Partial Oxidation of Methane in Hollow-Fiber Membrane Reactors Based on Alkaline-Earth Metal-Free CO₂-Tolerant Oxide

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The U-shaped alkaline-earth metal-free CO₂-stable oxide hollow-fiber membranes based on (Pr₀.₉La₀.₁)₂(Ni₀.₇₄Cu₀.₂₁Ga₀.₀₅)O₄₋₆(PLNCG) are prepared by a phase-inversion spinning process and applied successfully in the partial oxidation of methane (POM) to syngas. The effects of temperature, CH₄ concentration and flow rate of the feed air on CH₄ conversion, CO selectivity, H₂/CO ratio, and oxygen permeation flux through the PLNCG hollow-fiber membrane are investigated in detail. The oxygen permeation flux arrives at approximately 10.5 mL/min cm² and the CO selectivity is higher than 99.5% with a CH₄ conversion of 97.0% and a H₂/CO ratio of 1.8 during 140 h steady operation. The spent hollow-fiber membrane still maintains a dense microstructure and the Ruddlesden-Popper K₂NiF₄-type structure, which indicates that the U-shaped alkaline-earth metal-free CO₂-tolerant PLNCG hollow-fiber membrane reactor can be steadily operated for POM to syngas with good performance.

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Introduction

The economic use of natural gas has attracted extensive attention worldwide.¹ At present, natural gas is mainly converted into syngas (CO + 2H₂) by steam reforming. In a second step, a series of important chemical products such as liquid Fischer–Tropsch (F–T) fuels and methanol can be produced from syngas.² As a promising alternative for syngas generation, the catalytic partial oxidation of methane [POM, CH₄ + 1/2O₂ → CO + 2H₂, ΔH (25°C) = −36 kJ/mol] has attracted increasing attention in recent years.³ POM to syngas is a weakly exothermic reaction, and the reaction rate is 1–2 orders of magnitudes faster than that of steam reforming. Furthermore, the H₂/CO ratio is 2:1, which is a perfect stoichiometry for F–T and methanol syntheses. However, the downstream process requirements cannot tolerate nitrogen as ballast, that is, pure oxygen is required for POM. The investment cost in a cryogenic oxygen plant may cover 45% of the total investment cost of a POM to syngas plant.⁴ An alternative route following the concept of process intensification is the use of a mixed oxygen-ionic and electronic conducting (MIEC) membrane⁵ for the in situ oxygen separation from air combined with the catalytic POM in one device called catalytic membrane reactor.

To date, numerous studies have reported the development and application of MIEC membrane reactors in the POM to syngas, and the corresponding membrane materials, mainly perovskites, have been extensively investigated. Perovskites show a relatively high oxygen permeation flux compared with other oxygen-conducting oxides but their stability transpired to be a critical problem.⁶⁻¹⁵ A chemical decomposition to SrCO₃ was observed on the SrCo₃₀₆Fe₁₂₆O₃₅₆ hollow-fiber membrane reactor in syngas generation experiments.¹⁶ Bouwmeester¹⁷ also reported the formation of SrCo₃ on the membrane surface of La₀₉₂Sr₀₄Co₀₂Fe₁₂₆O₃₅₆ after POM operation for 3 days at 830°C. A BaCoₓFe₁₋ₓZrₓO₃₋₆ hollow-fiber membrane reactor coated with catalyst survived only 5 h in the POM.¹⁷ From the concept of “oxidation-reforming” mechanism for POM, the high CO₂-concentration from the methane total oxidation to CO₂ and H₂O near the membrane surface results in the formation of alkaline-earth metal carbonates. Caro et al.¹⁸ and Kleinert et al.¹⁹ also noted that the failure of the hollow-fiber membrane applied in POM was due to the formation of carbonate. In sum, most of the
Perovskites contain the alkaline-earth metal elements, which tend to react with CO$_2$ under POM conditions and form carbonates, although a proper membrane reactor operation can prevent the further decomposition of a perovskite membrane in the reducing atmosphere of a POM. The instability of alkaline-earth metal-containing materials will lead to the failure of a membrane reactor in the POM. Therefore, alkaline-earth metal-free CO$_2$-tolerant MIEC membranes with better stability will be a good choice for POM.

In recent years, intensive efforts have been made to develop CO$_2$-tolerant oxygen permeable membrane materials. A Ruddlesden-Popper K$_2$NiF$_4$-type phase of the composition (Pr$_{0.9}$La$_{0.1}$)$_2$(Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$)O$_4$ (PLNCG), which developed by Yashima et al., was also found to exhibit good oxygen permeability and good resistance to CO$_2$ in our previous work. However, only a few applications in the POM to syngas with these CO$_2$-tolerant materials have been published so far. Therefore, in this article, a membrane reactor based on the alkaline-earth metal-free CO$_2$-stable K$_2$NiF$_4$-type oxide PLNCG will be used for coupling the in situ oxygen separation from air and the POM to syngas. It has been reported that the reactor with smaller diameter (D) and greater length-to-diameter ratio (L/D) gives better performance in terms of high CH$_4$ conversion in POM. The hollow-fiber membranes exhibit many advantages, such as the large membrane area per unit volume for oxygen permeation, high oxygen permeation flux, easy assembly for large-scale module fabrications. Furthermore, the specific U-shaped hollow-fiber geometry can avoid the breakage of the membrane due to the expansion or shrinkage at changing temperatures. Therefore, the U-shaped PLNCG hollow-fiber membranes are chosen in this study.

**Experimental**

Powders of PLNCG, Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF), and BaCo$_{0.4}$Fe$_{0.6}$Zr$_{0.2}$O$_{3-δ}$ (BCFZ) were prepared through the sol-gel route and the U-shaped PLNCG hollow fibers were fabricated through a phase-inversion spinning process, which can be found in our previous work. The as-prepared PLNCG, BSCF, and BCFZ powders were treated in various atmospheres at 900°C for different time. The powder samples before and after gas treatment, as well as the fresh and spent PLNCG hollow-fiber membranes were characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu-Kα radiation). The microstructure and morphology of the fresh and spent PLNCG hollow-fiber were observed by a scanning electron microscope (SEM, JEOL JSM-6490LA) with energy dispersive X-ray spectrometer (EDXS).

The POM in the U-shaped PLNCG hollow-fiber membrane reactor was investigated in a high-temperature permeation cell, as shown in Figure 1. The Ni-based catalyst (an commercial steam reforming catalyst of Süd Chemie AG, now Clariant, BET surface area is 170–200 m$^2$/g, Ni: 42.7 wt %, Al: 14.1 wt %, Si: 5 wt %) was packed around the whole U-shaped hollow-fiber membrane above the quartz wool as support. The particle size of catalyst was between 0.2 and 0.4 mm, catalyst was diluted with silica of the same grain size (catalyst mass ≈60%) and the catalytic bed height was near 3 cm. The distance between the thermocouple and the catalytic bed was about 5 mm to ensure a more or less accurate temperature control. As the POM reaction is a weakly exothermic reaction, it cannot be excluded that the real temperature was slightly higher than detected. However, under most of our experimental conditions, methane was...
diluted with helium, which makes it easier to keep a constant reactor temperature. Therefore, the detected temperature seems to represent the real temperature within $\pm 10^\circ$C.

Air was fed to the core side while CH$_4$ or a mixture of He and CH$_4$ was fed to the shell side. Composition of the outlet gases was measured using an online coupled gas chromatograph (GC, Agilent 7890) with a thermal conductivity detector (TCD). CH$_4$ conversion ($X_{\text{CH}_4}$), CO selectivity ($S_{\text{CO}}$), and oxygen permeation flux ($J_{\text{O}_2}$) can be calculated through hydrogen balance and oxygen balance, which can be defined as follows:

$$X_{\text{CH}_4} = \frac{F_{\text{CH}_4}^{\text{in}} - F_{\text{CH}_4}^{\text{out}}}{F_{\text{CH}_4}^{\text{in}}}$$  

(1)

$$S_{\text{CO}} = \frac{F_{\text{CO}}}{F_{\text{CO}} + F_{\text{CO}_2}}$$

(2)

$$J_{\text{O}_2} = \frac{F_{\text{CO}} + 2F_{\text{CO}_2} + F_{\text{H}_2\text{O}} + 2F_{\text{O}_2} \text{ (unreacted)}}{2S}$$

(3)

where $F_{\text{gas}}$ is the flow rate of the corresponding gas, superscript of “in” and “out” is the gas direction, and $S$ is the effective hollow-fiber membrane area.

**Results and Discussion**

**Powder stability under syngas condition**

It is very important to test the stability of PLNCG under POM reaction conditions, that is, CO and H$_2$ containing atmosphere, even though it is stable in CO$_2$.$^{24,25}$ Therefore, PLNCG powder was treated in various atmospheres at 900$^\circ$C for 1 h, including He, CO$_2$, 15% CO balanced with He, 30% H$_2$ balanced with He, and syngas (15% CO + 30% H$_2$) balanced with He, which is shown in Figure 2. It can be found that PLNCG still keeps its K$_2$NiF$_4$-type structure under CO and H$_2$ atmosphere. To confirm the earlier statement, PLNCG powder was treated for different exposure times in a syngas atmosphere (15% CO + 30% H$_2$). The phase structures of PLNCG for the exposure time of 1, 5, and 12 h are shown in Figure 3. Compared with the fresh powder, the PLNCG powder exposed to syngas for even 12 h still exhibits the K$_2$NiF$_4$-type structure.

Conversely, BSCF and BCFZ were also chosen for comparison. As one of the most popular mixed conducting oxide with excellent oxygen permeability,$^{29,30}$ BSCF seems to be not stable enough in syngas atmosphere. As shown in Figure 4a, after exposure to syngas at 900$^\circ$C for 1 h, the material of BSCF decomposes and new reflections of BaCO$_3$, BaO, CoO, Co$_3$O$_4$ appear in the XRD pattern. As a much more stable mixed conducting oxide,$^{31}$ which can be applied in POM steadily for more than 2000 h,$^{32}$ BCFZ can maintain the primary reflections of the perovskite structure unchanged after syngas treatment, as shown in Figure 4b. However, some other phases of BaCO$_3$ and Co$_3$O$_4$ are formed. Table 1 summarizes the stability and decomposition products, respectively, of PLNCG, BSCF, and BCFZ powders after exposure to various atmospheres at 900$^\circ$C for 1 h. Compared with BSCF and BCFZ, PLNCG shows much better chemical and phase stability under these harsh atmospheres. In other words, PLNCG is stable not only in CO$_2$ but also in CO and H$_2$ containing atmospheres (POM conditions). Therefore, with the expectation of a good stability, PLNCG hollow-fiber membranes were applied in POM in the following work.

**Effect of different operation conditions on POM performance**

The time dependence of the oxygen permeation flux and the catalytic performance of the U-shaped PLNCG hollow-fiber membrane during the initial stage of POM are shown in Figure 5. The CH$_4$ conversion keeps constant at 100% in the first 20 h. In this period, the oxygen permeation flux through the membrane slightly increases from 11.2 to 11.8 mL/min cm$^2$, while the CO selectivity decreases from...
89% to 83%. Over this 20 h operation, the H₂/CO ratio was found to be 1.7. The missing hydrogen is attributed to the deep oxidation to H₂O while CO keeps at a relatively high selectivity. It can be found that it took only a short time for the membrane reactor to achieve a steady state from Figure 5. The performance in the initial stage is related to the reduction rate of the Ni-based catalyst which has been also found in other studies on POM in membrane reactors.33–35 Dong et al.33 showed that the initial catalyst was reduced from the oxidation state of NiO to Ni⁰ starting from the outer layer of the catalysts to the center gradually, and as a result, the catalytic performance of the catalyst was improved also gradually. Tsai et al.10 found that the oxygen permeation rate increased very slowly and reached its steady state after 500 h in a dense disk-shaped La₀₂Ba₀₅Co₀₂. Fe₀₇O₃.₆ membrane reactor in the POM reaction. But almost 21 h were needed for the BSCF disk-shaped membrane reactor to reach its steady state.33 In other words, the initial stage of membrane reactors based on different materials will be different, which might be related to the adjustment between the membrane and the new environment. However, a shorter initial time for POM was obtained in a tubular BSCF membrane reactor and only 1 h was needed to reach the steady state, which demonstrates that the initial stage is also affected by the membrane configuration.36 However, in our case during this initial stage in the PLNCG hollow-fiber membrane reactor, no sharp increase or decrease of the oxygen permeation flux, CH₄ conversion, or CO selectivity are observed. In addition, a probable reason for this experimental finding seems to be that the relative high operation temperature accelerates the reduction rate of the catalyst and shortens the activation time, which is also in agreement with Li’s finding.34 Therefore, the initial reaction process of the membrane reactor for POM is closely dependent on the membrane reactor configuration, feeding mode, methane partial pressure, membrane material, and the activation ability of the catalyst.35 After reaching the steady state, the effects of operation temperature, flow rate of CH₄ and air on the POM reaction are investigated to understand the catalytic performance of our PLNCG hollow-fiber membrane reactor and find the best and economical operation conditions for such a membrane reactor in POM.

Table 1. Stability and Decomposition Products, Respectively, of Different Oxygen Permeable Membrane Materials in Various Atmospheres (900 °C, 1 h)

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>CO₂</th>
<th>15% CO</th>
<th>30% H₂</th>
<th>syngas (15%CO + 30%H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLNCG</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
<td>Stable</td>
</tr>
<tr>
<td>BSCF</td>
<td>Stable</td>
<td>BaCO₃, CoO</td>
<td>BaCO₃, BaO, CoO</td>
<td>Sr(OH)₃, Co₃O₄, Co</td>
<td>BaCO₃, BaO, CoO, Co₃O₄</td>
</tr>
<tr>
<td>BCFZ</td>
<td>Stable</td>
<td>BaCO₃, Co₃O₄</td>
<td>BaCO₃, Co₃O₄</td>
<td>Co₃O₄, Fe</td>
<td>BaCO₃, Co₃O₄, Fe</td>
</tr>
</tbody>
</table>

Figure 4. XRD patterns of the (a) BSCF and (b) BCFZ powder before and after exposure to various atmospheres at 900 °C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
Figure 6 shows the temperature dependence of CH₄ conversion, CO selectivity, H₂/CO ratio, oxygen permeation flux, and that swept by He. It can be seen that the CH₄ conversion increases from 50% to 100%, and the oxygen permeation flux increases from 4.9 to 12.2 mL/min cm² with increasing temperatures from 800 to 950°C, while the CO selectivity decreases from 98% to 92% and the H₂/CO ratio keeps around 2. The increase of the oxygen permeation flux is due to the increase of the oxygen diffusion rate through the oxygen membrane and an enhanced surface exchange rate with increasing temperatures, which is in complete accordance with the conclusions in our previous work. Resulting from the increase of the oxygen permeation flux, the methane conversion increases because it is mainly controlled by the amount of the permeated oxygen. When the amount of the oxygen in the CH₄ side is more than the needed amount for the stoichiometric POM, the CO selectivity decreases due to the deeper oxidation of CO with increasing temperature. As presented in Figure 6, the oxygen permeation flux through the U-shaped PLNCG hollow-fiber membrane under the oxygen partial pressure gradient of air/CH₄ with Ni-based catalyst is an order of magnitude higher than that under an air/He gradient. Because the permeated oxygen prefers to react with CH₄ quickly, the oxygen partial pressure gradient in POM membrane reactors is much larger than that under conventional permeation conditions using nonreactive sweep gases. Yang and coworkers also compared the oxygen permeation flux under the POM reaction condition with that when using helium as sweep gas. They found that the presence of methane in the BSCF tubular membrane could lower the oxygen partial pressure deeply and the oxygen permeation flux was enhanced by 8–10 times. Li et al. also found that the oxygen permeation flux increased eightfold in the presence of a catalyst in the BaCe₀.₁Co₀.₄Fe₀.₅O₃₋₃ membrane reactor for POM.

Figure 7 shows the influence of the methane concentration on the performance of the POM membrane reactor. The different methane concentrations are obtained by adjusting the ratio of methane and helium. As shown in Figure 7, with increasing methane concentration, the CH₄ conversion first keeps 100% since enough oxygen is available, but then the CH₄ conversion begins to decrease once the methane concentration is higher than 32%, which can be ascribed to the high CH₄/O₂ ratio. On the contrary, the CO selectivity and the oxygen permeation flux increase with increasing methane concentration. A higher methane concentration means a higher partial pressure of methane, which leads to a higher oxygen partial pressure gradient as the driving force over the membrane. Therefore, the oxygen permeation flux increases as the methane concentration increases. However, the CH₄/O₂ ratio increases and as a result, a higher CO selectivity can be obtained at a higher methane concentration because the partial oxidation to produce CO is favored. In Figure 8, the effect of the methane flow rate on the POM performance is also investigated. Different from the conditions in Figure 7 where the He-diluted CH₄ is used, here we applied pure CH₄ as reactant. The CO selectivity and the oxygen permeation flux decrease while the CH₄ conversion decreases with increasing CH₄ flow rate. Under such reaction condition with a high methane flow rate, the permeated oxygen is not enough to completely consume the fed methane. As a result, the CH₄ conversion decreases and the CO selectivity increases with increasing methane flow rate. In both Figures 7 and 8, the H₂/CO ratio is around 2.

For the other side of the membrane reactor, the effect of the air flow rate on the performance of the POM membrane reactor is plotted in Figure 9. The CH₄ conversion keeps 100% for all air flow rates, which indicates that there is enough oxygen permeated through the membrane to consume the methane completely. With increasing air flow rate, the oxygen permeation flux increases while the CO selectivity decreases, but this trend is very slight. Compared to the effect of the methane flow rate on the performance of the PLNCG hollow-fiber membrane reactor, the influence of the air flow rate is less remarkable. For the BaCe₀.₁Co₀.₄Fe₀.₅O₃₋₃ POM membrane reactor, a similar phenomenon was also found by Li et al.
Stability of PLNCG hollow-fiber membrane in POM

The stability of a membrane reactor is very important for its practical application in POM. In recent decades, the lifetime of the membrane reactor has been prolonged by different methods, such as developing new materials which are stable under the POM reaction conditions, modifying the operation mode by adding a small amount of oxygen into the methane, precise temperature controlling by correct monitoring of the heat system in the POM process. For the disk-membrane reactor based on BaCe$_{0.1}$Co$_{0.4}$Fe$_{0.5}$O$_3$, a 1000 h continuous operation of POM was performed without any decrease of CH$_4$ conversion, CO selectivity and oxygen permeation flux. For the tubular membrane reactor based on La$_{0.5}$Sr$_{0.5}$FeO$_3$, the long-term test showed stable performance during more than 7000 h with the CH$_4$ conversion and CO selectivity of not less than 98.8% and 90%, respectively. For the disk-type and tubular membrane reactors, the lifetime can reach several hundreds or even thousands of hours under POM conditions. However, there is only a few literature about the long-term operation in hollow-fiber membrane reactors for POM. Because there are many factors which will block the POM reaction in hollow-fiber membrane reactors, such as material’s instability under reducing atmosphere, carbonate formation, solid state reaction between catalyst and membrane, coke deposition, and so forth. Therefore, the long-term operation of hollow-fiber membrane reactors in POM is reported rarely, and until now, only Caro et al. reported the 300 h long-term study in...
BaCoxFeyZrzO3-δ hollow-fiber membrane reactor for POM. In their study, the catalyst was separated from the hollow-fiber membrane by a porous tube, and steam was added into methane to avoid coke deposition. Turning back to our work, it has to be pointed out that our membrane is in direct contact with the catalyst and no steam is added to the

Figure 12. SEM micrographs of the cross-section of the fresh PLNCG hollow-fiber membrane (a and b); and that of the spent hollow-fiber membrane (c and d). (d) shows a cross-section area near to the outer surface of the hollow-fiber membrane which was in direct contact with the Ni catalyst. (e and f) show the EDX spectra of areas A and B as marked in (d). (g and h) show the Ni-Kα line scan of the spent membrane.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
methane feed. More than 140-hour continuous operation of POM is performed at 900°C in such a U-shaped alkaline-earth metal-free CO2-tolerant PLNCG hollow-fiber membrane reactor. As shown in Figure 10, the oxygen permeation flux reaches approximately 10.5 mL/min cm² and the CO selectivity is higher than 99.5% while the CH4 conversion is around 97.0%, the H2/CO ratio is about 2, exactly 1.8, the missing H₂ is due to the deep oxidation to H₂O. Over the 140 h operation, the performance of the PLNCG hollow-fiber membrane reactor remains stable with an only slightly decrease of the CH₄ conversion after 100 h, which is related to coke deposition. There are different methods to avoid coke formation. Using methane/steam mixtures as feed with CH₄/H₂O ≤ 1 allows to conduct the POM without coke deposition on the Ni-based catalyst. The coke deposition could also be slowed down by cofeeding CH₄ and CO₂ as feed due to the Boudouard reaction between CO₂ and coke. Efforts of avoiding the coke formation on the catalyst to extend the lifetime of PLNCG hollow-fiber membrane reactor for POM are under study. However, compared with other hollow-fiber oxygen permeable membrane reactors for POM, the PLNCG hollow-fiber membrane exhibits a good reaction performance and promising stability.

**Characterization of the spent membrane**

After 140 h steady POM operation, the PLNCG hollow-fiber membrane was still gastight. The spent membrane was characterized by XRD, SEM, and EDXS. Figure 11 presents the XRD phase structures of the starting PLNCG powder, the fresh and spent hollow-fiber membranes after 140 h operation in the POM. The XRD patterns indicate that all materials are pure K₂NiF₄-structures. Furthermore, after 140 h operation time, no carbonates or other new phases are observed. Although the XRD pattern alone cannot sufficiently prove the stability of the membrane because only the crystalline phases in a concentration higher than 5% can be detected, XRD is a helpful analytical tool to prove chemical as well as phase stability.

Figures 12a, b show the SEM micrographs of the cross-section of the fresh PLNCG hollow-fiber membrane. Finger-like structures can be observed in the wall of PLNCG hollow-fiber membrane near the inner surface, which is beneficial for improving the surface exchange rate during POM. Figures 12c, d show the cross-section of the spent hollow-fiber membrane and the wall part near the outer surface which was in direct contact to the Ni-based catalyst. It can be seen that the spent membrane maintains its compact structure. However, there are some μm-sized deposits on the outer surface of the membrane (Figure 12d). The EDX spectra of area A on the outer surface and area B in the membrane bulk in Figure 12d are shown in Figures 12e, f. From the EDX spectrum of area A (Figure 12e), a Ni enrichment on the surface is clearly indicated. The Ni signal at 0.85 keV stands for the electron transition L₂, the x-ray line at 7.5 keV reflects the Kx transition. This Ni-enriched layer could stem (a) from the Ni-containing catalyst or (b) from the membrane by demixing and segregation. From the Ni EDXS line scan across the membrane (Figures 12g, h, using the Ni-Kz₁ electron transition), we can learn that there is no Ni depletion in the bulk near to the surface of the PLNCG. In can be concluded, therefore, that the detected Ni enriched surface layer originates from the intimate contact of Ni catalyst and membrane (cf. Figure 1). It is reported in literature that a BaCo₃Fe₂ZrO₃ hollow-fiber membrane reactor failed after 9 h operation and the defect occurred at a position where the membrane was in direct contact with the Ni-based catalyst. However, the Ni transfer in a solid state reaction on the outer membrane surface resulting from the intimate contact with the catalyst showed little negative effect on the membrane performance from our long-term operation in the POM in Figure 10.

All these above results demonstrate that the U-shaped PLNCG hollow-fiber membrane reactor can be steadily operated in POM. Furthermore, such a hollow-fiber membrane reactor based on the alkaline-earth metal-free CO₂-tolerant material like PLNCG, exhibits a long lifetime among various hollow-fiber membrane reactors for POM with good reaction performance.

**Conclusions**

The U-shaped alkaline-earth metal-free CO₂-tolerant PLNCG oxide hollow-fiber membranes were successfully prepared by a phase-inversion spinning process and evaluated in the POM to syngas. With increasing temperatures, the CH4 conversion and the oxygen permeation flux increase, while the CO selectivity decreases. With increasing CH4 concentration or CH4 flow rate, the CO selectivity and the oxygen permeation flux increase while the CH4 conversion decreases. The oxygen permeation flux through the U-shaped PLNCG hollow-fiber membrane under an oxygen partial pressure gradient of air/CH₄ is an order of magnitude higher than that under an air/He gradient at 950°C. More than 140 h steady POM operation is performed at 900°C in such a U-shaped alkaline-earth metal-free CO₂-stable PLNCG hollow-fiber membrane reactor with the oxygen permeation flux of 10.5 mL/min cm², CO selectivity of 99.5%, CH₄ conversion of 97%, and a H2/CO ratio of 1.8. No carbonates or other new phases are observed after the long-term operation which indicates that PLNCG exhibits good chemical as well as phase stability under the POM reaction conditions. The spent membrane also maintains its compact dense structure except only a very thin Ni-enriched layer (around 5–10 μm) on the outer membrane surface resulting from the intimate contact with the catalyst, but without any negative effect on the membrane performance. To sum up, our hollow-fiber membrane reactor based on the alkaline-earth metal-free CO₂-tolerant PLNCG material exhibits promising stability in the POM with good performance in syngas production.

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**Literature Cited**


