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# *In situ* X-ray Diffraction Computed Tomography studies examining the thermal and chemical stabilities of working $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes during oxidative coupling of methane

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**Abstract:** In this study we present the results from two *in situ* X-ray diffraction computed tomography experiments of catalytic membrane reactors (CMRs) using  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) hollow fibre membranes and Na-Mn-W/SiO<sub>2</sub> catalyst during the oxidative coupling of methane (OCM) reaction. The negative impact of CO<sub>2</sub>, when added to the inlet gas stream, is seen to be mainly related to the C<sub>2+</sub> yield, while no evidence of carbonate phase(s) formation is found during the OCM experiments. The main degradation mechanism of the CMR is suggested to be primarily associated with the solid-state evolution of the BSCF phase rather than the presence of CO<sub>2</sub>. Specifically, *in situ* XRD-CT and post-mortem SEM/EDX measurements revealed a collapse of the cubic BSCF phase, formation of secondary phases, which include needle-like structures and hexagonal Ba<sub>6</sub>Co<sub>4</sub>O<sub>12</sub>, and formation of a BaWO<sub>4</sub> layer, the latter being a result of chemical interaction between the membrane and catalyst materials at high temperatures.

**Keywords:** membrane reactor; BSCF; Na-Mn-W/SiO<sub>2</sub>; XRD-CT; SEM; EDX

## 1. Introduction

Over the past decades, the potential of membrane reactors towards a cleaner and more sustainable future has become more apparent<sup>1-3</sup>. Catalytic membrane reactors (CMRs) are able to simultaneously perform separation and reaction processes offering a unique opportunity to increase the overall system efficiency and decrease the energy consumption in a single unit. More specifically, the application of oxygen permeable membranes with mixed ionic and electronic conductivity (MIEC) properties is an alternative technology for oxygen separation from air<sup>4-6</sup>. It offers both reduced costs and high oxygen permeation flux, and more importantly it can be directly integrated with the catalytic reactor systems<sup>7-10</sup>. The use of perovskite membranes in the oxidative coupling of methane (OCM) process<sup>11-15</sup> is believed to provide a more uniform distribution of oxygen along the axial direction when compared to conventional fixed bed reactors. This is believed to directly influence the C<sub>2+</sub> yield as the methane can be activated by the surface oxygen ionic species and the contribution of gas phase homogenous combustion reactions can be decreased<sup>16</sup>.

Wang *et al.*<sup>17</sup> studied the OCM reaction using a catalytic membrane reactor with a  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  tubular membrane and a La-Sr/CaO catalyst packed-bed. Both, packed-bed catalytic membrane reactor and catalytic membrane reactor (i.e. membrane material only)



configurations were tested using similar OCM conditions. Although both configurations showed similar performance regarding the CH<sub>4</sub> conversion and C<sub>2+</sub> yield, the packed-bed catalytic membrane reactor led to significantly higher C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio (12.5 as opposed to 1 for catalytic membrane reactor). Czuprat *et al.*<sup>18</sup> investigated the Na-Mn-W/SiO<sub>2</sub> catalyst packed inside the hollow fibre BaCo<sub>x</sub>Fe<sub>y</sub>Zr<sub>z</sub>O<sub>3-δ</sub> (x + y + z = 1) membrane. The highest C<sub>2+</sub> yield of 17 % and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 4 was obtained for a CH<sub>4</sub> conversion of 35 % (using a pure stream of air on the core/feed side). In the study of Bhatia *et al.*<sup>19</sup> three configurations were investigated for the OCM reaction: packed-bed reactor, packed-bed catalytic membrane reactor and catalytic membrane reactor with coated Na-Mn-W/SiO<sub>2</sub> catalyst. The latter configuration was found to perform the best among the three configurations, with the C<sub>2+</sub> yield of 35 % and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> ratio of 1.4. The changes in the catalytic membrane material were analysed postreaction with XRD and SEM analysis; catalyst components were found to migrate towards the reaction surface, whereas cation species from the membrane migrated towards the oxygen-enriched surface.

In this work we investigate a Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) hollow fibre membrane during the oxidative coupling of methane; this perovskite is known to have excellent oxygen permeability<sup>7,20-22</sup> at operating temperatures required for this reaction (~ 2 SmL · min<sup>-1</sup> · cm<sup>-2</sup><sup>23</sup>). However, there are still several challenges related to the long-term phase stability and chemical poisoning of this material that prevent its application under real industrial conditions. More precisely, at intermediate temperatures (i.e. below 850 °C) the cubic BSCF phase has been observed to decompose to secondary Ba and Co hexagonal phases with a simultaneous decrease in oxygen permeation<sup>24-29</sup>. The reason behind the instability of the cubic phase has been attributed to the change in the oxidation state of Co upon exposure to air below 850 °C, according to the Goldschmidt tolerance factor<sup>30</sup>, the cubic structure is not able to accommodate Co with higher oxidation states<sup>31</sup> and thus the more stable hexagonal phase is expected to form. The formation of the secondary hexagonal phase was identified to take place at the grain boundaries from the feed side (air exposed side), but over a long duration experiment (i.e. 1000s of hours of operation) this phase can also be identified in the grains<sup>32-34</sup>. The high internal stress resulting from this phenomenon was suggested to be responsible for the formation of cracks in the membrane reactor<sup>35</sup>.

The second major challenge is related to the interaction of the BSCF material with CO<sub>2</sub>. In many studies, the formation of BaCO<sub>3</sub> (or Ba<sub>x</sub>Sr<sub>1-x</sub>CO<sub>3</sub>) has been reported to have a detrimental effect on the oxygen permeation<sup>36,37</sup>. A thin layer of this carbonate phase forming at the surface of the membrane is considered to act as a barrier for the oxygen ion transport. In a study by Engels *et al.*<sup>38</sup>, 15 % of CO<sub>2</sub> in the permeated side gradually decreased the initial oxygen permeation flux by 80 % after 200 min of operation. Although the effect of CO<sub>2</sub> was found to be reversible, as the initial oxygen permeation flux could be restored when changing the composition of the sweep side to pure He, minor structural changes in the membrane were induced during this process; these may be considered important for the long term stability of BSCF membranes. Finally, as recently reported by Vamvakeros *et al.*<sup>39,40</sup>, Ba-containing membranes may also be susceptible to chemical poisoning by WO<sub>4</sub><sup>2-</sup> species. During the OCM reaction, a thin layer of BaWO<sub>4</sub> was found to form at the interface between a Na-Mn-W/SiO<sub>2</sub> catalyst and a hollow fibre BaCo<sub>x</sub>Fe<sub>y</sub>Zr<sub>z</sub>O<sub>3-δ</sub> (BCFZ) membrane. Although there was no direct change in the reactor performance, the loss of catalyst components coupled with the formation of the stable BaWO<sub>4</sub> layer was proposed to have a significant impact on the long-term performance of this integrated reactor system.

The aim of this work was to assess the aforementioned issues and their implication on the performance of working catalytic membrane reactors for the oxidative coupling of methane reaction. We employed the X-ray diffraction computed tomography (XRD-CT) technique<sup>41,42</sup> to investigate the evolution of the solid-state chemistry in the BSCF membrane in two experiments. The first experiment involved exposing the BSCF membrane to 20 % CO<sub>2</sub>/CH<sub>4</sub> gas stream (permeate side) for 11 h. In the second experiment, the Na-Mn-W/SiO<sub>2</sub> catalyst was placed inside the BSCF membrane and the packed-bed catalytic membrane reactor was tested for the OCM reaction with different concentrations of CO<sub>2</sub>



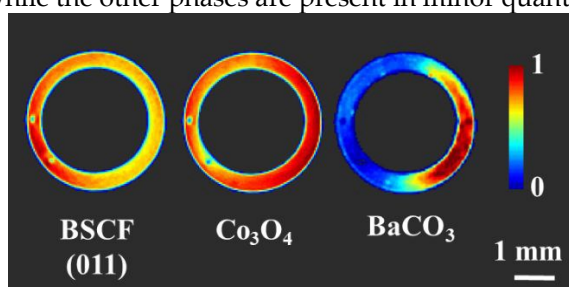
in the  $\text{CH}_4$  stream (permeate side). The solid-state changes observed from the XRD-CT data are discussed and compared with laboratory and post-reaction characterisation complementary measurements.

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## 2. Results

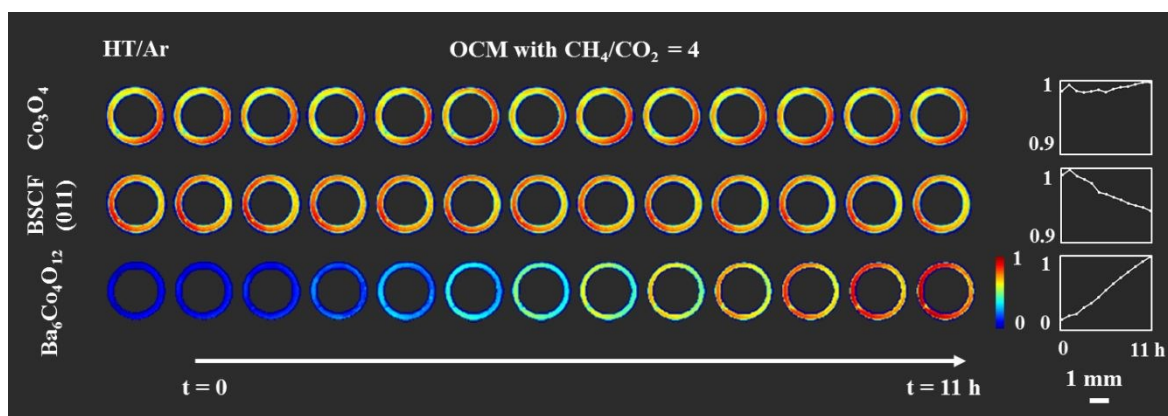
### 2.1. Catalytic membrane reactor

The initial distribution of the membrane components is presented in Figure 1. The membrane composition was found to be non-uniform, as two distinct regions can be observed in the acquired cross section. On the left side, the majority of the material consisted of cubic BSCF perovskite, whereas the right side contained  $\text{Co}_3\text{O}_4$ ,  $\text{BaCO}_3$  and an additional phase (Figures S1 and S2). This unusual distribution of membrane materials was not a measurement artefact and it was most likely formed during the membrane preparation. However, it is important to note that the membrane primarily consists of the BSCF phase while the other phases are present in minor quantities (Figure S2).



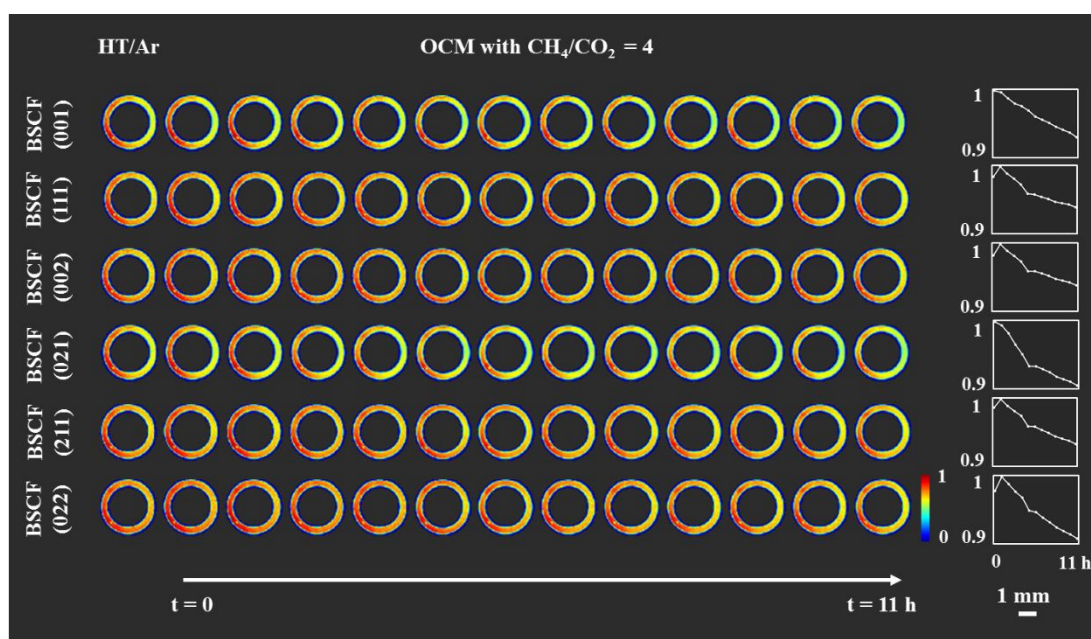
**Figure 1.** Distribution of the BSCF,  $\text{Co}_3\text{O}_4$  and  $\text{BaCO}_3$  phases in the as prepared membrane at room temperature.

Figure 2 shows the distribution of the membrane components ( $\text{Co}_3\text{O}_4$  and  $\text{Ba}_6\text{Co}_4\text{O}_{12}$ ) as well as distribution of the cubic perovskite (the main (011) reflection) during the high temperature scans under Ar and under OCM reaction conditions. It is important to note that the initially present  $\text{BaCO}_3$  decomposed during the temperature ramp and no other carbonate phase formed during the experiment. The results from the refinement analysis showed that the BSCF phase was not stable under OCM operating conditions (Figure S2). More precisely, after around 3 h of operation, a secondary hexagonal phase, identified as  $\text{Ba}_6\text{Co}_4\text{O}_{12}$ , started to form at the region where the cubic perovskite was initially present in the fresh material. As mentioned previously, the instability of the cubic perovskite is expected to occur during operation of the membrane at intermediate temperatures. Different compositions and morphologies of this secondary phase have been previously reported<sup>24,33,35</sup> however the hexagonal phase is expected to contain mainly Ba and Co. During the OCM reaction the intensities of all BSCF reflections were seen to gradually decrease, whereas the  $\text{Co}_3\text{O}_4$  remained stable for the duration of the experiment.



**Figure 2.** Distribution of membrane components during the high temperature XRD-CT scan and OCM reaction. Plots on the right correspond to changes in the normalised scale factors of  $\text{Co}_3\text{O}_4$  and  $\text{Ba}_6\text{Co}_4\text{O}_{12}$  and the peak intensity of the BSCF (011) reflection.

Although all BSCF reflections are seen to gradually decrease with time (Figure 3), an unusual behaviour can be observed between the 1<sup>st</sup> and 2<sup>nd</sup> XRD-CT scan; the intensity of the (011), (111), (002), (211) and (022) reflections increased whereas the intensity of the (001) and (021) reflections decreased. In addition, after the introduction of the OCM reaction mixture, the lattice parameter of the cubic perovskite instantly decreased from 4.015 to 4.013 Å (Figure S3). This observation can be explained by the contraction of the lattice parameter, through the oxidation of the transition metals occupying the perovskite B site. This would also suggest a decrease in oxygen vacancies in order to maintain the charge neutrality of the structure<sup>43</sup>. The gradual decrease in lattice parameter during the OCM reaction, from 4.013 to 4.011 Å is most likely caused by the change in the structure of cubic perovskite; the formation of hexagonal  $\text{Ba}_6\text{Co}_4\text{O}_{12}$  phase resulted in the decrease of Ba and Co in the resulting cubic perovskite, which is in agreement with previously reported studies<sup>34,44</sup>.



**Figure 3.** Distribution of membrane components – reflections of cubic BSCF phase during the high temperature XRD-CT scan and OCM reaction. Plots on the right correspond to changes in the normalised peak intensities for the various BSCF reflections.

In order to rationalise the subtle changes in the peak intensities, further analysis was performed focusing on how the structural changes in cubic BSCF (i.e. occupancy of each element at A and B sites, oxygen occupancy) affect the intensity of certain reflections. The simulation of BSCF diffraction patterns with different chemical composition can be found in the Supplementary Materials (section S2 Simulation of BSCF structure). Considering the relative changes in the simulated data, we conclude that the changes in the BSCF structure between HT/Ar and OCM XRD-CT scan were due to the increase in oxygen occupancy, which corresponds to decrease in oxygen vacancies (Table S1). Although the changes in the intensity for the (011) and (211) reflections are contradictory to the results of the simulated data, the relative changes in the simulated data are minor and therefore it is not possible to rule out that the changes in intensity may also be due to changes in the amounts of Co and Ba. The decrease in oxygen permeability is expected to occur during the introduction of the OCM reaction mixture (changing gas environment from He to  $\text{CH}_4$ ), as the  $\text{CO}_2$  produced from combustion reacts with the membrane forming a layer of  $\text{BaCO}_3$ . However, the XRD-CT measurements ( $40 \mu\text{m} \times 90 \mu\text{m}$ )

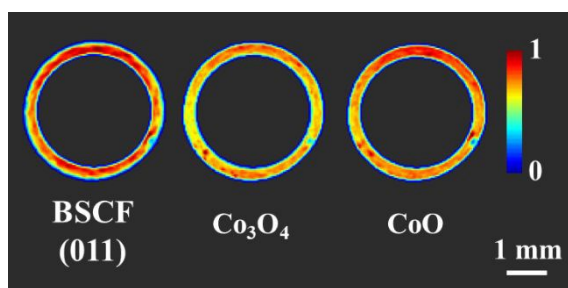


did not detect the presence of any carbonate phases. The relative changes in the BSCF structure though is a clear indication of oxygen permeation changing as a function of imposed operating conditions. As the perovskite was found to be unstable during the OCM reaction conditions, the decrease in intensity of all BSCF reflections during the experiment is attributed to the ongoing decomposition of this phase. The decomposition of BSCF during operation as well as the formation of  $\text{Co}_3\text{O}_4$ ,  $\text{BaCO}_3$  and the unidentified phase(s) during the preparation indicate inherent problems associated with the chemical stability of the perovskite phase.

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## 2.2. Catalytic membrane reactor with Na-Mn-W/SiO<sub>2</sub> packed-bed

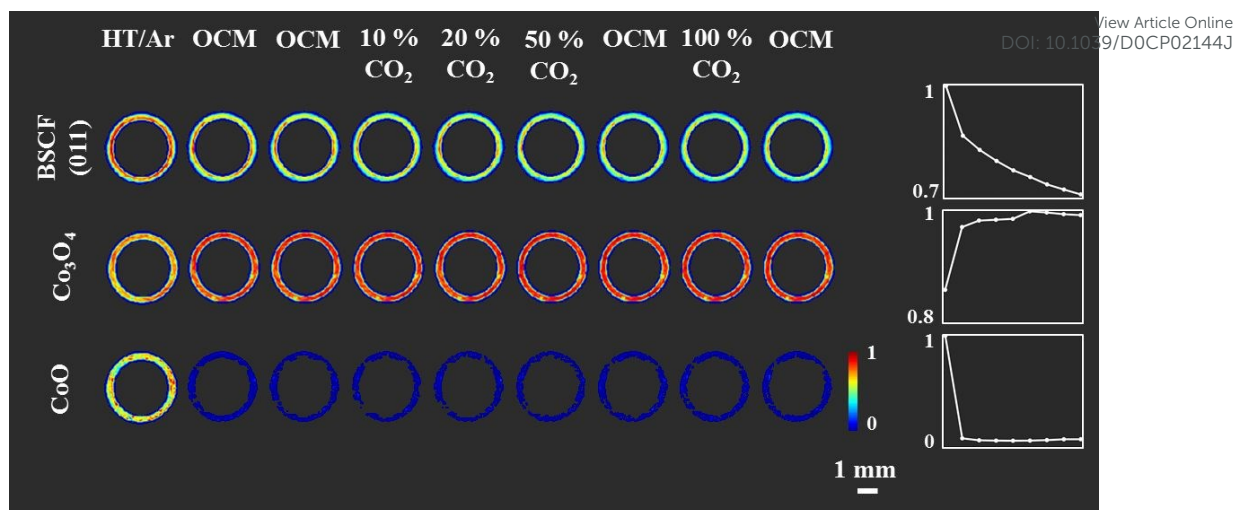
The distribution of the fresh membrane components at ambient conditions is presented in Figure 4. Initially, the membrane consisted primarily of the BSCF perovskite while minor quantities of CoO and  $\text{Co}_3\text{O}_4$  were also present. It is important to note that the  $\text{BaCO}_3$  phase seen in the case of the first experiment was not observed here (Figure S9). During the temperature ramp performed under air/Ar, the quantity of CoO significantly decreased which could be explained by the oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+}$  in the presence of air at high temperatures. The disappearance of CoO and simultaneous increase in  $\text{Co}_3\text{O}_4$  is clearly visible with the changes in the diffraction patterns collected at room temperature and operating temperature (Figure S9).



**Figure 4.** Distribution of the BSCF,  $\text{Co}_3\text{O}_4$  and CoO phases in the as prepared membrane at ambient conditions.

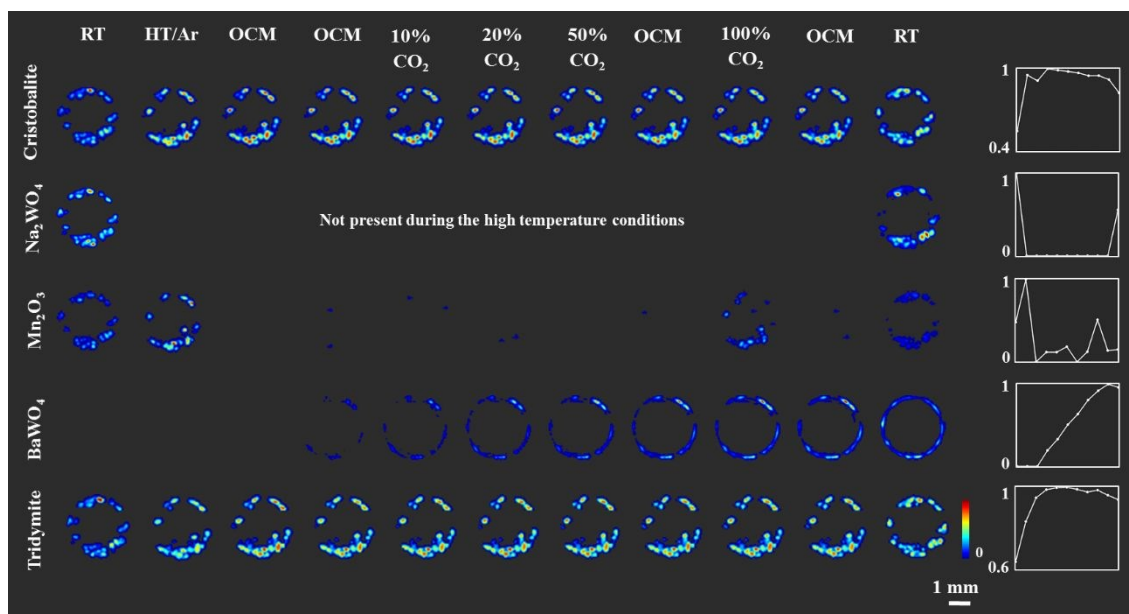
The distribution of the membrane components as well as the relative changes during the OCM reaction are shown in Figure 5. After the introduction of the OCM reaction mixture, the CoO was found to completely disappear from the membrane material, whereas the distribution and quantity of  $\text{Co}_3\text{O}_4$ , after the initial formation/growth from the CoO, was found to remain stable until the end of the experiment. Regarding the BSCF, the relative changes in its primary reflection ((011) at  $2\theta = 2.6^\circ$  in Figure S10) showed that the quantity of the perovskite gradually decreased with the greatest reduction observed after the introduction of the OCM reaction mixture. A similar trend was observed for the other cubic BSCF reflections (Figure S10). However, in contrast to the previous experiment, no changes in the lattice parameter of the cubic structure occurred with time; its value remained constant and was determined to be  $4.045 \text{ \AA}$  (Figure S11).





**Figure 5.** Distribution of crystalline components present in the membrane material during the OCM experiment. Plots on the right correspond to the relative changes in the normalised mean scale factor or peak intensity obtained through refinement.

The results of the refinements clearly show that the BSCF material was not stable during the OCM experiment. More importantly, a new phase, identified as  $\text{BaWO}_4$  was seen to form at the interface between membrane and catalyst material at the beginning of the second XRD-CT scan under OCM conditions with pure  $\text{CH}_4$ . The distribution of all catalyst components and the  $\text{BaWO}_4$  is presented in Figure 6.



**Figure 6.** Distribution of crystalline components present in the catalyst material during the OCM experiment. Plots on the right correspond to relative changes in the normalised mean summed peak intensity.

The  $\text{BaWO}_4$  was formed as a result of an interaction between the catalyst and membrane material. As observed previously<sup>39</sup>, the  $\text{Na}^+$  and  $\text{WO}_4^{2-}$  species are volatile and they can interact with the reactor vessel at high temperatures (i.e. above 780 °C)<sup>45</sup>. In this experiment the  $\text{WO}_4^{2-}$  species were found to migrate towards the membrane material where they interacted with  $\text{Ba}^{2+}$  present in the cubic perovskite, forming a continuous layer of  $\text{BaWO}_4$  at the membrane-catalyst interface. A similar



observation was made in the case of *operando* studies with a  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  perovskite membrane and a Na-Mn-W/SiO<sub>2</sub> catalyst<sup>39,40</sup>. It is possible that this phenomenon can have a detrimental effect on the overall long-term performance of the CMR reactor as the newly formed layer is expected to have a negative impact on the oxygen permeability while the loss of catalyst active species is also bound to affect its performance. Similarly to the first experiment, no significant changes in the membrane were detected when CO<sub>2</sub> was co-fed with CH<sub>4</sub>; there was no evidence for carbonate phases formation in this experiment.

Regarding the solid-state chemistry of the other catalyst components, the temperature induced a gradual transition between cristobalite and tridymite during the OCM reaction<sup>45,46</sup>. In addition, the Mn<sub>2</sub>O<sub>3</sub> phase was seen to disappear after the introduction of the OCM reaction mixture. However, it temporarily reappeared after the introduction of the reaction mixture containing pure CO<sub>2</sub> (possibly due to the CO<sub>2</sub> reduction by Mn<sup>2+</sup>/Mn<sup>3+</sup>). This observation is in good agreement with previous work on a Na-Mn-W/SiO<sub>2</sub> catalyst-membrane system<sup>45,47</sup>; the active catalyst does not need to contain the crystalline Mn<sub>2</sub>O<sub>3</sub> phase. It is also clear that in the presence of CH<sub>4</sub>, the crystalline Mn<sub>2</sub>O<sub>3</sub> loses its long-range order, most likely due to bulk reduction to Mn<sup>2+</sup>. However, no crystalline phase containing Mn<sup>2+</sup> (i.e. MnWO<sub>4</sub>) was identified to form during the OCM reaction. It should finally be noted that minor changes in the distribution of catalyst components between room temperature and high temperature XRD-CT scans were attributed to the movement of catalyst particles during the introduction of gas to the reactor (i.e. loose packing).

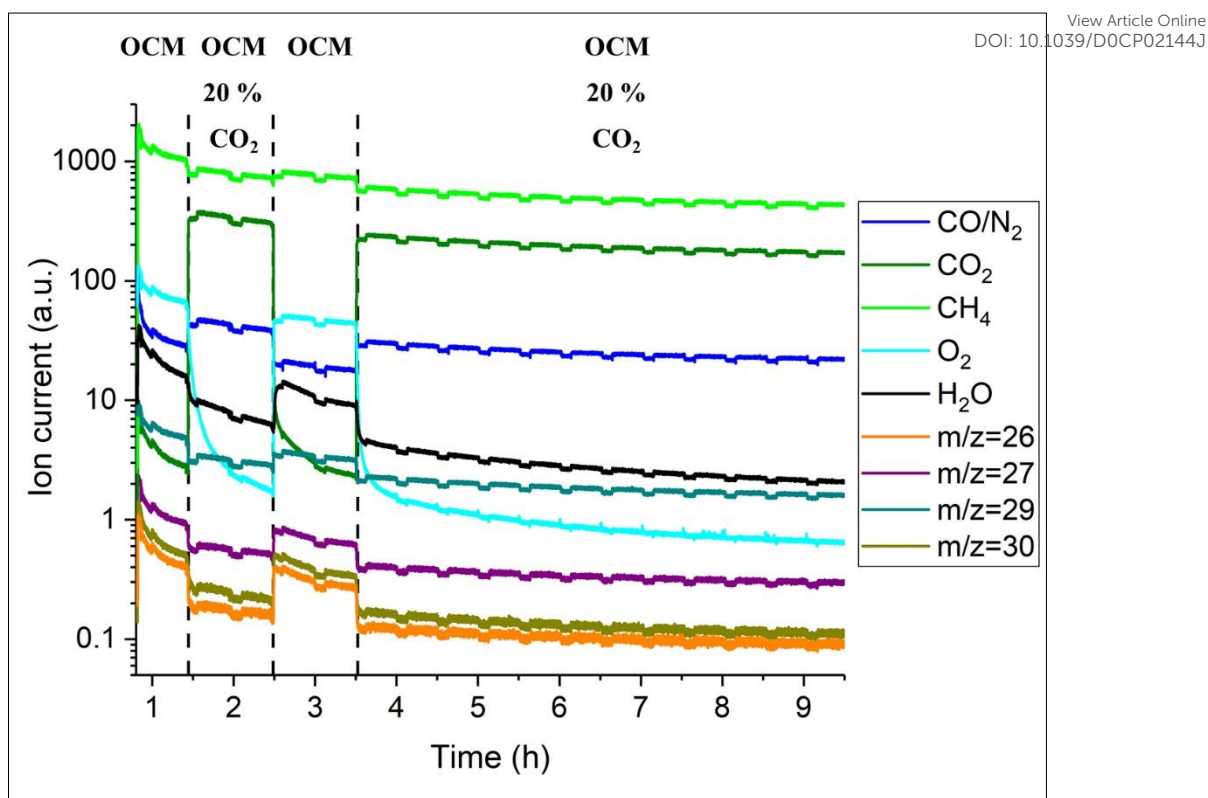
### 2.3. Laboratory performance testing and *ex situ* SEM/EDX characterisation

Complementary laboratory catalytic performance experiments were designed and performed in order to further support and rationalise the solid-state chemistry observations from the *in situ* XRD-CT measurements. However, small changes to the experimental protocol had to be made in order to advance our understanding of the working system (i.e. duration of experiment, additional steps related to co-feeding CH<sub>4</sub>/CO<sub>2</sub>). The reactor outlet gases were analysed with mass spectrometry (MS) and gas chromatography (GC); however, the analysis is only qualitative due to the dead volume of the experimental setup introduced by the large condenser/catch pot after the reactor and before the analytical instruments which led to diluted streams and a corresponding delay in observing the changes in gas phase composition. The recovered samples after the laboratory experiments were analysed with the scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX).

The results of the MS data collected during the OCM reaction with the catalytic membrane reactor are presented in the Figure 7. With the addition of CO<sub>2</sub> in the reactor inlet stream (inner side stream) the most apparent changes are related to the O<sub>2</sub> signal, as it was found to gradually decrease after the introduction of 20 % CO<sub>2</sub> in the CH<sub>4</sub> stream. Changing the gas composition to CH<sub>4</sub> (50 % of CH<sub>4</sub> in Ar) resulted in the recovery of the oxygen permeability which was found to decrease again in the second cycle with 20 % of CO<sub>2</sub>. However, during this second cycle, the oxygen MS signal was seen to decrease faster than during the first cycle. The O<sub>2</sub> signal continued to gradually decrease until the end of experiment. The GC measurements showed that the BSCF membrane exhibits poor activity for the OCM reaction and the additional CO<sub>2</sub> in the reactor inlet stream further decreases it (Figure S14).



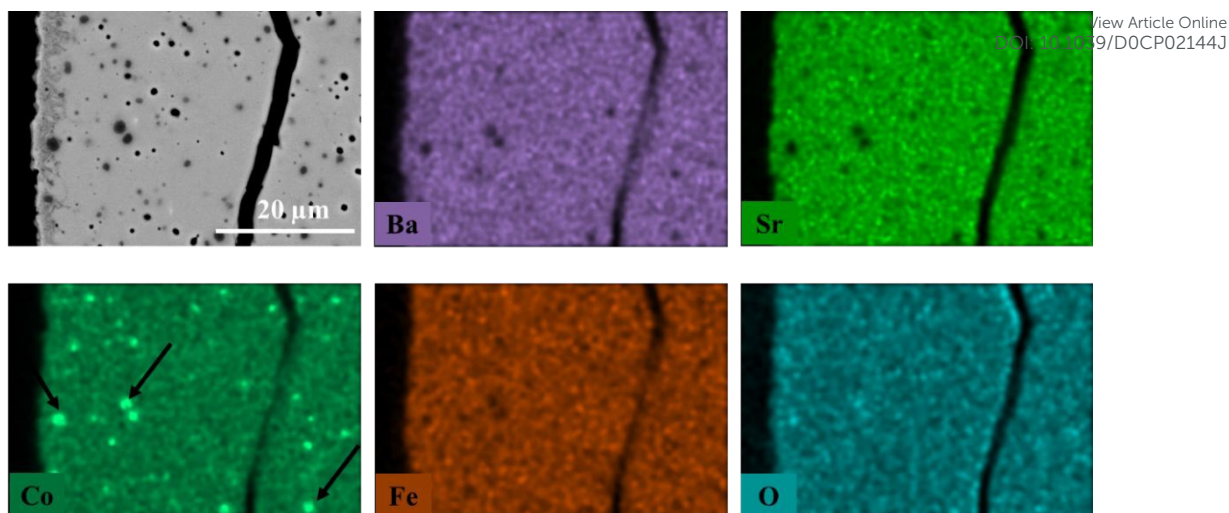




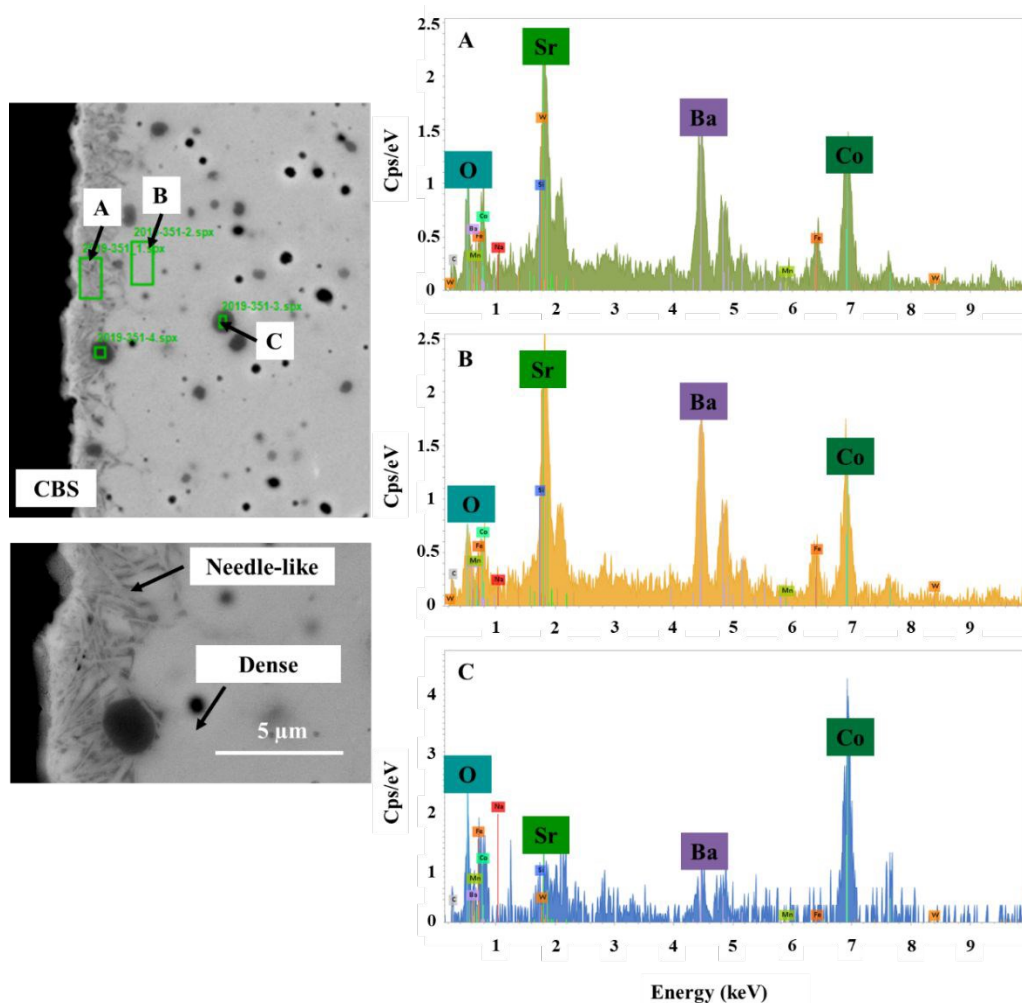
**Figure 7.** Results of mass spectrometry collected during the OCM experiment with catalytic membrane reactor. The y axis is in logarithmic scale and the ion current values were normalized with respect to the He signal (equivalent to instrument response with time). Note: oscillations in the mass spectrometry are due to the GC injection and corresponding valve movements.

The elemental distribution of the membrane components at the inner side of the membrane is presented in Figure 8. The results from the EDX mapping measurements showed that there is a segregation of  $\text{CoO}_x$  species in the membrane material (Figure 9). At the same time, the SEM images revealed the presence of a thin layer of  $\sim 5 \mu\text{m}$  on the membrane surface which possesses a different structure (needle-like) when compared to membrane bulk (dense structure). The formation of the needle-like structure in the BSCF membrane has been previously reported in the work of Engels et al.<sup>38</sup> however no exact information regarding its composition and structure was presented. The EDX mapping measurements showed that there was no significant difference in the elemental composition between the surface layer and the dense bulk of the membrane. The morphology of this new structure resembles the morphology of the secondary phases formed in the BSCF during operation under temperatures below  $900 \text{ }^\circ\text{C}$ <sup>34,48,49</sup>.





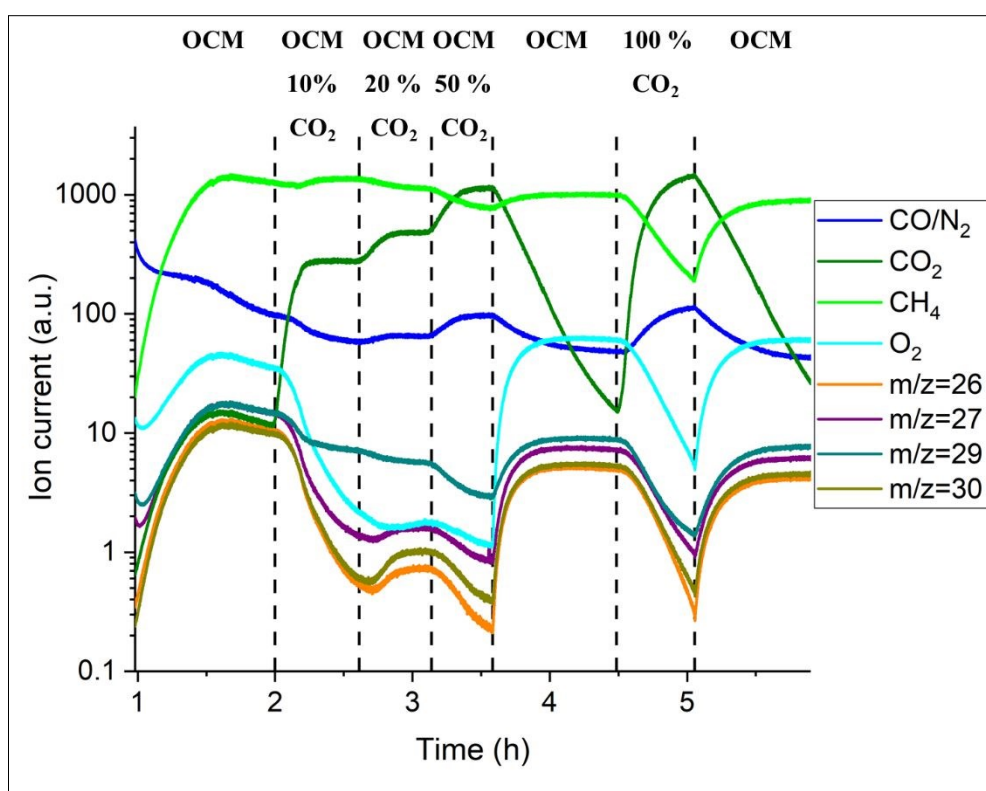
**Figure 8.** Elemental distribution of membrane components at the inner side of membrane obtained by EDX mapping. This fragment of membrane cross section was obtained from the reactor inlet.



**Figure 9.** SEM image of the inner side of the membrane and the corresponding energy spectrum from chosen regions. This fragment of the membrane cross section was obtained from the reactor inlet.



The mass spectrometry results collected with the packed-bed catalytic membrane reactor are shown in Figure 10. As mentioned previously, the changes in the MS signal were slower due to the large dead volume after the reactor, however it is still possible to observe the general trend in the gas phase composition. The gradual introduction of CO<sub>2</sub> into the OCM reaction mixture (from 10 to 50 %) resulted in a decrease of oxygen permeation as well as lower production of C<sub>2+</sub> molecules (Figure S15). It is important to note that the difference in the C<sub>2+</sub> production between the 1<sup>st</sup> and 2<sup>nd</sup> stage of the OCM reaction (1-2 h and 3.5 – 4.5 h respectively) was mainly caused by the introduction of another CH<sub>4</sub>:O<sub>2</sub> ratio (3.5 vs 2.5). As reported previously<sup>50,51</sup>, at higher CH<sub>4</sub>:O<sub>2</sub> ratios the production of C<sub>2+</sub> is seen to increase. However, a lower production of C<sub>2+</sub> molecules, when compared to the 2<sup>nd</sup> and 3<sup>rd</sup> OCM measurement performed at the same CH<sub>4</sub>:O<sub>2</sub> ratio, can be explained by the solid-state changes in the membrane primarily associated with the formation of the BaWO<sub>4</sub> layer.



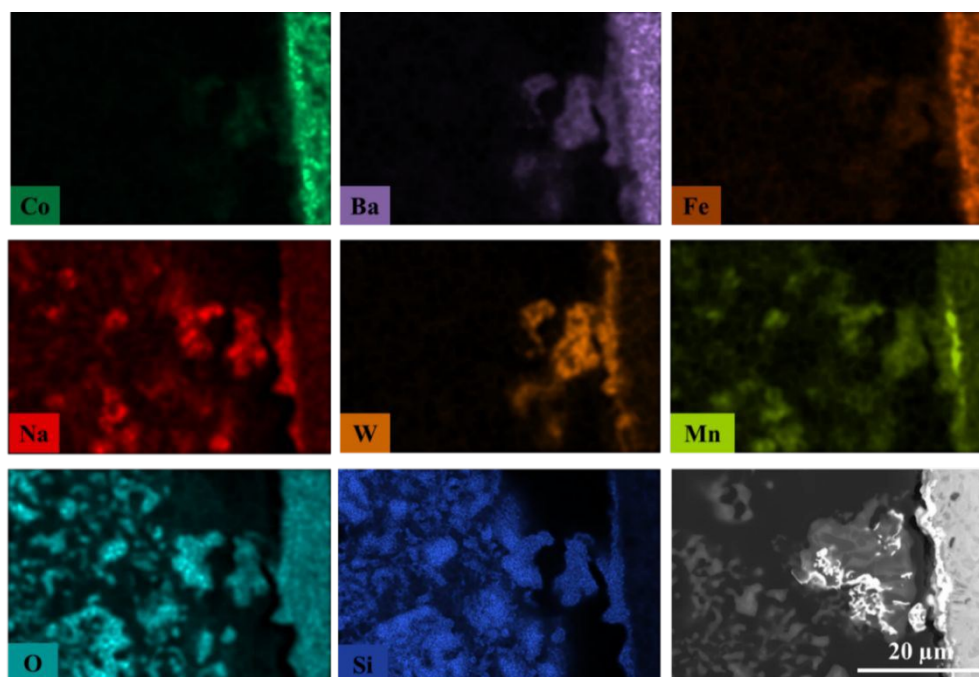
**Figure 10.** Mass spectrometry results collected during the OCM experiment with packed-bed catalytic membrane reactor. The y axis is in logarithmic scale and the ion current values were normalized with respect to the He signal (equivalent to instrument response with time). Note: the 1<sup>st</sup> OCM measurements were performed with CH<sub>4</sub>:O<sub>2</sub> of 3.5 whereas the 2<sup>nd</sup> and 3<sup>rd</sup> OCM measurements were performed with CH<sub>4</sub>:O<sub>2</sub> of 2.5.

The elemental distribution of the catalyst and membrane components at the inner side of the membrane near the reactor inlet is presented in Figure 11. The results from the EDX mapping revealed that during the OCM reaction there was an interaction between volatile W-containing species and the BSCF membrane which led to the formation of thin deposits on the membrane surface, at the interface between membrane and catalyst particles. This observation further supports the results obtained from the *in situ* XRD-CT data where it was shown that a BaWO<sub>4</sub> formed during the OCM experiment. In addition, these deposits were seen to contain Na and Mn species. Similarly to the previous experiment with the BSCF membrane, Co species were present in the form of large agglomerates containing CoO<sub>x</sub>.



species but in addition they were also seen to agglomerate at the membrane surface, forming a uniform layer.

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**Figure 11.** Elemental distribution at the inner side of membrane obtained by EDX mapping. This fragment of the membrane cross section was obtained from the reactor inlet.

The EDX mapping measurements were also performed for inter and intra particle investigation of the distribution of the catalyst active components (Figure S17). The Na and Mn containing species are seen to be present in the catalyst particles as well as in the deposits on the membrane surface, whereas the W-containing species are seen to be present in the deposits and in the particles interacting with the membrane. These observations suggest that all catalyst active components are seen to migrate towards the membrane surface during the OCM reaction, with the W-containing species being the most prone to migration/volatilisation. In addition, the remaining Na and Mn containing species in catalyst particles are seen to have similar and rather uniform distribution; no formation of agglomerates with high concentration of material.

### 3. Materials and Methods

#### 3.1. Preparation of hollow fibre BSCF membrane

The BSCF perovskite hollow membranes were supplied by the Flemish Institute for Technological Research (VITO), prepared from the BSCF mixed ionic-electronic conducting perovskite powder obtained from CerPoTech (Norway). Membranes were prepared using the spinning and phase inversion technique previously reported in the work of Di Felice *et al.*<sup>23</sup>. The dimensions of the BSCF membranes used for both experiments were: 3.6 – 3.7 mm outside diameter and 2.8 -2.9 mm inside diameter.

#### 3.2. In situ XRD-CT measurements at ID15A, ESRF

XRD-CT measurements were performed at ID15A beamline at the ESRF<sup>52</sup> using a monochromatic beam of 95keV with a size of 40μm × 90μm (H × V). For both experiments BSCF membranes were placed inside a quartz reactor (6 mm outside diameter and 4 mm inside diameter). A schematic representation of the experimental setup can be found in Figure S18. Two different experiments were performed: (1) with catalytic membrane reactor and (2) with packed-bed catalytic membrane reactor using 60 mg of



Na-Mn-W/SiO<sub>2</sub> catalyst placed inside the BSCF membrane and supported between glass wool. During the first experiment (with pure membrane reactor) the sample was scanned using 150 translation steps (with 40 μm step) and 100 angular steps (with 1.8° step), whereas during the experiment with packed-bed catalytic membrane reactor sample was scanned using 140 translation steps (with 40 μm step) and 120 angular steps (1.5° step). Diffraction patterns were collected using a PILATUS3 X CdTe (Dectris) area detector. The calibration of the detector was performed using a CeO<sub>2</sub> NIST standard. Every collected 2D diffraction image was converted to 1D powder diffraction patterns using PyFAI software<sup>53</sup> using the nDTomo software<sup>54</sup> with implemented trimmed mean filter (20 %) to remove the artefacts due to hot spots of (single) crystalline materials<sup>55</sup>. The reconstructed images were obtained using the filtered back projection algorithm. For both experiments the XRD-CT data were corrected for the self-absorption using a zero-order approximation. The detailed description of the self-absorption correction strategy can be found elsewhere<sup>56</sup>.

### 3.3. *In situ* OCM experiments at ID15A, ESRF

Figure S15 shows the photograph of the experimental setup used during the *in situ* measurements. In both experiments two separate gas streams were delivered to the reactor cell. During the temperature ramp up to 820 °C, the sample was heated under atmosphere of 50 sccm Ar (inner side gas stream) and 50 sccm air (outer side gas stream) with a temperature ramp of 20 °C·min<sup>-1</sup>. Pure gases of air, CH<sub>4</sub>, CO<sub>2</sub> and Ar were delivered to the reactor by mass flow controllers (Brooks). The OCM reaction was performed at atmospheric pressure and the outlet gases were analysed by mass spectrometry using an Ecosys portable mass spectrometer. The sample was heated using an in-house developed box furnace. In the case of the first experiment, we investigated the long-term stability (11 h) of the BSCF membrane during the OCM reaction, using a CH<sub>4</sub> stream co-fed with 20 % of CO<sub>2</sub>. The outer side gas stream delivered 50 sccm of air and the inner side gas stream delivered 80 sccm of CH<sub>4</sub> and 20 sccm of CO<sub>2</sub>. In the case of the second experiment, the solid-state interaction between the membrane and catalyst materials was investigated, testing different compositions of OCM reaction mixtures (CH<sub>4</sub> stream also co-fed with CO<sub>2</sub>). The outer side gas stream delivered 50 sccm of air and the inner side gas stream delivered OCM mixture co-fed with 0, 10, 20, 50 and 100 % of CO<sub>2</sub> in CH<sub>4</sub>/CO<sub>2</sub> mixture, keeping the 100 sccm as total flow of inner side gas stream. The experimental protocol details for both experiments can be found in the Supplementary Materials (Figure S20-S21).

### 3.4. Analysis of reconstructed diffraction patterns

The summed diffraction patterns from each XRD-CT dataset were analysed with the X'Pert HighScore Plus software to identify which phases were present and create the model necessary for the Rietveld refinement. The identified phases together with crystallographic information are presented in Table S2. The analysed diffraction patterns were extracted only from pixels where the membrane or catalyst particles were present (the regions of air, reactor and voids between particles were masked). The batch refinement analysis using the reconstructed diffraction patterns was performed using the software Topas v5<sup>57</sup>. For both measurements, individual reflections of the cubic perovskite (space group *Pm-3m*) were fitted to experimental data, in order to follow the relative changes in peak intensities (referred as *hkl\_phase* in Topas). In addition, the use of a 20 % trimmed mean filter for data correction<sup>55</sup>, especially in the case of second experiment, affected the relative intensity of each peak (i.e. spotty data). Therefore, Pawley instead of Rietveld refinement analysis was used as a means to overcome the intensity mismatch problem. In addition, due to the significant thermal expansion of the ceramic material during the temperature ramp, the relative changes in peak intensities were compared only for measurements performed at high temperatures. The scattering signal originating from catalyst particles (low absorbing and weakly scattering material) was highly altered by the membrane signal (high absorbing and strongly scattering material) and therefore it was not possible to perform refinement analysis of these diffraction patterns. The distribution of each component is based on the summed intensity of a corresponding diffraction peak in the XRD-CT data.



### 3.4. Laboratory mass spectrometry and gas chromatography measurements

Complementary laboratory OCM experiments to the *in situ* experiments performed at the ID15A beamline were also performed. In contrast to the *in situ* measurements, the reactor used in the laboratory measurements was closed from both ends; two inlet streams and two outlet streams were connected to the reactor using nonporous alumina rods. The sample was placed inside a quartz reactor, itself placed inside a horizontal tubular furnace (Carbolite). In the case of packed-bed catalytic membrane reactor, 68 mg of Na-Mn-W/SiO<sub>2</sub> catalyst was placed inside the BSCF membrane supported by quartz wool.

A schematic representation of the experimental setup used in the laboratory measurements is presented in Figure S22. Gases: 20 % of O<sub>2</sub>/He, 50 % of CH<sub>4</sub>/Ar, CO<sub>2</sub> and N<sub>2</sub> were delivered to the reactor by mass flow controllers (Brooks). The OCM reaction was performed at atmospheric pressure and the outflow gases were analysed by mass spectrometry, using an Ecosys portable mass spectrometer, and by gas chromatography, using the SRI 8610C Gas Chromatograph (Molecular Sieve 13X and Haysep 6D columns) equipped with FID and TCD detectors. The inner side gas stream was cooled with an ice bath to collect the produced water (in the case of the experiment with packed-bed catalytic membrane reactor). The experimental setup allowed, by adjusting accordingly the valves, switching between the two streams and choosing which one was probed by mass spectrometry. Prior to the experiments, the membrane sealing was tested by measuring the gas flow from the sweep outlet 2 (outer side gas stream) while using only an inert gas to the reactor through inlet 1 (inner side gas stream). This way the sealing of both membrane sections was tested. During the temperature ramp, only the gas stream flow outlet 2 was probed in order to ensure the sealing did not fail during the high temperature treatment. Before introducing the OCM reaction mixture the valves were adjusted to probe the outlet 1 (inner side gas stream). The experimental protocol for both experiments can be found in Table S3 and Table S4.

## 4. Summary and conclusions

In this work we presented an *in situ* XRD-CT study of two catalytic membrane reactors consisting of BSCF hollow fibre membranes and a Na-Mn-W/SiO<sub>2</sub> catalyst. The spatially-resolved diffraction data obtained under operating conditions coupled with laboratory MS measurements and SEM/EDX post-reaction measurements revealed that there are several challenges that need to be addressed before the BSCF membrane can be used for the industrial application of the OCM process.

More specifically, the long-term operation of the BSCF membrane at intermediate temperatures (i.e. 825 °C) resulted in the gradual decomposition of the BSCF to secondary phases; the XRD-CT measurements identified the formation of a hexagonal phase containing in majority Ba and Co species (Ba<sub>6</sub>Co<sub>4</sub>O<sub>12</sub>) while the SEM measurements indicated the formation of a new structure (needle-like) around the edge of membrane. However, the EDX mapping measurements did not reveal any chemical difference between the needle-like structure and the membrane dense structure. In addition, the formation of the secondary phases during operation of the BSCF membrane was shown to cause a gradual decrease in oxygen permeation.

In the case of the packed-bed catalytic membrane reactor, a chemical interaction between the membrane and catalyst was observed; at high temperature the W species were seen to migrate towards the membrane surface forming a layer of BaWO<sub>4</sub>. The additional SEM/EDX measurements on the recovered samples revealed that also Na and Mn species migrated towards the membrane but to a lesser extent. With the MS measurements, the formation of the BaWO<sub>4</sub> layer was directly shown to have a detrimental effect on the membrane performance, as the production of C<sub>2+</sub> molecules was seen to decrease during the OCM measurements performed in between the CO<sub>2</sub> cycling. The BaWO<sub>4</sub> formed at the interface between the catalyst particles and membrane is believed to suppress the oxygen permeation and may have indirectly led to a reactor type change, specifically to fixed-bed type with co-fed CH<sub>4</sub> and O<sub>2</sub>. The behavior of the W species results from the intrinsic instability of Na-Mn-W/SiO<sub>2</sub> catalyst at high temperatures and under operating conditions; this problem could potentially be solved through the chemical promotion and/or thermal treatment<sup>45,46</sup>.



Regarding the poisoning effect of CO<sub>2</sub>, the laboratory measurements showed that the addition of CO<sub>2</sub> (from 10 % to 100 %) to the reaction mixture significantly affected the oxygen permeation and thus the production of C<sub>2+</sub> molecules. In all measurements, the CO<sub>2</sub> effect was reversible and the initial performance could be recovered when removing the CO<sub>2</sub> from the reaction mixture. It should be noted that both *in situ* XRD-CT and *ex situ* SEM/EDX mapping of the recovered membrane samples did not provide any evidence for carbonate species formation or elemental segregation. This implies that if any carbonate species formed at the membrane surface, these are in not in large quantities and indeed below the detection limit of the techniques applied in this work (i.e. instruments and experimental conditions). The structural changes and formation of BaWO<sub>4</sub> were seen to be the main mechanisms behind the long-term degradation of the investigated CMRs. It is concluded that the CO<sub>2</sub> produced from CH<sub>4</sub> combustion/oxidation processes during the OCM reaction does not significantly affect the oxygen permeation. However, as shown in this work, using the CO<sub>2</sub> as the reactor diluent has a negative effect on the membrane reactor performance and should be avoided.

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