 present these results.

Figure 9a shows $J_{\text{O}_2}$ as a function of $T$ and $X_{\text{CH}_4}^{\text{in}}$. At $T = 750$ °C, $J_{\text{O}_2}$ is constant at $\sim0.5 \text{ mol/cm}^2/\text{s}$ and independent of $X_{\text{CH}_4}^{\text{in}}$. However, as $T$ increases, $J_{\text{O}_2}$ rises as a function of $X_{\text{CH}_4}^{\text{in}}$. As discussed earlier, this is related to the rate-limiting steps of the O$_2$ permeation process. Surface reactions on the CH$_4$ side are rate limiting at $T \leq 800$ °C (in addition to bulk diffusion), and they are accelerated at $T \geq 850$ °C. The $J_{\text{O}_2}$ increase as a function of $X_{\text{CH}_4}^{\text{in}}$ at $T = 850–900$ °C, as shown in Figure 9a, suggests that a low $P_{\text{O}_2}$ is developed in the presence of La$_2$O$_3$ when CH$_4$ is added. This will be confirmed in the next section.

In addition to the above, we also make a note about the nonreactive $J_{\text{O}_2}$ measurements ($X_{\text{CH}_4}^{\text{in}} = 0\%$) at 800–900 °C, as shown in Figure 9a. At this temperature range, comparing with Figure 5a reveals that $J_{\text{O}_2}$ has decreased slightly in the presence of La$_2$O$_3$. Given that the thickness of the BFZ91 membrane was almost the same for both experiments, we suspect that the slight decrease in the nonreactive $J_{\text{O}_2}$ could be related to the presence of the La$_2$O$_3$ powder on the CH$_4$ side of the membrane. La$_2$O$_3$ could restrict gaseous diffusion through its porous structure thus decreasing $J_{\text{O}_2}$. In any case, the performance drop observed in our measurements was not remarkable, and hence, if the slight drop in $J_{\text{O}_2}$ is not related to experimental uncertainties but is...
because of the presence of La$_2$O$_3$, we conclude that the latter does not significantly impact $J_{CH}$, especially when CH$_4$ is added in the reactor. Figure 9b shows $C_{CH}$ as a function of $T$ and $X^{in}_{CH_4}$. Higher $C_{CH}$ is achieved as $T$ increases given the Arrhenius activated behavior of gas phase and surface (membrane and catalyst) reactions. At the same $T$, adding more fuel decreases $C_{CH}$, showing that less fraction of CH$_4$ can be converted to the products. Figure 9c,d shows $S_{CH_2}$ and $S_{CH_4}$, respectively. The system is less selective to the formation of CH$_2$ and CH$_4$ as $T$ increases. The trend is opposite for CH$_2$, whose selectivity increases as a function of $T$ except at 900 °C. At the same $T$, adding more CH$_4$ increases the selectivity with the exception of $S_{CH_2}$ at 900 °C and of $S_{CH_4}$ at 750 °C, where nearly constant values are observed. These trends can be explained by the conversion of CH$_2$ to CH$_4$, which, in general, can happen in the gas phase and on the La$_2$O$_3$ catalyst through oxidative and non-oxidative pathways.

To obtain further insights about the aforementioned reactions, we examined the NODHE in the absence and presence of La$_2$O$_3$ between $T = 750$–900 °C; this experiment is described in the Supporting Information (Section 7). Supporting Information Figure S9 shows that at equilibrium, CH$_2$ is fully converted to products even at $T = 750$ °C. The mole fraction of CH$_2$ is finite but low and the system favors the production of CH$_3$, H$_2$, and CH$_4$. Under non-equilibrium conditions, Supporting Information Figure S9 shows identical CH$_2$ thermal decomposition with and without La$_2$O$_3$. As a result, we can safely conclude that La$_2$O$_3$ is not active toward the CH$_2$ and CH$_4$ non-oxidative dehydrogenation, which can only happen in the gas phase. Supporting Information Figure S9 reveals that the conversion of CH$_2$ at $T = 750$ °C approaches ≈80%, while full conversion to products is achieved at $T = 850$ °C. Most of CH$_2$ is converted to CH$_2$ and H$_2$ with CH$_2$ and CH$_4$ also being present but at lower mole fractions. The produced CH$_2$ peaks at $T ≈ 780$ °C, and then, it decreases because of decomposition to CH$_2$, CH$_4$, and H$_2$. These results confirm the presence of both CH$_2$ and CH$_4$ non-oxidative dehydrogenation in the gas-phase, which depend on the residence time and become more intense as the temperature rises. Hence, we demonstrate that one pathway for CH$_2$ production is the NODHE in the gas-phase; this reaction does not proceed on La$_2$O$_3$. The possibility of the oxidative dehydrogenation of CH$_2$ (ODHE) to CH$_2$ and H$_2$O (either in the gas phase or on La$_2$O$_3$) will be discussed in the next section.

The yields (Figure 9e,f) and activities (Figure 9g,h) of CH$_2$ and CH$_4$ show similar trends. For the same $X^{in}_{CH_2}$, $Y_{CH_2}$, and $n_{CH_2}$, increase at 800 °C compared to 750 °C, but a sharp drop is observed at 850 °C and 900 °C because of C$_2$H$_6$ conversion to CH$_3$. In contrast, $Y_{CH_4}$ and $n_{CH_4}$ clearly increase as $T$ rises. However, the increase at 900 °C compared to the 850 °C case is small, confirming that CH$_3$ either pyrolyzes at high $T$ similar to CH$_2$ (see Supporting Information Figure S9) or reacts with other products. At the same $T$, both $n_{CH_2}$ and $n_{CH_4}$ increase as more fuel is introduced in the CH$_4$ side, which is consistent with the known trend of higher C$_2$ selectivity under fuel-rich conditions. Figure 10 shows the selectivities and yields of the rest of the species produced within the reactor. Figure 10a–d demonstrates that the La$_2$O$_3$ catalyst is selective toward the formation of H$_2$O and CO$_2$ with yields higher than those of C$_2$H$_4$ and C$_2$H$_2$. This suggests that, in addition to CH$_4$ coupling to C$_2$, hydrocarbon full oxidation to H$_2$O and CO$_2$ also takes place. For both H$_2$O and CO$_2$ and at the same $X^{in}_{CH_4}$, Figure 10a–d shows that between $T = 750$–900 °C, the selectivity and yield increase as $T$ rises because of the Arrhenius-activated nature of the reactions. However, at the same $T$, addition of more CH$_4$ in the reactor decreases $S_{H_2}$ and $S_{CO_2}$. Comparison with Figure 9c,d confirms that the system becomes more selective toward the formation of C$_2$ by adding more fuel in the reactor. As discussed earlier, this is consistent with the literature suggesting that increased C$_2$ selectivities can be achieved at high CH$_4$ to O$_2$ ratios.

At $T = 750$–850 °C, Figure 10e–h shows that the selectivities to H$_2$ and CO are below 15%, while the corresponding yields are lower than 2%. This confirms that the system is not very active toward syngas production. However, a different trend is observed at 900 °C. At this $T$, an increase in the yields of H$_2$ and CO is observed. As will be discussed in the next section, this behavior is related to several competing reactions leading to syngas production because of enhanced gas-phase reactivity at 900 °C.

3.6. Mixture Composition near the CH$_4$ Side Gas–Membrane Interface and Comparison with Outlet Values. In Section 3.5, we analyzed the steady-state performance of BFZ91 with La$_2$O$_3$ toward CH$_4$ conversion to products. Based on Figures 9, 10, and Supporting Information Figure S9, significant information was obtained about the primary reactions of the OCM chemistry with and without La$_2$O$_3$. However, Figures 9 and 10 focus on measurements at the outlet of the reactor. It has already been demonstrated in Section 3.3 that measurements at the outlet can be different compared to measurements near the membrane surface. This is true when the mixture composition includes species with significant gas-phase reactivity (such as CH$_3$, C$_2$H$_4$ and C$_2$H$_2$) and becomes more important as $T$ rises. In the presence of La$_2$O$_3$, measurements with an alumina micro-probe near the membrane surface allow us to identify the reactions taking place due to the membrane-catalyst interaction. At the same time, these measurements provide information about gas-phase reactions not related to the membrane-catalyst presence such as the ones happening in the reactor’s post-catalytic zone. Figures 11 and 12 compare the CH$_4$ side membrane (i.e., near the membrane surface but still in the gas-phase and within the La$_2$O$_3$ bed) and outlet (i.e., at the outlet of the reactor) mole fractions of O$_2$, CH$_4$, CO$_2$, CO, C$_2$H$_2$, C$_2$H$_4$, H$_2$O, and H$_2$. For the entire data set, mole fractions less than 0.01% were measured for propane, propene, propadiene, and propyne. C$_2$H$_2$ was zero at 750–850 °C, while mole fractions between 0.01 and 0.05% were measured at 900 °C.

In the absence of fuel (i.e., for the cases with $X^{in}_{CH_4} = 0$%), Figure 11a shows that $X^{mem}_{O_2}$ increases as $T$ rises, consistent with the higher $J_{O_2}$ observed in Figure 9a. When CH$_4$ is added, the presence of the catalyst reduces $X^{mem}_{O_2}$ significantly and leads to conditions where C$_2$O$_2$ ≈ 100% (Figure 11b). At $T = 750$–800
°C, surface reactions at the CH4 side limit \( I_{O_2} \), and hence, \( I_{O_2} \) is almost constant despite the fact that a low \( P_{O_2} \) environment evolves in the vicinity of the membrane. At higher \( T \), surface reactions are accelerated, and hence, \( I_{O_2} \) increases at \( T = 850-900 \) °C as more CH4 is added. Figure 11b shows that \( X_{\text{out}} \) follows the same trend as \( X_{\text{mem}} \), with \( X_{O_2}^{\text{mem}} > X_{\text{out}}^{\text{mem}} \) for all experimental points. For nonreactive cases, the trend is consistent given that a higher mole fraction of O2 is expected near the membrane surface, which then decreases at the outlet because of gaseous diffusion. For reactive cases, the results demonstrate that most of the reaction of O2 with CH4 (or other products) takes place near the OCM catalyst with the remaining O2 reacting in the gas phase with CH4 or other products as the mixture exits the reactor.

Figure 11c,d shows that a significant fraction of CH4 remains nonreactive both near the membrane surface and at the outlet, consistent with the relatively low \( C_{CH_4} \), as reported in Figure 9b. However, mole fractions at the outlet are lower than the ones near the membrane; the trend is more apparent as the temperature increases and is consistent with gas-phase reactivity as the mixture exits the reactor. For the same \( X_{\text{mem}}^{\text{CH_4}} < \) CH4 is measured at higher \( T \), which explains the higher \( C_{CH_4} \) observed as \( T \) rises.

Figures 11e and 12e show that significant quantities of CO2 and H2O form within the La2O3 catalyst. The fact that \( X_{H_2O}/X_{CO_2} > 2 \) suggests the full oxidation of CH4. The full oxidation of CH4 and H2 to CO2 and H2O results in \( X_{CO_2}/X_{H_2O} \) equal to 1.5 and 1, respectively. Clear evidence of CH4 full oxidation is also shown in Supporting Information Figure S12a (partial O2 consumption experiment discussed in section 3.7). At \( T = 750-850 \) °C, the mole fractions of CO2 and H2O near the membrane surface are nearly the same as the ones at the outlet (see Figures 11f and 12f). This demonstrates that CH4 full oxidation takes place within the La2O3 bed, and then, the produced H2O and CO2 transport to the exit of the reactor without reacting much with CH4 or with other products. In addition, Figure 12a,c shows that both CH4 and H2O form near the membrane surface and within the La2O3 bed. This observation coupled with the fact that \( X_{H_2O}/X_{CO_2} > 2 \) suggests that CH4 full oxidation to CO2 and H2O is happening simultaneously with CH4 oxidative coupling to CH4 and H2O (reaction 1). Both are facilitated by the presence of the La2O3 catalyst as the aforementioned reactions are not observed at considerable rates in the absence of La2O3 (Figure 5). CH4 is known to precede the formation of CH4; this is verified by the aforementioned results and has also been confirmed by others.59,90

Next, we attempt to identify the pathway of the C2H4 formation from C2H2. To do so, we consider the results, as shown in Figures 11 and 12. These plots confirm the existence of the following primary species within the La2O3 catalyst: H2O, CO2, C2H4, C2H6, CH4, H2, and CO, and unreacted CH4. We note that because O2 is fully consumed near the membrane, the formation of C2H4 and H2 through NODHE takes place in the oxygen-free zone between the La2O3 catalyst and the exit of the reactor (compare Figure 12a with Figure 12b etc.). This is known from our previous work and that of others.37,58,89,91 To remove the effect of this reaction from the analysis of the reactions happening on La2O3, we will focus on the measurements near the membrane surface and within the La2O3 catalyst (i.e., we do not consider the outlet data). By looking at Figure 12c,g, we observe that for a fixed \( T \), \( X_{CO_2}^{\text{mem}} \) and \( X_{H_2}^{\text{mem}} \) increase as \( X_{CH_4}^{\text{mem}} \) increases. Based on this observation, the production of C2H4 and H2 can be the result of the following pathways:

- **Pathway 1**: ODHE to C2H4 and H2O followed by reaction to syngas. This pathway can be described through the following global reactions:

\[
C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \tag{11}
\]

\[
C_2H_4 + \frac{x}{a-c}O_2C_2C \rightarrow ax CO + \left( \frac{y}{2} + \frac{bx}{2(a-c)} \right)H_2
\]

\( a \neq c \)

Regarding syngas production (reaction 12), we note that in general, syngas can be produced through oxidation, steam- or dry-reforming of CH4, C2H4, and C2H2. In this analysis, we are interested in the fact that syngas is produced through any reaction after ODHE. Hence, we can consider only one of these reactions without the loss of generality.

If this is the pathway taking place on La2O3, then, at a fixed \( T \), both \( X_{CO_2}^{\text{mem}} \) and \( X_{H_2}^{\text{mem}} \) should increase as \( X_{CH_4}^{\text{mem}} \) increases. At \( T = 750-850 \) °C, Figure 11g reveals an almost constant \( X_{CO_2}^{\text{mem}} \) at \( X_{CH_4}^{\text{mem}} \approx 0.10\% \), while Figure 12g clearly shows that \( X_{H_2}^{\text{mem}} \) is increasing. The constant \( X_{CO_2}^{\text{mem}} \) confirms that this pathway is not taking place at high rates. The production of H2 should be accompanied by the production of CO if syngas production is taking place on La2O3 after ODHE. The constant value of \( X_{CO_2}^{\text{mem}} \) also rules out the possibility of H2 being produced through the water gas shift (WGS) as this would lead to decrease in \( X_{CO_2}^{\text{mem}} \).

- **Pathway 2**: NODHE to C2H4 and H2. This pathway can be described through the following reaction:

\[
C_2H_6 \rightarrow C_2H_4 + H_2 \tag{13}
\]

At \( T = 750-850 \) °C, Figure 12c,g shows that \( X_{C_2H_4}^{\text{mem}} = X_{CH_4}^{\text{mem}} \), but \( X_{H_2}^{\text{mem}} \) is always slightly higher than \( X_{C_2H_4}^{\text{mem}} \). In conjunction with the fact that \( X_{CO_2}^{\text{mem}} \) is nearly constant at \( X_{CO_2}^{\text{mem}} \approx 0.10\% \), this confirms the validity of this pathway. We have already shown that NODHE does not happen on La2O3 (Supporting Information Figure S9). The produced H2 of this pathway has 2 contributions: (a) from one or multiple reactions producing syngas, which, however, are slow and kinetically frozen at \( T = 750-850 \) °C after some CO and H2 have been produced at low \( X_{CH_4}^{\text{mem}} \) and (b) from NODHE.

The aforementioned analysis confirms that ODHE is not a major reaction within our membrane reactor. However, this does not mean that the reaction does not happen at all on La2O3 but rather, that within our reactor, the rate of ODHE on La2O3 is smaller than the rate of the primary reaction, NODHE (in the gas phase). However, evidence of ODHE has been reported in the literature, although the investigated catalysts were not pure La2O3 as in our study. For example, Stansch et al.91 proposed ODHE to proceed on La-impregnated CaO, and they also added ODHE in their proposed reaction mechanism. However, SEM images were not provided in that work to identify whether the impregnation results to discrete La2O3 particles on CaO or to a full coating of CaO with La2O3. If the former is true, then a question that arises is whether the ODHE takes place on La2O3.
or CaO or at their interface. In a similar way, Choudhary et al.\textsuperscript{92} investigated ODHE over a Sr- and La-impregnated SA5205 support (consisting primarily of Al\textsubscript{2}O\textsubscript{3} with some SiO\textsubscript{2}). Although this paper confirms the presence of the ODHE reaction, it does not provide any data or conclusions in terms of whether this reaction proceeds in the gas phase or on the surface of the catalyst (on SrO or on La\textsubscript{2}O\textsubscript{3} or at the SrO

or La\textsubscript{2}O\textsubscript{3} interface) or both. SEM images were not provided to investigate the catalyst’s microstructure. In addition, the catalyst support was considered to be inert but results validating this hypothesis were not provided. Hence, given the different materials and the unknown microstructure of these catalysts compared to pure La\textsubscript{2}O\textsubscript{3} as well as the lack of key evidence, we conclude that the work by Stansch et al.\textsuperscript{91} and Choudhary et al.\textsuperscript{92} do not clearly support an ODHE pathway over pure La\textsubscript{2}O\textsubscript{3}.

The discussion above focuses on measurements between $T = 750$–$850 \, ^\circ\text{C}$, for which, the low and constant values of $X_{\text{CO}}$ suggest that syngas reactions in the vicinity of La\textsubscript{2}O\textsubscript{3} are slow and kinetically frozen, respectively. At $T = 900 \, ^\circ\text{C}$, our results show that reactions producing syngas are not kinetically frozen anymore and that gas-phase reactions are accelerated significantly. This is true even in the absence of La\textsubscript{2}O\textsubscript{3} (see Figure 5). At $T = 900 \, ^\circ\text{C}$, there are several competing reactions leading to syngas production that should be considered, which complicates the analysis. First, under the operating T of this study, it is known that CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{2}H\textsubscript{4} can be partially oxidized or reformed (with H\textsubscript{2}O and/or CO\textsubscript{2}) into syngas.\textsuperscript{26,91} Second, the formation of CO and H\textsubscript{2}O through the reverse WGS reaction is favored thermodynamically at $T > 818 \, ^\circ\text{C}$, while the formation of CO\textsubscript{2} and H\textsubscript{2} is favored at lower $T$. Third, decomposition of C\textsubscript{2}H\textsubscript{4} is also accelerated as $T$ increases. For example, at $T = 900 \, ^\circ\text{C}$, we attribute this to the additional non-oxidative dehydrogenation of C\textsubscript{2}H\textsubscript{4} in the gas phase. Therefore, although our proposed mechanism is clear for $T = 750$–$850 \, ^\circ\text{C}$ given that the aforementioned reactions are sluggish within this temperature regime, the multiple competing pathways because of the enhanced gas-phase chemistry at $T = 900 \, ^\circ\text{C}$ make the analysis at this $T$ difficult. At this $T$, a safe conclusion about the reactions leading to syngas production is only possible through the use of computational models, and hence, no further analysis
on the reactions resulting to syngas production will be attempted here. To enable the comparison of the results of this work with other studies in the literature, we decided to plot the most important performance metrics as a function of $T$ and $X_{\text{CH}_4}^{\text{in}}$, that is, the ratio of the CH$_4$ mole flow rate at the inlet of the CH$_4$ side over the mole flow rate of O$_2$ through the membrane. This definition is consistent with the standard used in traditional OCM, where results are plotted as a function of $T$ and $X_{\text{CH}_4}^{\text{in}}$/O$_2$ given that CH$_4$ and O$_2$ are co-fed at the inlet of the reactor. Figure 13 summarizes the results and reveals some very interesting trends. First, although the independent variables of our measurements are $T$ and $X_{\text{CH}_4}^{\text{in}}$, we observe that $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}}$ is not constant at each $T$. Given that $J_{\text{O}_2}$ increases at higher $T$ and as more CH$_4$ is introduced in the reactor, the operating window of $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}}$ narrows down. Second, the results reveal that the highest C$_2$H$_6$ and C$_2$H$_4$ yields are obtained as $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}}$ decreases while the highest selectivities are obtained as $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}}$ increases. The highest C$_2$ yield is Y$_C = 10.3\%$ obtained at $T = 850$ °C for $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}} \approx 3.1$, which is very close to a stoichiometric ratio of 2. Finally, we observe that for some of the performance metrics (C$_2$H$_6$, S$_{\text{H}_2}\text{O}_2$, Y$_{\text{H}_2}\text{O}_2$, S$_{\text{C}_2}\text{O}_2$ and Y$_{\text{CO}_2}$), all data points collapse into the same curve demonstrating that they depend exclusively on $n_{\text{CH}_4}^{\text{in}}/n_{\text{O}_2}^{\text{mem}}$ (recall, though, that $n_{\text{O}_2}^{\text{mem}}$ is a function of $T$ and $n_{\text{CH}_4}^{\text{in}}$); however, this is not the case for the species of interest, that is, S$_{\text{C}_2}\text{H}_4$, Y$_{\text{C}_2}\text{H}_4$, S$_{\text{C}_2}\text{H}_2$, and Y$_{\text{C}_2}$, although some similarity is observed for a part of the data (e.g., for Y$_{\text{C}_2}\text{H}_4$ at $T = 750–800$ °C and for Y$_{\text{C}_2}$, at $T = 850–900$ °C). Based on the activation barriers ($E_a$) reported by Stansch et al.,$^{91}$ $E_a = 48–68$ (kJ/mol) for CH$_4$ oxidation (partial and full) while $E_a = 168–182$ (kJ/mol) for C$_2$H$_4$ and C$_2$H$_6$ formation. Such high $E_a$ values do not support the observed temperature independence for some performance metrics given that $E_a/RT \approx 5–18$. They do explain, however, the temperature dependency for C$_2$. Because the C$_3$H$_6$ and C$_2$H$_4$ non-oxidative dehydrogenation happens in the gas phase within oxygen-free zones, the residence time is another variable that affects the aforementioned trends for C$_2$. However, further studies are required to elucidate the reasons why an explicit temperature independence is observed for C$_2$H$_6$, S$_{\text{H}_2}\text{O}_2$, Y$_{\text{H}_2}\text{O}_2$, S$_{\text{C}_2}\text{O}_2$ and Y$_{\text{CO}_2}$. To the best of our knowledge, this is the first time that such similarity curves are reported for OCM and can be very useful as first-order estimates when designing commercial-scale reactors.

3.7. Performance and Stability of BFZ91 and La$_2$O$_3$ under Partial O$_2$ Consumption and under an Undiluted CH$_4$ Stream. In the previous sections, we demonstrated the stability of BFZ91 with La$_2$O$_3$ under conditions of full O$_2$ consumption (Figure 11a,b). However, Hayek et al. have reported that OCM catalysts may still undergo deactivation, which is masked if operating at C$_2$, approximately 100%; they confirmed this behavior for the Mn$_x$O$_{1-x}$Na$_2$WO$_4$/SiO$_2$ catalyst.$^{93}$ Although this catalyst is known to be very unstable and to exhibit different phase transformations leading to OCM performance loss as a function of time,$^{14}$ we decided to conduct another stability test, this time under conditions of partial O$_2$ consumption. The experiment was conducted using a new BFZ91 pellet and fresh La$_2$O$_3$ powder. Given that $J_{\text{O}_2}$ is a function of $T$, $X_{\text{CH}_4}^{\text{in}}$ and membrane thickness, we fixed the temperature at $T = 850$ °C, and the membrane thickness at 0.66 mm while varying $X_{\text{CH}_4}^{\text{in}}$. To cover more than one values of C$_2$H$_6$, we conducted long-term measurements at different $X_{\text{CH}_4}^{\text{in}}$. 

![Figure 14. Long-term performance of BFZ91 with La$_2$O$_3$ at $T = 850$ °C under partial O$_2$ consumption conditions.](https://dx.doi.org/10.1021/acscatal.0c04888)
Figure 14. Long-term performance of BFZ91 with La₂O₃ at T = 850 °C under pure CH₄. (a) \( J_{O_2} \) (black) and C_{CH₄} (red) as a function of time and (b) \( \dot{n}^\text{out}_{C_2H_6} \) (pink), \( \dot{n}^\text{out}_{C_2H_4} \) (orange), and \( \dot{n}^\text{out}_{C_2} \) (green) as a function of time. Measurements were conducted every 4 min. During the experiment, ambient air was flowing in the air side at \( Q_{in} = 200 \text{ sccm} \) while pure CH₄ with \( Q_{CH₄} = 100 \text{ sccm} \) was introduced in the CH₄ side. The thickness of the membrane was 0.66 mm, while the thickness of the La₂O₃ catalyst layer was 1.5 mm.

Although the air side BFZ91 and the La₂O₃ catalyst microstructures shown in Supporting Information Figure S15ac, respectively, do not reveal any differences when compared to the ones, as shown in Figure 8, this is not the case for the CH₄ side BFZ91 surface. As shown in Supporting Information Figure S15b, several particles with different sizes and shapes have evolved on this surface. EDS mapping (Supporting Information Figure S16) confirms that these particles are enriched in Fe but depleted in Ba and Zr, although this depletion is not significant (i.e., Ba and Zr still exist within the Fe-enriched zones); it does not point out to the formation of metallic Fe (Fe₀) or Fe oxides (FeOₓ). These results suggest that secondary Fe-enriched Ba₆Fe₇ZrOₓ phases formed on the CH₄ side of the BFZ91 membrane and are possibly related to the decomposition of the BFZ91 membrane because of the extremely reducing environment \( (\dot{n}^\text{in}_{CH₄}/\dot{n}^\text{in}_{O_2} \approx 45) \). These particles do not exist on the CH₄ side of BFZ91 between \( X^\text{in}_{CH₄} = 0 – 30\% \) (Figure 8d).

This Fe-enriched Ba₆Fe₇ZrOₓ phase is not amorphous (because it is analyzed through SEM-EDS), so a possible reason why it was not observed through XRD is because XRD is a bulk characterization technique, and this phase is probably located primarily on the surface of BFZ91 and not within its bulk.

We do not currently know at which stage of the 3-day experiment with pure CH₄ this Fe-enriched Ba₆Fe₇ZrOₓ phase started forming. One hypothesis is that this phase formed progressively as a function of time. If this is the case, then Figure 15 confirms that it did not impact the performance of BFZ91 because no degradation was observed. However, longer trials are required to demonstrate if the performance can be compromised under prolonged exposure to pure CH₄. Another hypothesis is that this phase formed soon after pure CH₄ was introduced in the reactor. This could explain the reason of the observed equilibration within the first few hours of the experiment. If the aforementioned Fe-enriched Ba₆Fe₇ZrOₓ phase formed during this stage, it resulted in performance enhancement both in terms of \( J_{O_2} \) as well as C₂ production (Figure 15); and some studies have shown that similar perovskite oxides (e.g., Ba₉SeyFeO₃₋ₓ) are active OCM catalysts. The performance...
remained stable for the rest of the measurement, confirming that if this phase forms at the beginning of exposure to CH₄, it does not degrade the performance of BFZ91 with La₂O₃. Further studies are required to fully identify the stoichiometry of the proposed Fe-enriched BaₐFeₐZr₋O₃₋δ phase and whether it is indeed active for OCM. Finally, some carbon deposition is observed on the CH₄ side of the BFZ91 membrane (Supporting Information Figure S16), which is confined to a few discrete locations and does not appear to degrade the performance of the investigated materials.

3.8. OCM Mechanism of BFZ91 with La₂O₃: Global Reactions, Rate-Limiting Steps, and Species Activation on the Catalyst. Based on the results, as shown in Figures 9–12, and the discussion in Sections 3.5–3.7, we have clearly identified the following global reactions on a macroscopic level when using BFZ91 membranes coupled with La₂O₃:

\[
\frac{1}{2} \text{O}_2(g) + V^{**} + 2\text{Fe}^\delta_{\text{Fe}} \xrightarrow{\text{BFZ91}} \text{O}_\delta^\delta + 2\text{Fe}^\delta_{\text{Fe}} \tag{14}
\]

\[
\text{CH}_4(g) + 2\text{O}_2(g) \xrightarrow{\text{La}_2\text{O}_3} \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \tag{15}
\]

\[
2\text{CH}_4(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{\text{La}_2\text{O}_3} \text{C}_2\text{H}_6(g) + \text{H}_2\text{O}(g) \tag{16}
\]

\[
\text{C}_2\text{H}_6(g) \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2(g) \tag{17}
\]

For reactions 14–17, (g) denotes a species in the gas phase. Reaction 14 is written assuming that electrons are the main charge carriers for electronic conductivity, which is consistent with the defect chemistry of BaₐFeₐZr₋O₃₋δ. Although the determination of the exact defect chemistry of BFZ91 is outside the scope of this work and will be addressed in future publications, it is reasonable to conclude that the defect chemistry between BFZ91 and BaFe₀.₉₅Zr₀.₀₅O₃₋δ will be similar. The forward step of reaction 14 takes place on the air side gas-membrane interface and incorporates O₂ into the membrane; the reverse reaction occurs on the CH₄ side interface and releases O₂ into the gas phase. As discussed earlier, we have excluded the possibility of the CH₄ reaction with Ō; on the gas-membrane interface or with O₂ in the gas phase based on measurements in the absence of the La₂O₃ powder (Section 3.3).

According to Figures 9–12, the CH₄ conversion increases significantly in the presence of La₂O₃. The analysis of the species composition near the CH₄ side membrane interface and at the outlet allows us to conclude that reactions 15 and 16 occur on the surface of the La₂O₃ catalyst. C₂H₄ formed via reaction 16 is then converted to C₂H₆ and H₂ in the gas phase according to reaction 17. As discussed earlier, CO (and H₂) may form because of oxidation and/or reforming of CH₄, C₂H₄, and C₂H₂ as well as through the (reverse) WGS. At T = 750–850 °C, syngas production is low and kinetically frozen within the La₂O₃ catalyst but it is accelerated significantly at T = 900 °C. At this T, identifying the presence and rate of reactions producing syngas requires the use of computational models and is outside the scope of this work. A schematic of the global reaction pathways identified in our work is shown in Figure 16. With the exception of ODHE, these reactions are in agreement with the primary OCM reactions proposed by Stansch et al. who investigated the conventional OCM using a La₂O₃/Co₃O₄ catalyst.

Reactions 14–17 provide a macroscopic description of the OCM chemistry for BFZ91 and La₂O₃. Microscopically, several studies have already provided insight about the elementary steps of the OCM chemistry but significant disagreement still exists about the CH₄–O₂ activation process even for the same material. Early experiments have shown that CH₄ does not adsorb on the surface of La₂O₃. This has been confirmed by computational studies suggesting that the CH₄ physisorption on La₂O₃ is very weak. As a result, CH₄ is not expected to bind on La₂O₃ at any practical temperature. Instead, the CH₄ activation proceeds via a reaction that involves CH₃ adsorbed on La₂O₃ as an activated oxygen species (O²⁺) already adsorbed on La₂O₃ as follows:

\[
\text{O}_2(g) + (s) \rightarrow \text{O}_2^+(s) \tag{18}
\]

\[
\text{CH}_4(g) + \text{O}_2^+(s) + (s) \rightarrow \text{CH}_3^+(s) + \text{HO}_2^+(s) \tag{19}
\]

\[
\text{CH}_3^+(s) \rightarrow \text{CH}_2^+(s) + (s) \tag{20}
\]

\[
2\text{CH}_2^+(g) \rightarrow \text{C}_2\text{H}_4(g) \tag{21}
\]

In reactions 18–21, (s) denotes an empty site or a species on the surface of the catalyst. Reaction 18 corresponds to the gaseous O₂ adsorption on the surface of the catalyst and its activation to form O²⁺, while reaction 19 denotes the hydrogen abstraction from CH₄ in the presence of O²⁺ leading to the formation of methyl radicals (CH₃⁺) on the surface of the catalyst. The process continues with CH₃⁺ desorption into the gas phase through reaction 20, whose existence has been confirmed experimentally. Two CH₂⁺ will combine in the gas phase to form gaseous C₂H₄ through reaction 21. Then, C₂H₄ can in general be dehydrogenated to C₂H₂ through oxidative or non-oxidative pathways, as proposed in other studies. Our results show that, within our membrane reactor, the NODHE in the gas phase (reaction 17) is the primary reaction for producing C₂H₂. Reaction 19 is probably the most important step of the OCM chemistry as it is typically considered rate limiting toward C₂ formation. However, the exact mechanism is still under debate and depends strongly on the catalyst’s properties. On the one side, it has been proposed that the C–H bond cleavage is homolytic and is activated by a surface O²⁺ in a single step, as proposed by reaction 19. In contrast, a heterolytic C–H bond
Fundamentally, this could explain the results shown in Figure 2. A computational study by Palmer et al.98 performed by Lacombe et al. demonstrated that the adsorption of molecular O2 on La2O3 happens dissociatively;89 they also hypothesized that the electronophilic site formed during the O2 adsorption on La2O3 is either O2− or O22−. Earlier electron paramagnetic resonance spectroscopy measurements performed by Wang and Lunsford had already shown evidence of O2− on the surface of La2O3.99 A computational study by Palmer et al. confirmed the dissociative adsorption of molecular O2 on the (001) plane of La2O3.98 However, further binding with an oxygen ion on the La2O3 surface resulted in the formation of O22−, which did not agree with the results of Wang and Lunsford.98 A recent computational study predicted O2− as the activated oxygen species on La2O3 during the second step of reaction 19.95 Note, however, that the aforementioned studies99,95,98,99 dealt exclusively with the determination of the active site upon O2 adsorption on La2O3 without correlating it with the OCM activity of the catalyst; the latter has been demonstrated for other OCM catalysts and a link between the C2 yield and the concentration of the activated O2 species was established.109 Identifying and quantifying active species on the surface of OCM catalysts using in situ characterization techniques and correlating these with the C2 yield is expected to advance the start-of-the-art on OCM.

Finally, based on Supporting Information Figure S9, we have shown that the non-oxidative dehydrogenation of C2H6, C2H4, and CH4 does not take place on La2O3 between T = 750–900 °C. Given that CH4 does not adsorb on La2O3,95 it is reasonable to assume the same for C2H6 and C2H4. Fundamentally, this could explain the results shown in Supporting Information Figure S9. However, further studies based on isotope-exchange measurements are required to confirm this hypothesis.

4. CONCLUSIONS

This work investigates OCM in CMRs as a means to produce C2 hydrocarbons from CH4. A BFZ91 membrane was used for O2 separation from air and La2O3 was selected as the OCM catalyst. Long-term experiments were conducted in a button-cell reactor at T = 750–900 °C and XCH4 = 0 – 30%. These measurements reveal that the BFZ91-La2O3 combination is chemically and structurally stable for 23 days, during which no loss of performance was observed. The performance of the materials was also investigated under partial O2 consumption and pure CH4 conditions. The BFZ91 membrane and La2O3 catalyst were characterized before and after the OCM measurements and significant information about each was obtained, especially regarding their stability under OCM conditions. The highest C2 yield is ~10% obtained at C2 selectivity of ~93%. These values were achieved at T = 850 °C and XCH4 = 5% during which fO2 ≈ 0.91 (μmol/cm2/s). Experimental measurements in the absence of La2O3 revealed that the membrane does not catalyze CH4 pyrolysis or oxidation on its surface at high rates, and hence, undesired CH4 conversion to species other than C2 because of the membrane presence is avoided. Based on the results presented in our work, the primary OCM chemistry within our reactor is identified to consist of: (1) the CH4 full oxidation to CO2 and H2O, (2) the CH4 oxidative coupling to C2H6 and H2O, (3) the C2H4 non-oxidative dehydrogenation to C2H2 and H2, and (4) the oxidation/reforming of CH4, C2H2, and C2H4 combined with the (reverse) WGS to produce syngas. The first two reactions happen on La2O3 and the third takes place exclusively in the gas phase. The reactions in the fourth category are slow and kinetically frozen at T = 750–850 °C but they accelerate at T = 900 °C and can happen both in the gas phase and on the La2O3 catalyst. Based on early and recent experimental-computational results, the mechanism of C–H bond breaking and the oxygen activation on La2O3 was presented in an effort to deepen our understanding on the OCM chemistry from a microscopic level.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c04888.

Experimental setup for OCM measurements; loading of the La2O3 powder on the BFZ91 membrane; system of equations to estimate the performance metrics and XH2O

XRD of the BFZ91 raw ash and calcined BFZ91 powder; CH4 conversion using BFZ91 in the absence of a catalyst; La2O3 sintering at high T; C2H6 and C2H4 non-oxidative dehydrogenation in the presence and absence of La2O3; and BFZ91-La2O3 performance and characterization under partial O2 consumption and pure CH4 conditions (PDF)

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