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Oxygen Selective Ceramic Hollow Fiber Membranes for Partial Oxidation of Methane

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A $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ) perovskite hollow fiber membrane was used to construct reactors for the partial oxidation of methane (POM) to syngas. The performance of the BCFZ fibers in the POM was studied (i) without any catalyst, (ii) with catalyst-coated fibers, and (iii) with catalyst packed around the fibers. In addition to the performance in the POM, the stability of the BCFZ hollow fiber membranes was investigated for the different catalyst arrangements. Best stability of the BCFZ hollow fiber membrane reactor in the POM could be obtained if the reforming catalyst is placed behind the oxygen permeation zone. It was found that a direct contact of the catalyst and the fiber must be avoided which could be achieved by coating the fiber with a gold film. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2657–2664, 2009
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Introduction

Large amounts of natural gas resources are still not utilized due to their remoteness and the small scale of the individual gas fields (so called stranded gas resources). According to estimates, these stranded gas resources account to roughly 60% of the available gas resources[1] and today these resources are usually flared or reinjected in associated oil fields to increase oil recovery. Gas-to-Liquids (GTL) technologies like Fischer-Tropsch-Synthesis (FT)[2] can convert such stranded gas reserves into easily transportable liquid fuels. FT consists of three stages, the synthesis-gas (a mixture of H_2 and CO) generation, the production of higher hydrocarbons and waxes in a Fischer-Tropsch-synthesis step, and the upgrading of the heavy products by catalytic hydro cracking. The synthesis-gas generation usually done by autothermal reforming or steam-reforming accounts to a significant part of the total investment and operational costs[3]

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so its optimization has a large impact on the applicability of the FT process. The partial oxidation of methane (POM) is a promising alternative for syngas generation because it is a mildly exothermic reaction and could produce syngas with the H_2/CO ratio of 2:1, which is a preferable feed stock for methanol synthesis or the Fischer-Tropsch reaction. However, due to commercial reasons, nitrogen in the syngas must be avoided, so applicability of POM depends on the availability of cheap oxygen. Recently developed ceramic membrane reactors can integrate oxygen separation and POM into a single step and therefore show a great potential for the cost reduction of syngas generation.[4]

For practical applications, a dense oxygen selective membrane has to show (1) stability for long-term operation at elevated temperatures (>800°C) under strongly reducing atmospheres such as the mixture of carbon monoxide and hydrogen, (2) considerable high oxygen permeability under operation conditions, and (3) the necessary strength to withstand the mechanical stress in the membrane reactor. Furthermore, the material and the membrane should be cheap enough for large-scale industrial applications. To fulfil these requirements, extensive R&D work has been performed since Teraoka et al. published their first article on the oxygen permeability through $La_{1-x}A_xCo_{1-y}Fe_yO_{3-\delta}$.[5] For example, Yang's group has developed a novel material named $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, which shows high oxygen permeability and good operational stability under POM reaction conditions.[6,7] To further improve the stability of the membrane materials, ions with constant valence (Zr^{4+}, Ga^{3+}, Al^{3+})[8–13] were used to partially substitute reducible B-site ions (Co^{3+}, Fe^{3+}). Recently, several cobalt-free perovskite materials were reported to meet the stability requirements under reducing environments. However, the improvement of stability seems to be at the cost of the oxygen permeability.[14–16] In addition to POM,[17–21] the perovskite membranes have been widely evaluated in the oxygen production,[22,23] the generation of oxygen enriched air,[24] the selective oxidation of hydrocarbons,[25–27] and for power plants with carbon sequestration.[28,29]

At the same time, different membrane geometries such as disks, tubes, monoliths, capillaries, and hollow fibers as full or graded materials have been developed. However, most of these geometries do not fulfill industrial requirements. For example, disk-shaped membranes that can be prepared quite easily by a pressing and sintering method show a low surface-to-volume ratio and significant problems associated with the high-temperature sealing.[14] As a result, tube membranes in the cm-scale were developed to reduce the engineering difficulties, especially the sealing problems. However, their small surface area to volume ratio makes them also unfavorable in practice. A very interesting concept to overcome these restrictions is the application of flat membranes stacked to larger units as proposed by Air Products and Chemicals.[30] Increasing activities can be observed in the preparation of oxygen ion conducting membranes in a hollow fiber geometry. Examples are the pioneering articles from the groups of Li and coworkers,[31–36] Liu et al.,[37–39] and Schiestel et al.,[40–42] as well as the articles by Trunec[43] and Luyten et al.[44] showing that thin-walled ceramic fibers can be prepared by wet-spinning. Such hollow fiber membranes possess several advantages: (1) a large membrane area per unit volume for oxygen permeation (about 2500 m^2 per m^3 permeator assuming a bunch of fibers of 0.75 mm diameter); (2) high oxygen permeation flux due to thin walls; and (3) easy assembly for large-scale module fabrications. These advantages recommend the hollow fiber as potential and promising configuration in future industrial applications.

In previous studies, we investigated the possible reaction pathway of the POM in a hollow fiber membrane reactor[45] and the effect of carbon deposit on the stability of fiber during the POM reaction.[46] In this article, the performance of the $BaCo_xFe_yZr_zO_{3-\delta}$ ($x + y + z = 1$, BCFZ) hollow fiber in the POM reaction with/without catalyst and coated/packed catalyst as well as the operation stability of the hollow fiber membrane reactor for different catalyst arrangements are investigated in detail. The aim of the present article is to optimize the operation conditions and the catalyst arrangements for the POM in the hollow fiber membrane reactor. The material BCFZ was chosen because it can be operated steadily for POM for more than 2200 h and was the best material reported in open literatures so far.[47]

Experimental

The dense $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ, $x + y + z = 1$) perovskite hollow fiber membrane was prepared by phase inversion spinning followed by sintering.[40–42] Two ends of the hollow fiber were coated by Au paste (C5754, Heraeus). After sintered at 950°C for 5 h, a dense Au film was obtained. Therefore, such Au-coated hollow fibers can be sealed outside the oven at room temperature and the uncoated part can be kept in the middle of the oven ensuring isothermal conditions for the oxygen transport. Air of 150 ml/min was fed to the core side and a mixture of CH_4 and He was fed to the shell side. Under these conditions, the fiber was subjected to synthesis gas production in different reactor configurations, as shown in Figure 1. In Configuration A, no catalyst was used. In Configuration B, a commercial Ni-based steam reforming (SR) catalyst (Süd-Chemie) was coated on the fiber by a dip-coating procedure. In Configuration C, 0.4 g Ni-based SR catalyst was packed around the active oxygen transporting part of the hollow fiber membrane. In Configuration D, 0.6 g Ni-based SR catalyst was packed around and behind the uncoated part of the hollow fiber membrane. In Configuration E, 0.4 g Ni-based SR catalyst was packed only behind the active zone of the hollow fiber membrane. The gas composition at the outlet of the shell side was determined by gas chromatography (Agilent 6890 with a Carboxen 1000 column supplied by Supelco). The H_2O amount was determined from the hydrogen atom balance. CH_4 conversion (X_{CH_4}) and product selectivities (S_i) were defined as follows:

$$X_{CH_4} = 100 - \frac{F^{out}_{CH_4}}{F^{in}_{CH_4}} \times 100\% \quad (1)$$

$$S_i = \frac{n_i F_i}{F^{in}_{CH_4} - F^{out}_{CH_4}} \times 100\% \quad (2)$$

where n_i is the number of carbon atoms in the carbon-containing product molecules i and F_i is the flow rate of species i in ml/min, respectively.

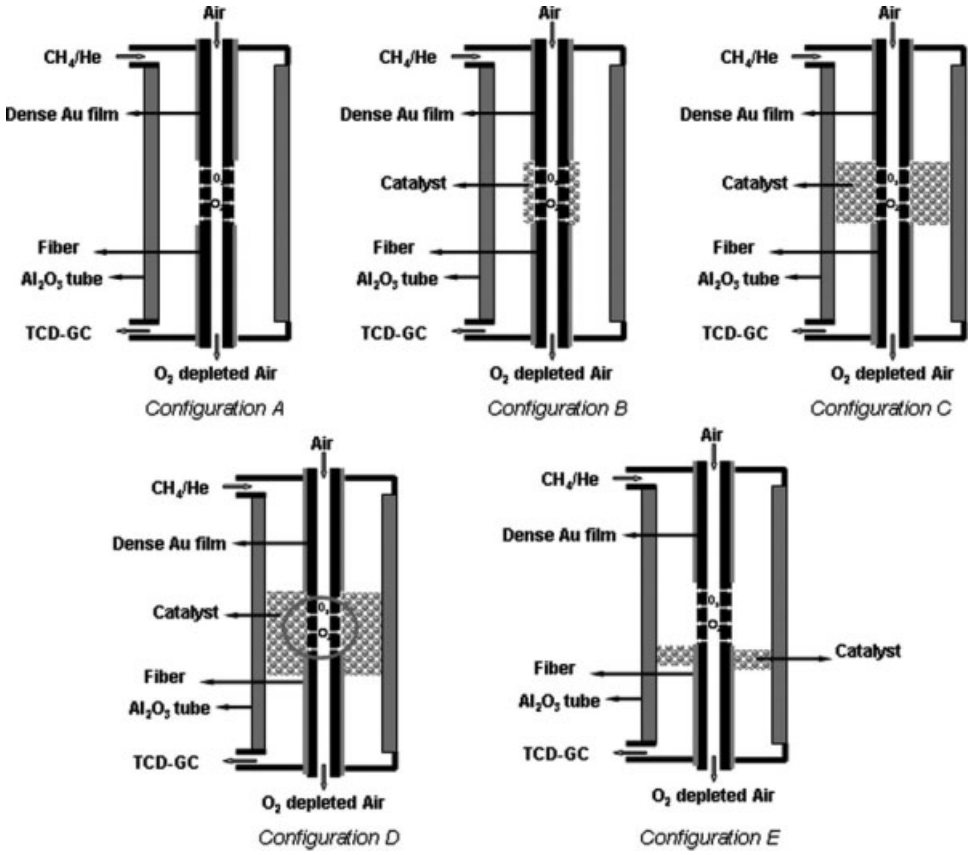

Figure 1. Schematic diagram of different operation modes of BCFZ hollow fiber membrane reactor for POM.

The circle indicates the broken position of the BCZ fiber during POM.

Results and Discussion

POM performance in the BCFZ hollow fiber membrane reactor without catalyst (Configuration A)

Perovskites show some catalytic activity and selectivity to light hydrocarbons, for example, for the POM, the oxidative coupling of methane and the oxidative dehydrogenation of ethane. Especially in the oxidative coupling of methane, perovskites show a rather high selectivity to C_2.[48–50] Therefore, it is informative to investigate the catalytic performance of the pure BCFZ hollow fiber itself without any additional catalyst.

Table 1 shows that under our reaction conditions only CO_2 rather than other carbon-containing products (CO and C_{2+} hydrocarbons) were observed in the outflow when the BCFZ perovskite hollow fiber membrane was used in the POM at 875°C without any catalyst. The methane conversion is lower than 3%. Some amount of unreacted oxygen was found at the outlet of the membrane reactor together with unconverted methane.

Similar results were reported by Balachandran et al. who found that the permeated oxygen reacted with methane yielding CO_2 and H_2O in a $SrFeCo_{0.5}O_x$ tubular membrane reactor in the absence of a reforming catalyst.[17] The presence of CO_2, H_2O, CH_4, and O_2 was also reported by Tsai et al. in the effluent gas of a $La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-\delta}$ disc-shaped membrane reactor without catalyst.[51] Therefore, it is reasonable to use a suitable catalyst, which will catalyze the POM.

POM performance in the BCFZ hollow fiber membrane reactor coated with Ni-based SR catalyst (Configuration B)

The surface of the hollow fiber was coated with the Ni-based SR-catalyst by dip-coating with a solution of the crashed catalyst. The modified hollow fiber membrane was characterized by field-emission scanning electron microscopy (Figure 2). From the cross-section it can be concluded that the catalyst layer is homogeneous and a few micrometer

Table 1. Catalytic Performance of the BCFZ Hollow Fiber Membrane Reactor Without Reforming Catalyst in the POM

Methane Concentration in the Feed (%)	CO Selectivity (%)	CO_2 Selectivity (%)	CH_4 Conversion (%)
10	0	100	1.5
20	0	100	2.6
50	1	99	2.4

Air flow rate on the shell side: 150 ml/min, total flow rate on the core side: 30 ml/min, CH_4 concentration: 10–50 vol %, membrane surface area: 3.3 cm^2, temperature: 875°C.

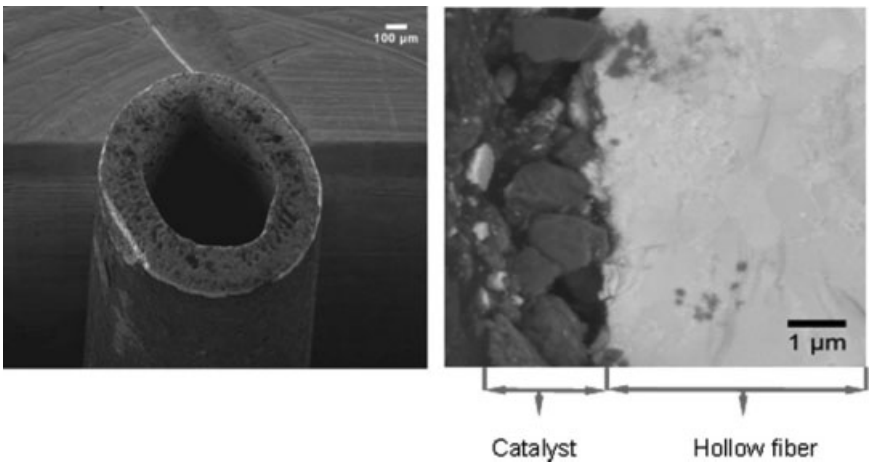

Figure 2. SEM images of the modified hollow fiber membrane with Ni-based catalyst layer.

thick. However, the catalyst layer shows some porosity, so oxygen permeation can occur.

Table 2 shows the CO and CO_2 selectivities as well as the methane conversion as a function of the methane flux on the shell side. Compared with Configuration A, almost no gaseous oxygen was found in the outflow of the reactor in Configuration B. The CH_4 conversion is much higher than that in the absence of the catalyst, which indicates that the permeated oxygen had reacted with methane thus decreasing the oxygen partial pressure and increasing the driving force for oxygen permeation. As a result, a higher oxygen flux through the hollow fiber membrane compared with the uncoated fiber is obtained. However, the CO selectivity is very low. This means that the deep oxidation of methane is the controlling reaction.

Dissanayake et al.[52] studied a Ni-based catalyst for the POM in the conventional packed bed reactor. They found that an effective catalyst bed consists of three different regions. In the first one at the reactor inlet, the catalyst is in contact with the CH_4/O_2/He feed mixture and the catalyst is present as $NiAl_2O_4$, which has only moderate activity for the complete oxidation of methane to CO_2 and H_2O. In the second region NiO/Al_2O_3 is present, where the complete oxidation of methane to CO_2 occurs, resulting in a strong temperature increase in this section of the bed. As a result of the complete consumption of O_2 in the second region, the catalyst in the third region consists of a reduced Ni/Al_2O_3 phase. Formation of CO and H_2, corresponding to the thermodynamic equilibrium at the catalyst bed temperature, occurs in this final region via reforming reactions of CH_4 with the CO_2 and H_2O produced during the complete oxidation on the NiO/Al_2O_3 phase.

In our experiment, a thin layer of Ni-based SR catalyst was coated on the surface of the hollow fiber membrane (see Figure 2). Because of the continuous oxygen permeation through the membrane, Ni can easily be oxidized to NiO. Therefore, the Ni species of the catalyst layer are presumably NiO or $NiAl_2O_4$, which are active for the total oxidation of methane to produce CO_2 and H_2O instead of the POM to synthesis gas. So it can be easily understood that a lot of CO_2 was observed in the coated hollow fiber membrane reactor. To increase the CO selectivity, more catalyst is needed for CH_4 reforming with CO_2 and H_2O and additional catalyst will be packed in the section behind the active part of the hollow fiber membrane.

It should be pointed out that in Configuration B the coated BCFZ hollow fiber membrane survived only 5 h when it was operated as a reactor for the POM reaction at 875°C. One possible reason for this behavior is the high CO_2-concentration near the membrane surface. Details of the effects of CO_2 on microstructure and oxygen permeation of a different perovskite are reported elsewhere.[53] The consideration of Ellingham diagrams allows estimating critical conditions for the operation of materials containing alkaline-earth cations.[15,54] For the conditions chosen in the experiments under discussion, it is reasonable to assume that the structure of the hollow fiber membrane was destroyed by $BaCO_3$ formation because of the high CO_2 partial pressure. An alternative explanation for the degradation of the fiber could be the local temperature increase near the membrane surface caused by the total oxidation of methane.

POM performance in the BCFZ hollow fiber membrane reactor packed with Ni-based catalyst (Configurations C and D)

The Ni-based SR catalyst was applied as a packed bed ($\sim$0.16 to 0.4 μm particle size) around the perovskite fiber

Table 2. Catalytic Performance of the POM in the Modified BCFZ Hollow Fiber Membrane Reactor Coated with Ni-Based Catalyst According to Configuration B

CH_4 Flow Rate (ml/min cm^2)	CO Selectivity (%)	CO_2 Selectivity (%)	CH_4 Conversion (%)
5	0.1	99.9	76.5
10	0.1	99.9	59.2
15	0.2	99.8	63.7
20	7.2	92.8	63.2
25	9.7	90.3	56.7

Air flow rate on the core side: 150 ml/min, total flow rate on the shell side: 10–50 ml/min, methane concentration: 50%, membrane surface area: 3.3 cm^2, catalyst amount: 0.4 g, temperature: 875°C.

Table 3. Catalytic Performance of the Membrane Reactor with a BCFZ Hollow Fiber with a Ni-Based SR Catalyst (Configurations C and D) in the POM Reaction

Catalyst Position	Temperature (°C)	CO Selectivity (%)	CO_2 Selectivity (%)	CH_4 Conversion (%)	H_2/CO Ratio
Around the fiber	825	81.6	18.4	38.7	1.86
	850	79.4	20.6	49	1.85
	875	74.6	25.4	60.9	1.85
	900	60.6	39.4	65.9	1.64
	925	49.1	50.9	71.4	1.4
Around and behind the fiber	825	98	2	43.9	2.33
	850	98.4	1.6	59.6	2.38
	875	97.8	2.2	85	2.48
	900	97.1	2.9	92.2	2.22
	925	96.6	3.4	95.8	2.08

Air flow rate on the shell side: 150 ml/min, total flow rate on the shell side: 20 ml/min, methane concentration 50 %, catalyst amount: 0.4 g (for cf. C) and 0.6 g (cf. D), membrane surface area: 0.56 cm^2.

(shell side, Configuration C). From Table 3 it can be seen that the CH_4 conversion is considerably higher than in the absence of catalyst (Table 1). This result suggests that the oxygen permeation flux in Configuration C is much higher than without Ni-catalyst. Furthermore, the CO selectivity is much higher than in Configuration B. However, the CO selectivity is lower than 82% and decreases with increasing temperature. A considerable amount of unreacted methane is also found. At 925°C, both CO_2 and CO selectivities reach 50% at only 70% CH_4 conversion. These experimental findings indicate that the methane reforming with the produced CO_2 and H_2O was not complete.

In the case of additional catalyst behind the active part of the membrane (Configuration D in Figure 1), a considerable improvement can be stated and CO and H_2 become the main reaction products (cf. Table 3). At 925°C, the CO selectivity is above 97% at roughly 96% CH_4 conversion and the H_2/CO ratio is around 2.08 as expected for POM. The temperature increase in the CH_4 conversion is ascribed to the temperature-accelerated oxygen permeation flux.

The changes in the catalytic performance of the membrane reactor in the presence of the Ni-based SR catalyst can be explained as follows: As the BCFZ membrane has very low intrinsic activity for methane oxidation (Table 1), methane conversion occurs nearly exclusively over the Ni-based SR catalyst. Previous research showed that synthesis gas formation from methane in a mixed conducting perovskite membrane reactor may be called an "oxidation-reforming process," that is, a total oxidation followed by steam and dry reforming steps. In the second step, the concentration of H_2O and CO_2 is reduced by further SR and dry reforming of unreacted CH_4 giving CO and H_2.[21] By applying more and more catalyst, the catalyst-based residence time is enlarged so this oxidation-reforming-process can be completed.

Operational stability and performance of the membrane reactor in the POM (Configurations D and E)

The stability of the hollow fiber membrane was studied for two Configurations (D and E in Figure 1). Figure 3 shows the stability measurements for the POM reaction in the hollow fiber membrane reactor at 875°C in the Configuration D. CO and H_2 are the main reaction products. CO selectivity of 97% with CH_4 conversion of 96% is obtained and the H_2/CO ratio is 2.0 as expected for the POM. However, the hollow fiber membrane was broken after 9 h time on stream. The defect occurred at a position in which the membrane was in contact with the Ni-based SR catalyst (as shown in Configuration D in Figure 1 with a circle).

The destroyed membrane was studied by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS). As can be seen from Figure 4, the fiber became amorphous and porous, especially on its outer parts in contact with the catalyst/methane side. From the initial wall thickness of 170 μm, only 40 μm remained as a dense perovskite phase showing some cracks. About 110 μm of the fiber in contact with the catalyst and about 20 μm on the air side became porous. Different positions of the spent hollow fiber membrane were examined by EDXS. Surprisingly, in the outer and to some extent in the middle parts of the cross section of the porous fiber, Al from the SR catalyst was found. The Al diffusion into the perovskite fiber may be a possible reason for its failure. No Al was observed in the spectrum of the inner intact part (40 μm) of the hollow fiber membrane.

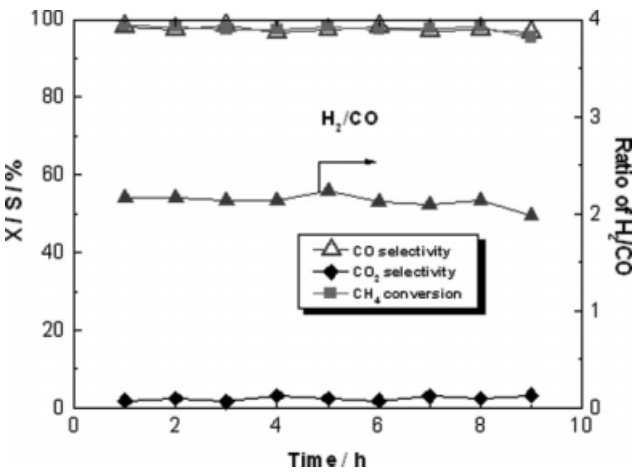

Figure 3. Performance and stability of the fiber during POM reaction in the Configuration D.

Air flow rate on the core side: 150 ml/min, total flow rate on the shell side: 20 ml/min, methane concentration: 50%, catalyst amount: 0.6 g, membrane surface area: 0.56 cm^2, temperature: 875°C.

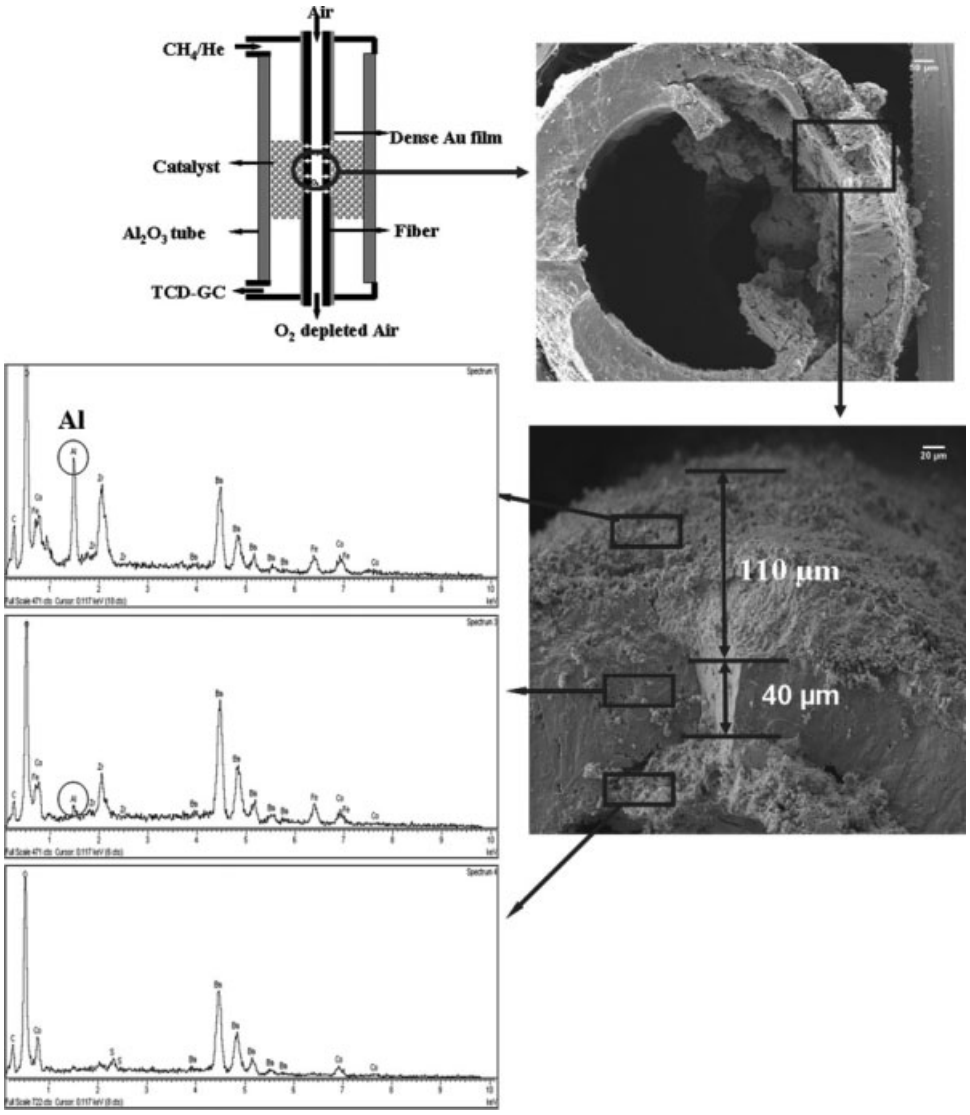

Figure 4. SEM and EDXS of spent fiber after 9 h operation in the POM in Configuration D (cf. Figure 3).

By avoiding physical contact between fiber and catalyst, the stability of the membrane in the POM reaction should be improved. In Configuration E, the catalyst was positioned only behind the oxygen permeation zone where the fiber was coated with Au. Figure 5 shows the stability measurements for the POM reaction in the hollow fiber membrane reactor at 875°C. A CO selectivity of above 90% with a methane conversion of 93% and a H_2/CO ratio around 2 are obtained. It is obvious that the fiber in this case survives longer than in Configuration D because the Au film avoids the contact of catalyst and fiber. Compared with the other configurations, the stability of the fiber in Configuration E is significantly improved. By separating catalyst and fiber, the hollow fiber membrane reactor could be steadily operated more than 300 h in the POM.[55]

It follows from literature analysis that in most of the POM studies the catalyst was in direct contact with the membrane and usually problems such as the impact of reducing atmospheres and solid-state reactions between catalyst and membrane were not mentioned. In this study, we found as the best choice to pack the catalyst behind the membrane. At first sight, a coupling of the three steps (i) oxygen permeation, (ii) membrane total oxidation, and (iii) carbon dioxide/SR with methane look promising for several reasons. The continuous consumption of the permeated oxygen will establish a constant high driving force for the oxygen flux and the combination of the exothermal combustion with the endothermal reforming could guarantee optimal heat management in Configurations C and D. However, there are also reasons speaking against these concepts, as high concentrations of reducing gases produced by the reforming step (CO, H_2) could reduce the BCFZ fiber and the direct contact between catalyst and fiber can initiate an exchange of mobile species between BCFZ and catalyst by solid-state ion diffusion (Fe, Co).

Obviously, in our best Configuration E, the oxygen permeation zone of the BCFZ hollow fiber is in contact with methane and one could assume a reduction of the perovskite by methane. However, this reduction does not take place, most probably due to a continuous flow of oxygen released from

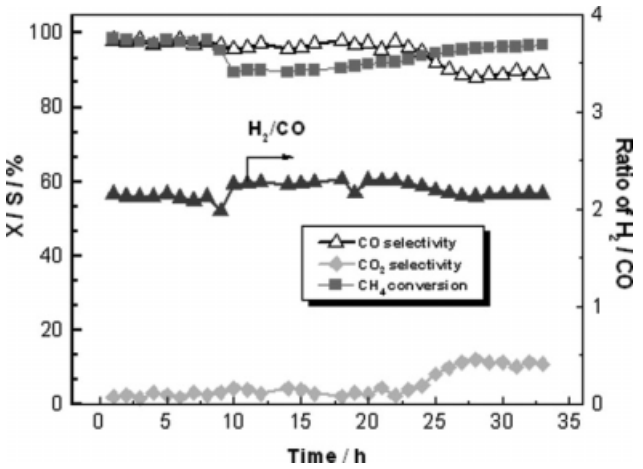

Figure 5. Stability of the fiber during POM reaction in the Configuration E.

Air flow rate on the core side: 150 ml/min, total flow rate on the shell side: 20 ml/min, methane concentration: 50%, catalyst amount: 0.4 g, membrane surface area: 0.56 cm^2, temperature: 875°C.

the perovskite. With other words, there is always a nonzero oxygen partial pressure at the perovskite surface which means that no pure methane as reducing agent is in contact with the perovskite. Furthermore, the benefit of Configuration E is that no major CO_2, CO, or H_2 concentrations are in contact with the unprotected perovskite fiber because the formation of these products is kinetically suppressed in the homogeneous gas phase reaction without catalyst. And even if these products are formed, the oxygen flow from the perovskite surface would reduce their impact.

In the conventional technology, pure oxygen is needed for the POM. This oxygen is conventionally produced by cryogenic fractionation technology, which requires a large-scale plant and high-operation costs. In the membrane reactor technology, the membrane can be used to in-situ produce pure oxygen from air which is competitive to the conventional technology.

Conclusion

The POM to syngas was investigated at 825–925°C using a membrane reactor based on BCFZ hollow fibers with and without SR catalyst in different catalyst arrangements. It was found that to get a high CO selectivity, an additional amount of catalyst was needed behind the active membrane area to ensure that the reforming reactions can take place completely. Stability studies of the hollow fiber membrane in the POM reaction showed that the stability of the fiber can be significantly improved if the contact between fiber and catalyst is avoided. A stable reactor concept is proposed with an arrangement of the reforming catalyst behind the oxygen permeation zone. In this case, the BCFZ perovskite is not attacked by strongly reducing components like CO and H_2 or by carbonate formation with CO_2 because the formation of these components at the perovskite site is kinetically suppressed without catalyst. Furthermore, the continuous release of oxygen from the perovskite surface results in a nonzero oxygen partial pressure at the surface and prevents a reduction of the perovskite by, for example, methane.

Acknowledgments

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