The U-shaped hollow-fiber membranes based on the perovskite-type oxide BaCo$_{0.7}$Fe$_{0.2}$Ta$_{0.1}$O$_3$ (BCFT) were prepared by phase inversion spinning process and were used to construct membrane reactor for partial oxidation of methane (POM) to syngas (CO + H$_2$) successfully. The effects of the temperature, CH$_4$ concentration and the CH$_4$ flow rate on the performance of the BCFT hollow-fiber membrane reactor were investigated in detail. At 875 °C, an oxygen permeation flux of 20 ml/min cm$^2$ with 96% methane conversion and 99% CO selectivity were obtained. SEM, XRD, XPS and EDS of the fresh and spent hollow-fiber membranes show that carbonate was formed and the metal ion reduction, as well as the elements segregation took place in the membrane, which led to the fracture of the membrane reactor after 83 h operation.

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1. Introduction

Nowadays, highly efficient conversion of natural gas into value-added chemicals has attracted great attentions [1-9]. However, the direct conversion of the natural gas has not been applied in industry till now because the desired products are more active than the starting materials. This eventually leads to deep oxidation which results in low selectivity of the aimed products. The alternative conversion approach for natural gas is to produce syngas (CO + H₂) through selective oxidation of methane, then synthesize a series of important chemical products by methanol synthesis or Fischer–Tropsch technology [10,11]. At present there are several ways for syngas production, e.g. catalytic methane partial oxidation (POM) and the steam reforming (SRM). Although the main technology for syngas production is SRM, it still has several disadvantages, such as the product ratio of H₂/CO is 3, which is not suitable for the further syngas conversion to produce liquid fuel. Additionally, it is a strongly endothermic reaction, which makes the process energy intensive [12,13]. As a promising alternative for syngas generation, POM has attracted increasing attentions due to its potential advantages. The ratio of H₂ to CO is 2, which is suitable for the downstream process. It is also a slightly exothermic reaction and can be operated at lower pressures, which less cost-intensive compared with the endothermic SRM.

In recent years, great attention has been paid to the POM for syngas production using the dense ceramic membrane reactors [3,14-24]. In membrane reactors, air instead of oxygen can be directly used as the oxidant so that the costly separation of oxygen can be avoided, which makes it more commercially feasible. Furthermore, such membranes can couple the oxygen separation and the POM reaction in one unit, which simplifies the process and reduces the operation costs. The hot spots in the conventional co-feed reactor can also be eliminated due to the gradual feeding of oxygen through the membrane. However, the oxygen permeable membranes used in POM reaction should meet the following requirements: high oxygen permeation flux, good chemical stability under reducing atmosphere and suitable membrane configuration for scaling up. It is believed that the mixed-conducting materials with perovskite structure would be promising materials for POM because of its excellent oxygen permeability. Dong et al. found that the Ba₅SrxSr₀.5Co₁₋₀.₁₅Fe₂₋₀.₁₅O₃₋ₐ showed an oxygen permeation flux of 11.5 ml/min cm² with the methane conversion >97% and CO selectivity >95% at 875 °C in the POM reaction [21]. Tong et al. investigated BaCo₀.₄FeₓZr₀.₂O₃₋ₐ membrane reactor for POM. In this membrane reactor a CH₄ conversion of 96-98% with CO selectivity of 98-99% and an oxygen permeation flux of 5.4-5.8 ml/min cm² was achieved at 850 °C [25]. Jin et al. developed Ba₀.₅Sr₀.₅CoₓFe₂₋ₓO₄₋ₓ membrane reactor for POM, the CH₄ conversion was higher than 96% with the CO selectivity higher than 97% at 1098–1158 K [17].

In the previous studies, most oxygen permeable membranes used for POM to syngas were disk or tubular membranes, because they could be easily fabricated by the pressing method or the plastic extrusion. However, disk-shaped membranes have a very limited membrane area and the sealing problem at high temperature. The thickness of tubular membrane is relatively higher, which leads to a low oxygen permeation flux due to the big resistance of ionic bulk diffusion in the membranes. So far, large research efforts are recently being focused on the linear hollow-fibers due to the high oxygen permeation flux resulted from thin thickness. However, when both ends of the linear hollow-fiber are tightly fixed on the outer host tube at room temperature, the linear hollow-fiber will be broken due to the expansion during increasing temperatures. In our previous work, a U-shaped hollow-fiber configuration was proposed to solve the problem mentioned above [26-28]. And we also found that the U-shaped hollow-fiber membrane based on the BaCo₀.₄FeₓZr₀.₂O₃₋ₓ [12,28,29] exhibit good oxygen permeation and stability. In order to accelerate the practical application of membrane reactor, the U-shaped hollow-fiber membrane reactors with a high surface/volume was chosen in this study. The POM for syngas production in the U-shaped BCFT hollow-fiber membrane reactor with Ni-based catalyst was investigated. The oxygen permeation and the reaction performance of the POM in the membrane reactors were systematically studied.

2. Experimental

2.1. Preparation of powder

The BCFT powder was synthesized through a solid state reaction. BaCo₃ₓFe₀.₄Zr₀.₂O₇₋ₓ (all reagents with A.R. purity) were weighted according to their stoichiometry and mixed in an agate mortar for 3 h and then ball-milled for 24 h with ethanol. Then, the mixtures were calcined at 950 °C for 10 h with heating and cooling rates of 2 °C/min. For the spinning of the hollow-fiber membranes, the powder was ball-milled for 24 h and then dried using a spray dryer (Büchi Mini Spray Dryer, B-290) with a nozzle of 1 μm. The obtained fine powder was used for the preparation of the U-shaped hollow-fiber membranes.

2.2. Preparation of BCFT hollow-fiber membrane

The dense BCFT perovskite hollow-fiber membrane was prepared by a phase inversion spinning technology. The spinning solution was composed of 6.96 wt% poly(ethersulfone) (PESI, A-300, BASF), 27.84 wt% 1-methyl-2-pyrrolidinone (NMP, AR-grade, purity >99.8%, Kernel Chem Inc., Tianjin, China), 0.70 wt% poly(vinylpyrrolidone) (PVP, K30, Boao Biotech Co., Shanghai, China), and 64.50 wt% BCFT powder. A spinneret with orifice and inner diameters of 1.5 and 1.0 mm, respectively, was used to obtain the hollow-fiber precursors. Deionized water and tap water were used as the internal and external coagulants, respectively. Afterward, the BCFT hollow-fiber precursors were sintered at 1150 °C for 5 h with an air flow rate of 60 ml/min to remove the polymers and obtain the gastight membranes. The preparation conditions of obtaining the U-shaped BCFT hollow-fiber are summarized in Table 1. The length of the U-shaped hollow-fiber is 4 cm, and the outer and inner diameter are 1.10 mm, 0.63 mm respectively in this experiment.

2.3. Characterizations of XRD, SEM, EDS and XPS

The phase structures of the as-prepared BCFT powder and the hollow-fiber membrane were characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu Kα radiation). The microstructure and morphology of the U-shaped BCFT hollow-fiber precursors

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of the starting solution</td>
<td></td>
</tr>
<tr>
<td>BCFT power</td>
<td>64.50 wt%</td>
</tr>
<tr>
<td>PESI, A-300</td>
<td>6.96 wt%</td>
</tr>
<tr>
<td>NMP</td>
<td>27.84 wt%</td>
</tr>
<tr>
<td>PVP, K30</td>
<td>0.70 wt%</td>
</tr>
<tr>
<td>Spinning temperature</td>
<td>25 °C</td>
</tr>
<tr>
<td>Injection rate of internal coagulant</td>
<td>2.8 ml/min</td>
</tr>
<tr>
<td>Spinning pressure</td>
<td>0.65 bar</td>
</tr>
<tr>
<td>Air gap</td>
<td>0.5 cm</td>
</tr>
<tr>
<td>Sintering temperature</td>
<td>1150 °C</td>
</tr>
<tr>
<td>Spinning time</td>
<td>5 h</td>
</tr>
<tr>
<td>Air flow rate for sintering</td>
<td>60 ml/min</td>
</tr>
</tbody>
</table>

Table 1
Preparation conditions for the U-shaped BCFT hollow-fiber membranes.
and the sintered BCFT hollow-fibers were observed by scanning electron microscopy (SEM, S-3700N, Japan). The element compositions of the fresh and spent membrane were determined by energy dispersive spectroscopy (EDS). The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Kratos Axis Ultra XPS instrument with the mono Al Kα radiation (1486.6 eV) under a pressure of $5 \times 10^{-9}$ Torr. The samples were referenced to the standard calibrated value of the adventitious carbon, C1s hydrocarbon peak at 284.6 eV prior to fitting the spectrum of samples.

2.4. Measurements of membrane reactor for the POM

The membrane reactor configuration for the POM to syngas is presented in Fig. 1. The U-shaped BCFT hollow-fiber membrane was sealed in a corundum tube with two channels by a commercial ceramic sealant (HT767, Hutian, China). The Ni-based catalyst (Süd-Chemie), mixed with 60% 40–60 mesh SiO2 to disperse catalyst and avoid coke deposition was packed around the whole U-shaped hollow-fiber membrane above the support of the quartz wool. Air was fed to the core side while CH4 or a mixture of He and CH4 was fed to the shell side. The gas flow rates were controlled by mass flow controllers (MFC, Seven Star D08-4F/ZM) calibrated using a soap bubble flow meter. The composition of the outlet gases were measured using an online gas chromatograph (GC, Agilent 7890) with a TCD detector. The leakage of the oxygen due to the imperfect sealing at high temperatures was less than 0.5% during all the experiments. The CH4 conversion ($X_{\text{CH}_4}$), CO selectivity ($S_{\text{CO}}$) and the oxygen permeation flux ($J_{\text{O}_2}$) can be

![Fig. 1. Configuration of the U-shaped BCFT hollow-fiber membrane reactor for POM.](image)

![Fig. 2. SEM micrographs of the sintered BCFT hollow-fiber membranes: (A) cross section; (B) wall of the sintered hollow fiber.](image)

![Fig. 3. Temperature dependence of the CH4 conversion, CO selectivity and the oxygen permeation flux in POM. Conditions: $F_{\text{air}} = 180$ ml/min, $F_{\text{He+CH}_4} = 60$ ml/min, $C_{\text{CH}_4} = 55.8\%$.](image)
permeation measurement at room temperature. Depending on above phenomena, the methane conversion mechanism in hollow-fiber membrane reactor packed with a Ni-based catalyst is possibly the combustion reform reaction (CRR) mechanism. If the oxidation reaction of methane in the membrane reactor obeys the direct partial oxidation (DPO) mechanism, the oxygen partial pressure near the membrane surface exposed to methane would decrease with increasing the methane flow rate, which led to the increase of the oxygen diffusion and the surface exchange kinetics with increasing temperature, which is in complete accordance with the conclusions in our previous work [28]. As shown in Fig. 3, the CH₄ conversion is 49.2% at 775 °C; however, the CH₄ conversion increase to 96.2% at 875 °C, and the selectivity of CO maintains above 98% from 775 °C to 875 °C. Among the products, only small amount of CO₂ is observed and there is no C₂ products. For the excess feed of methane, the methane conversion is mainly controlled by the oxygen permeation flux, the increase of the oxygen permeation flux spontaneously lead to the increase of the methane conversion. When the amount of the available oxygen on the reaction side is more than the stoichiometric amount for POM, the CO selectivity decreases due to the deeper oxidation of CO to CO₂ with increasing temperature.

Fig. 4 shows the influence of the methane concentration on the POM performance. The different methane concentrations are obtained by adjusting the ratio of methane and helium, and the total feed flow rate is 60 ml/min. As shown in Fig. 4, the CH₄ conversion maintain above 97%. The CH₄ conversion decreases slightly and the CO selectivity increases with the increase of the methane concentration. The oxygen permeation flux increases dramatically with increasing the methane concentrations from 36.6% to 45.5%, but as the methane concentration further increases to 55.8%, the oxygen permeation flux increases slowly or is kept nearly constant. The oxygen permeation flux increases with increasing CH₄ concentration because the oxygen partial pressure on the permeated side of membrane decreases as CH₄ concentration increases, thus the driving force of the oxygen permeation increases. Furthermore, the CH₄/O₂ ratio increases with increasing CH₄ concentration, which leads to the increase of the CO selectivity. But when the CH₄ concentration is higher than 45.5%, the permeated oxygen is not enough to completely consume the feed CH₄, which results in the decrease of the CH₄ conversion. Depending on above phenomena, the methane conversion mechanism in hollow-fiber membrane reactor packed with a Ni-based catalyst is possibly the combustion reform reaction (CRR) mechanism. If the oxidation reaction of methane in the membrane reactor obeys the direct partial oxidation (DPO) mechanism, the oxygen partial pressure near the membrane surface exposed to methane would decrease with increasing the methane flow rate, which led to the increase of the

Fig. 3 shows the temperature dependence of CH₄ conversion, CO selectivity and oxygen permeation flux. The CH₄ conversion and the oxygen permeation flux increase rapidly with the increase of temperature and the CO selectivity decreases slowly in contrast. The increase of the oxygen permeation flux is due to the increase of the oxygen diffusion and the surface exchange kinetics with increasing temperature, which is in complete accordance with the conclusions in our previous work [28]. As shown in Fig. 3, the CH₄ conversion is 49.2% at 775 °C; however, the CH₄ conversion increase to 96.2% at 875 °C, and the selectivity of CO maintains above 98% from 775 °C to 875 °C. Among the products, only small amount of CO₂ is observed and there is no C₂ products. For the excess feed of methane, the methane conversion is mainly controlled by the oxygen permeation flux, the increase of the oxygen permeation flux spontaneously lead to the increase of the methane conversion. When the amount of the available oxygen on the reaction side is more than the stoichiometric amount for POM, the CO selectivity decreases due to the deeper oxidation of CO to CO₂ with increasing temperature.

3. Results and discussion

Fig. 2 shows the SEM micrographs of the cross-section and the wall of the U-shaped BCFT hollow-fiber membrane after sintering at 1150 °C for 5 h. It can be seen that the U-shaped BCFT hollow-fiber membrane connects to each other firmly. Before the experiment, the N₂ permeation measurement at room temperature confirms that the U-shaped BCFT hollow-fiber membrane is gastight.

Fig. 4. The influence of methane concentration in the reaction side on the CH₄ conversion, CO selectivity and the oxygen permeation flux in POM. Conditions: T = 875 °C, F_air = 180 ml/min, F_in = 60 ml/min.

Fig. 5. Effect of the pure methane flow rate in the reaction side on the CH₄ conversion, CO selectivity and the oxygen permeation flux in POM. Conditions: T = 875 °C, F_air = 180 ml/min, C_in = 100%.

Fig. 6. Time dependence of POM performance in the U-shaped hollow-fiber membrane reactor. Conditions: T = 875 °C, F_air = 180 ml/min, F_in = 60 ml/min, C_in = 55.8%.
the oxygen permeation flux. So under direct partial oxidation mechanism, the oxygen permeation flux would continuous increase with increasing the methane concentration. However, this phenomenon does not occur in our experiment. Therefore, the methane conversion mechanism in the membrane reactor is possibly the CRR mechanism. Similar results were found by other researchers [21,23].

Fig. 5 presents the effect of the methane flow rate swept in the reaction side on the POM performance at 875°C. Air flow rate is kept at 180 ml/min and the methane is used in this experiment. From Fig. 5, we can see that the oxygen permeation is kept constant when the methane flow rate varies from 34 to 27.3 ml/min, but as the methane flow rate decreases to 24.6 ml/min, the oxygen permeation flux decreases with the decrease of the methane flow rate. These results are in accordance with that in Fig. 4, which verifies that the methane conversion mechanism in the membrane reactor is possibly the CRR mechanism. As shown in Fig. 5, the CH₄ conversion is higher than 90% when the methane flow rate is lower than 31 ml/min, and the CO selectivity is higher than 94%, which shows an excellent reaction performance of membrane reactor.

For practical application, the stability of the membrane reactor is an important issue. Fig. 6 shows the CH₄ conversion, the CO selectivity and the oxygen permeation flux as a function of time.

![Fig. 7. SEM micrographs of the BCFT hollow-fiber: (A) outer and (B) inner surfaces of the fresh hollow-fiber membrane; (C) outer and (D) inner surfaces of the spent hollow-fiber membrane after POM for 83 h.](image)

![Fig. 8. XRD patterns of the BCFT powder, fresh and spent hollow-fiber membrane after 83 h operation for POM.](image)

![Fig. 9. (a) Co 2p XPS spectra of the fresh hollow-fiber membrane and (b) Co 2p XPS spectra of the spent hollow-fiber membrane.](image)
During a period of 83 h, the CH₄ conversion is higher than 98% with the CO selectivity of 93% and the oxygen permeation flux of 19–20 ml/min cm² at 875 °C. However, the oxygen permeation flux through the membrane begin to decay and the membrane is broken after 83 h operation. The spent BCFT hollow-fiber membrane sample is characterized by XRD, SEM, XRS and EDS. Fig. 7 presents the SEM images of the fresh and spent BCFT hollow-fiber membranes. Fig. 7A and B show the outer and inner surfaces of the fresh hollow-fibers after sintering respectively. It can be observed that the grains with clear grain boundaries are obvious, and the BCFT particles connect to each other firmly. Fig. 7C and D show the outer and inner surfaces of the spent BCFT hollow-fiber after POM for 83 h. We can see that there are some carbonate producing on the outer surface, because of the membranes containing alkaline-earth elements such as Ba tends to react with acid gas CO₂ to form carbonates [30,31], which could be one of the reasons that the hollow fiber membrane is broken after 83 h for POM. Fig. 8 compares the X-ray diffraction (XRD) patterns of the original BCFT powder, the fresh membrane and the spent membrane. As shown in Fig. 8, no changes are observed in the crystalline structure of the BCFT material resulting from the sintering and sintering processes after the hollow-fiber membranes are prepared. However, after the 83 h POM reaction there are some carbonate phase observed. Fig. 9 shows Co 2p XPS spectra of the hollow-fiber membrane. As shown in Fig. 9a, the Co₂P½ and Co₂P⅓ peaks of the fresh hollow-fiber membrane are observed at binding energies of 779.3 eV and 794.6 eV, which are characteristic of a CoO₂ phase. However, after POM reaction, the Co₂P½ and Co₂P⅓ peaks are observed at binding energies of 780 eV and 795.3 eV, which are characteristic of a CoO phase. The result shows that complicated metal ion reduction takes place after POM reaction. Similar results were found by other researchers [32,33]. The Co reduction is possible another reason for the redistribution of the metal ions across the membranes. This provided the driving force for the redistribution of the metal ions across the membranes. This redistribution may have weakened the mechanical strength of the membrane tube, leading to the fracture of the membrane tube after the membrane ran for some hours.

### 4. Conclusions

The partial oxidation of methane (POM) to synthesis gas was performed in a BaCo₃FeO₆Ta₂O₃ membrane reactor in the presence of the Ni-based catalyst. At 875 °C, an oxygen permeation flux of 20 ml/min cm² with 96% methane conversion and 99% CO selectivity were obtained. However, the CH₄ conversion and the oxygen permeation flux began to decrease after 83 h operation. A metal ion reduction and element segregation of the surface elements and redistribution of the metal compositions across the membrane were found after continuous operation in the membrane reactor. These may have weakened the strength of the membrane and cause the fracture of the hollow-fiber membrane under the POM reaction conditions.

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