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Partial oxidation of methane in $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor

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ABSTRACT

A new perovskite material, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ used as dense oxygen permeable membrane for partial oxidation of methane (POM) reaction was investigated. In order to improve the synergetic effects between membrane and catalyst, LiLaNiO/γ-Al_2O_3 catalyst was directly packed onto the surface of the membrane to carry out POM. In $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor, high oxygen permeation flux, high CH_4 conversion and CO selectivity were obtained. At 950 °C, oxygen flux of 9.5 ml cm^{-2} min^{-1}, CH_4 conversion of 99% and CO selectivity of 93% were achieved with a membrane thickness of 1.0 mm. There was an induction process at the initial stage of POM, which was related to the reduction of NiO to Ni^0 in LiLaNiO/γ-Al_2O_3 catalyst. Experiments illustrated that higher reaction temperature would shorten the induction time. During continuously operating for 1000 h at 875 °C, no degradation of performance of the membrane reaction was observed. SEM characterization also demonstrated that the membrane disc maintained an integral structure without any cracks after long-term operation.

1. Introduction

Catalytic conversion of methane is an important process for high-efficiency utilization of natural gas which is mainly composed of methane. Amongst the proposed catalytic conversion routes, only steam reforming of methane (SRM) to produce synthesis gas (syngas, $H_2 + CO$) is commercialized in large-scale application. However, SRM is a capital and energy-extensive process due to highly endothermic nature of the reaction. Moreover, the ratio of H_2/CO is always higher than the optimum required for further syngas conversion to produce hydrocarbons and methanol, etc. [1]. Partial oxidation of methane (POM) to syngas can make up the drawback of SRM because POM is a mildly exothermic reaction which can save much energy, and provide a suitable H_2/CO ratio [2]. However, POM process should consume a great deal of pure oxygen, and the cost of oxygen production is 40–50% of the investment of the whole POM process. In addition, a risk of explosion exists in POM due to direct contact of methane and pure oxygen at elevated temperature [3]. Fortunately, oxygen permeable membrane reactors hold a promise of being energy efficient and operation safe in comparison with conventional POM process [4,5]. In such membrane reactor, the oxygen permeable membrane can directly yield pure oxygen from air and simultaneously avoid the contact of oxygen and methane. Therefore, to develop oxygen permeable membrane reactor used in POM is very desirable in commercial production.

At present, the extensive investigated membrane materials are perovskite and perovskite-related oxides, because they usually possess higher oxygen permeability compared with other structural materials [6,7]. In the past decades, many perovskite-type membrane reactors have been employed in POM [8,9]. Ysai et al. [10] studied the direct conversion of methane to syngas in $La_{0.2}Ba_{0.8}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane reactor. They revealed that the direct packing of catalysts on membrane disks can lead to a fivefold increase in oxygen flux and a fourfold increase in methane conversion. In our group, we reported the utilization of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ in POM reaction which had high oxygen permeation flux of above 10 ml cm^{-2} min^{-1}[11]. Despite excellent oxygen permeability of some materials, their poor stability limits their industrial application. Especially at reducing atmospheres, membrane materials are easily reduced and decomposed so that membrane reactors would break into several pieces in operation. For example, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membrane reactor would rupture shortly after the methane was introduced in the reactor [12]. And although the stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has been much improved, it cannot work stably for more than 500 h under syngas conditions. Researchers attributed their poor stability to decomposition of membrane surface [13]. With operational time increasing, the decomposition depth of membrane surface gradually increased and finally resulted in the destruction of the whole membrane reactor. In order to enhance the stability of oxygen permeable membranes,

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some stable metal ions (Al^{3+}, Ga^{3+}, Zr^{3+}) were introduced into B-site of perovskite lattices. However, the enhancement of the stability was usually at the cost of oxygen permeability. Kharton et al. [14] developed $SrAl_xFe_{1-x}O_{3-\delta}$ membrane material which had higher stability, but oxygen flux generally was low. Tong et al. [15] reported that $BaZr_{0.2}Co_{0.4}Fe_{0.4}O_{3-\delta}$ membrane reactor work stably for more than 2200 h at 850 °C and its oxygen permeation flux reached at 5.6 ml cm^{-2} min^{-1}. Ga-containing perovskite oxides, $La_xSr_{1-x}Ga_yFe_{1-y}O_{3-\delta}$, were reported as a kind of high stable membrane materials, but the high cost and poor permeability of this material restrict its application [16]. Therefore, to develop a novel membrane material with high stability and high permeability is much desirable for POM industrial application.

Based on our previous work [17,18], a new perovskite material, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$, was synthesized and employed in POM. Ba–Ce–O-based perovskite oxides were usually utilized in hydrogen permeable membranes which possessed strong resistance to reducing atmospheres [19,20]. Simultaneously, the doping of cerium ions with large radius and changeable valence (Ce^{4+}/Ce^{3+}) can improve oxygen permeability markedly. Hence, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ oxygen permeable membrane could possess both high structural stability and high oxygen permeability. The POM performance of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor was investigated detailedly in this paper.

2. Experimental

The precursor powder of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ oxide was synthesized by the wet chemical method (EDTA–citrate acid combined complexing method) [21]. The obtained oxide powders were pressed into disks by using a stainless mold with a diameter of 18 mm. The green disks were sintered in a muffle oven at 1160 °C in stagnant air for 5 h with a heating/cooling rate of 2 °C min^{-1}. Finally, the dense disks could be obtained with a diameter of 16 mm. The catalyst, LiLaNiO/γ-Al_2O_3, was prepared via the impregnation method. The γ-Al_2O_3 was fully impregnated into the nitrate solution containing different metal ions with calculated concentration for 24 h. Then the sample was dried at 80 °C and subsequently was calcined at 550 °C for 1 h, and finally LiLaNiO/γ-Al_2O_3 catalyst could be obtained [22].

The fresh disk used for POM membrane reactor was polished to 1.0 mm with 1000 mesh sand papers. The assembly sketch of apparatus and the membrane configuration was presented in Fig. 1. The disk was sealed on the top of quartz tube with a gold ring, and another quartz tube was used to press the membrane disk from the below with two springs. During the sealing process, the membrane reactor was heated to 1140 °C, and then kept at this temperature for 10 min for the softening of the gold ring. Subsequently, the temperature was dropped to 950 °C. First, the blank membrane experiment without any catalyst was performed. After the blank experiment, the as-prepared LiLaNiO/γ-Al_2O_3 catalyst was directly packed onto the top of membrane disc. The effective area of the disc was controlled around 0.9–1.0 cm^2. Dried synthesized air (O_2, 21%) was fed to the membrane (air side). Highly pure methane without any dilution flowed onto the top of the membrane (reaction side), where there existed LiLaNiO/γ-Al_2O_3 catalyst on the membrane. Flow rate of all gases was controlled with mass flow controllers (Models MT50-4J, Beijing Huibolong Co., Ltd). The effluents were analyzed with a gas chromatograph (GC, Agilent 6890) equipped with 3 m 13× zeolite and Porapar Q columns. In the experiment, H_2, O_2, N_2 and CO were identified with 13× zeolite columns, and CH_4, CO_2, C_2H_4 and C_2H_6 were measured through Porapar Q columns. The switching of two columns was controlled by two automatic switching valves and one damping valve so that all the product components of POM could be analyzed with one chromatograph. CH_4 conversion (C_{CH_4}) and product selectivity (S_i) were defined as follows:

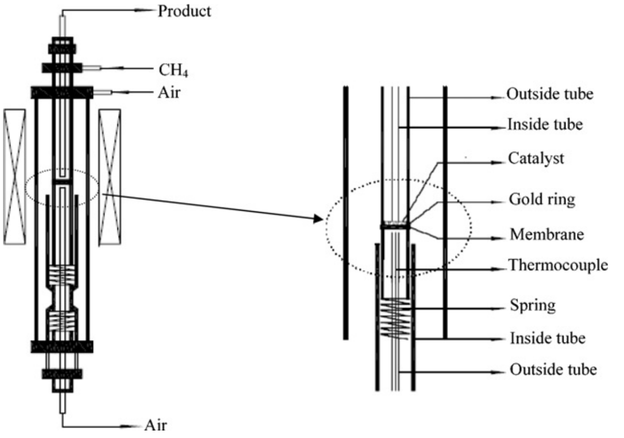

Fig. 1. The configuration of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor for POM.

$$C_{CH_4} = 1 - \frac{n_{CH_4} Y_{CH_4}}{\sum n_i Y_i}, \qquad S_i = \frac{n_i Y_i}{\sum n_i Y_i - n_{CH_4} Y_{CH_4}}$$

where C_{CH_4} is the conversion of methane, S_i is the selectivity to products, n_i is the carbon atom number of product i and Y_i is the volume concentration of product i in effluents.

The phase structure of perovskite oxide was determined by X-ray diffraction (XRD) using a Rigaku D/Max-2500 diffractometer (Cu Kα radiation, operating at 40 kV and 200 mA) in the 2θ range of 20–80° with a scanning rate of 5° min^{-1}. The surface microstructure of fresh and used membrane disc was studied with a scanning electron microscopy (SEM, Quanta 200 FEG, FEI Company, operating at 20 kV). The element analysis of the membrane disc surface and cross-section was evaluated by SEM-EDX.

3. Results and discussion

3.1. POM reaction performance of bare membrane

It is well known that perovskite oxides themselves were catalytic materials which could be used in many catalytic reactions. Hence, it was indispensable to measure the intrinsic catalytic activity of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ in order to distinguish the different functions of the membrane reactor and the catalyst in POM. Therefore, a blank POM experiment of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor was performed without any catalyst. In blank experiment, methane flow rate was 15 ml min^{-1} and air flow rate was 250 ml min^{-1}. As shown in Fig. 2, CH_4 conversion and oxygen flux as well as the selectivity to CO and CO_2 increased with the increasing temperature, and the selectivity to C2 components gradually decreased. When there was no catalyst packed on the membrane, CH_4 conversion was lower than 8%. And oxygen flux was only 1.26 ml cm^{-2} min^{-1} at 950 °C. Moreover, among all the products, the selectivity to CO_2 was highest (above 70%) which was much higher than CO selectivity. Therefore, the blank experimental results demonstrated that $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane had poor catalytic activity to POM reaction and a suitable catalyst was necessary for $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor for POM reaction.

In the past decades, two types of catalysts have been used for POM, i.e., noble metal-based catalyst and Ni-based catalyst. Noble metal-based catalyst, Rh and Ru, had higher activity and stability than Ni-based catalyst, but with high-cost [23–25]. Due to appreciable catalytic activity and low cost, Ni-based catalyst was generally investigated in POM [26]. Here LiLaNiO/γ-Al_2O_3

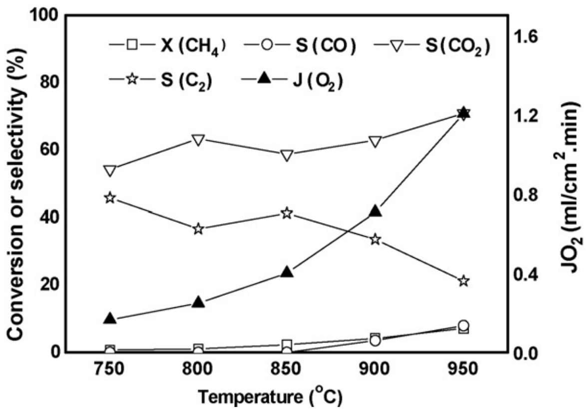

Fig. 2. Temperature dependence of blank experiment for $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane air flow rate: 250 ml min^{-1}; CH_4 flow rate: 15 ml min^{-1}; thickness of the membrane: 1.0 mm; $X(CH_4)$ denotes the conversions of CH_4; S(CO or CO_2) denotes selectivity to CO or CO_2; $J(O_2)$ denotes oxygen flux.

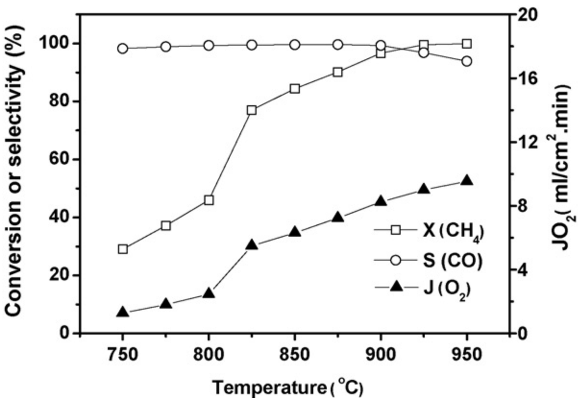

Fig. 4. Effects of temperature on the catalytic reaction in the membrane reactor. Air flow rate: 250 ml min^{-1}; CH_4 flow rate: 15 ml min^{-1}; thickness of the membrane: 1.0 mm.

catalyst was used in $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor, which exhibited high activity and stability [27–29].

3.2. POM performance of the membrane reactor with LiLaNiO/γ-Al_2O_3 catalyst

The blank experiment demonstrated that the addition of the catalyst was necessary for POM membrane reactor. Thus, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor with LiLaNiO/γ-Al_2O_3 catalyst was further investigated. In the experiment, the unreduced LiLaNiO/γ-Al_2O_3 catalyst was directly packed onto the membrane disc. There need a reduction process to activate LiLaNiO/γ-Al_2O_3 catalyst. Metallic Ni^0 reduced from LiLaNiO/γ-Al_2O_3 functioned as the active component for POM reaction. Therefore, the reaction performance of membrane reactor exhibited a gradual increasing at the initial stage which was related to the gradual reduction of LiLaNiO/γ-Al_2O_3. Fig. 3 illustrated the comparison of the activation process of LiLaNiO/γ-Al_2O_3 catalyst at 875 °C and 950 °C. As shown in Fig. 3, the activation time of the catalyst at 875 °C was longer than that at 950 °C. It took about 280 min to finish the activation process at 875 °C, but it took 35 min to reach steady state at 950 °C. The results indicated that higher temperature could accelerate the reduction rate of LiLaNiO/γ-Al_2O_3 catalyst and shorten the activation time of the catalyst. After reaching steady state, the effects of operation temperature, flow rate of methane and air on POM reaction were investigated to understand the catalytic performance of the perovskite membrane reactor.

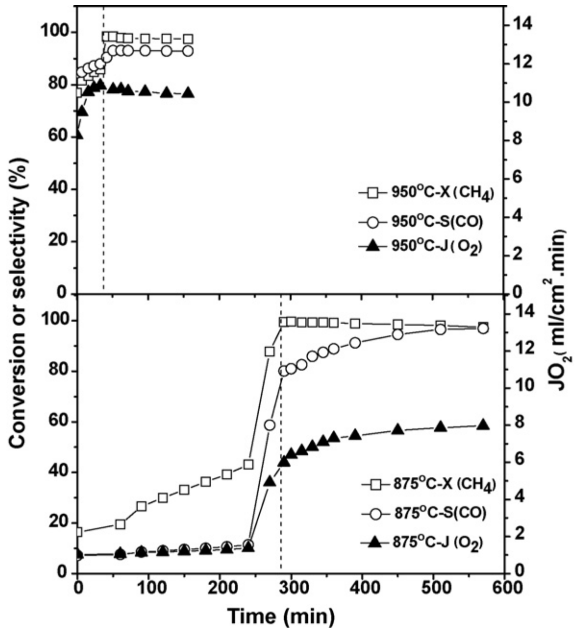

Fig. 3. Influence of temperature on initial processes of the catalytic membrane reactor. Air flow rate: 250 ml min^{-1}; CH_4 flow rate: 20 ml min^{-1}; thickness of the membrane: 1.0 mm.

Fig. 4 presented the temperature dependence of the performance in $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor. Oxygen permeation flux increased with the increasing of the temperature and the highest oxygen flux reached about 9.5 ml cm^{-2} min^{-1} at 950 °C. The oxygen flux increased eightfold in the presence of catalyst. This was because permeated oxygen would quickly react with methane in reaction side, and oxygen partial pressure gradient in POM membrane reactor was much larger than that at conventional permeation condition without catalytic reaction. As shown in Fig. 4, due to participation of LiLaNiO/γ-Al_2O_3 catalyst, the conversion of CH_4 and selectivity to CO was very high within the studied temperature range, for instance, the conversion of CH_4 reached 90% above 875 °C, and the selectivity to CO maintained above 93% from 750 °C to 950 °C. Among the products, only a little CO_2 was observed and there was nearly no C2 products. Simultaneously it was found from Fig. 4 that the selectivity to CO slightly decreased with the increase of temperature because of excessive oxidation of CO at higher temperature.

In general experiments of membrane reactor, the methane usually diluted with helium was fed into POM membrane reactor to avoid the deactivation of catalyst during long-term operation. However, diluted methane could not be used as feed gas in practical application because it would increase the cost of product separation. Thus, highly pure methane without any dilution was used as feed gas in all our experiments. As shown in Fig. 5, variations in methane flow rate caused fluctuations on CH_4 conversion and selectivity to products. The CH_4 conversion decreased with the increase of flow rate of methane; however, oxygen flux and selectivity to CO increased with the increase of flow rate of methane. The conversion of CH_4 dropped to about 80% when the flow rate of methane increased to 28 ml cm^{-2} min^{-1}. In the experiment, when methane flow rate did not exceed 25 ml cm^{-2} min^{-1}, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor could maintain CH_4 conversion of >90%. Fig. 5 also shows the effects of methane flow rate on the selectivity to CO, which was higher than 90% only if methane flow rate was higher than 16 ml cm^{-2} min^{-1}. Oxygen permeation flux was also greatly influenced by methane

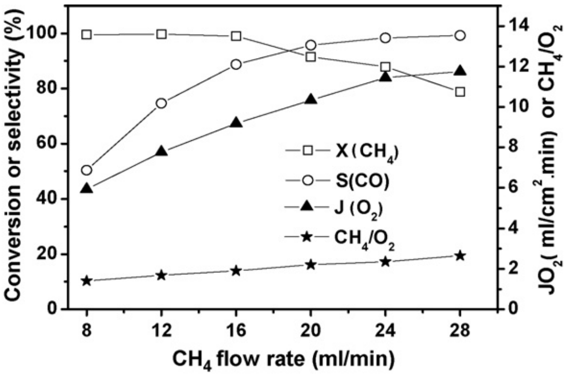

Fig. 5. Effects of methane flow rate on catalytic performance in the membrane reactor. Air flow rate: 250 ml min^{-1}; thickness of the membrane: 1.0 mm; temperature: 875 °C.

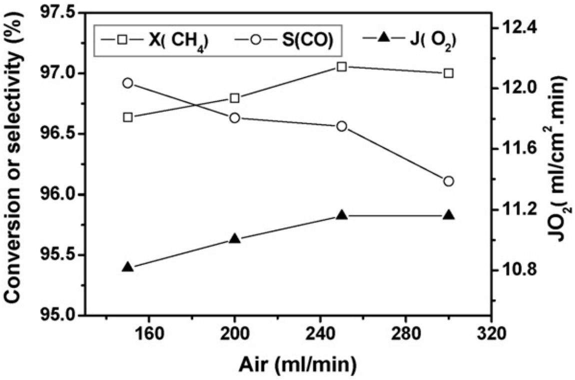

Fig. 6. Effects of air flow rate on catalytic performance in the membrane reactor. Air flow rate: 250 ml min^{-1}; CH_4 flow rate: 20 ml min^{-1}; thickness of the membrane: 1.0 mm; temperature: 875 °C.

flow rate and it increased from 5.9 ml cm^{-2} min^{-1} to 11.7 ml cm^{-2} min^{-1} when methane flow rate increased from 8 ml cm^{-2} min^{-1} to 28 ml cm^{-2} min^{-1}.

The effects of air flow rate on the performance of membrane reactor were plotted in Fig. 6. As shown in Fig. 6, with the increase of air flow rate both conversion of CH_4 and oxygen flux increase, but the increasing trend was very slight although air flow rate increased twofold from 150 ml cm^{-2} min^{-1} to 300 ml cm^{-2} min^{-1}. The result demonstrated that the effect of air flow rate on $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor was less remarkable than that of CH_4.

3.3. Stability of the membrane reactor

Oxygen permeation flux and structural stability were two key parameters for POM membrane reactor. Especially for practical application of POM membrane reactor, the membrane reactor should operate continuously for more than one year or more and should survive rigorous reaction conditions. As most perovskite-related oxygen permeable membrane reactors were concerned, the problem in the stability was always more serious than that in oxygen permeability. Hence, it was necessary to investigate the stability of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor under POM reaction condition.

A 1000-h continuous operation of POM was performed at 875 °C. In long-term operation, optimal conditions were selected according to the above experiments: flow rate of CH_4: 17.90 ml cm^{-2} min^{-1}, flow rate of synthesized air: 250 ml cm^{-2} min^{-1}. As shown in Fig. 7, oxygen flux reached approximately 8.9 ml cm^{-2} min^{-1}, and both conversion of CH_4 and selectivity to CO were higher than 97%. Over 1000-h operation, the performance of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor remained stable without any decrease of CH_4 conversion, CO selectivity and oxygen flux. Nevertheless, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane reactor packed with a Ni/γ-Al_2O_3 catalyst only operated for 7 h and fractures occurred [30]. Although $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was comparably stable, the fractures in membrane reactor took place after 500-h operation [31]. The comparison demonstrated that $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane material was the promising candidate for constructing POM reactor.

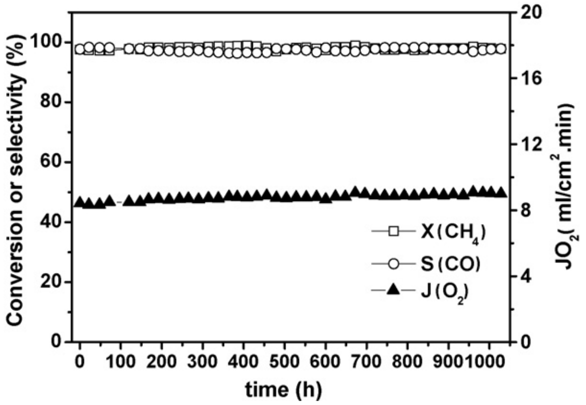

Fig. 7. Life test of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor for 1000 h. Air flow rate: 250 ml min^{-1}; CH_4 flow rate: 17.90 ml min^{-1}; thickness of the membrane: 1.0 mm; temperature: 875 °C.

In general, the reason of POM catalyst deactivation was that the coke accumulating on Ni^0 grain surface impeded the access of methane to catalyst. The activity of the catalyst would degrade gradually with coke accumulating. However, POM performance in $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor was maintained stably for 1000 h. CO selectivity and CH_4 conversion were hardly affected in long-term operation because high permeability of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane ensured the continuous supply of oxygen. And the activity of Ni-based catalyst could be recovered after the surface carbon filament was scavenged efficiently. The oxygen permeable membrane provided continuous oxygen supply to remove carbon deposition on the catalyst in time [32].

It was reported that the membrane always decomposed or cracked in long-term POM operation [33]. Researchers found that there were some remarkable changes in surface microstructure of used membranes compared with fresh membranes. Fig. 8 shows the SEM micrographs from a top view and cross-sectional view of the used membrane disc after 1000-h life experiment. Also Fig. 8B presented the cross-sectional image of fresh membrane disc which demonstrated that no open pores existed in the bulk of the membrane. As shown in Fig. 8C and D, although the surface microstructure of syngas side was different from that of air side, both of them were compact. Furthermore, it can be seen in Fig. 8C and D that the morphologies of the membrane surface exposed to syngas became more loose and porous than those of air side. The micrograph of cross-section near the reaction side shows that the thickness of the porous layers was very thin. Compared with the whole thickness of membrane disc, the porous layer could be neglected. The comparably high stability of $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane is related to low cobalt content and high stable Ba–Ce–O-based framework structure. Therefore, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor could work stably under POM reaction conditions.

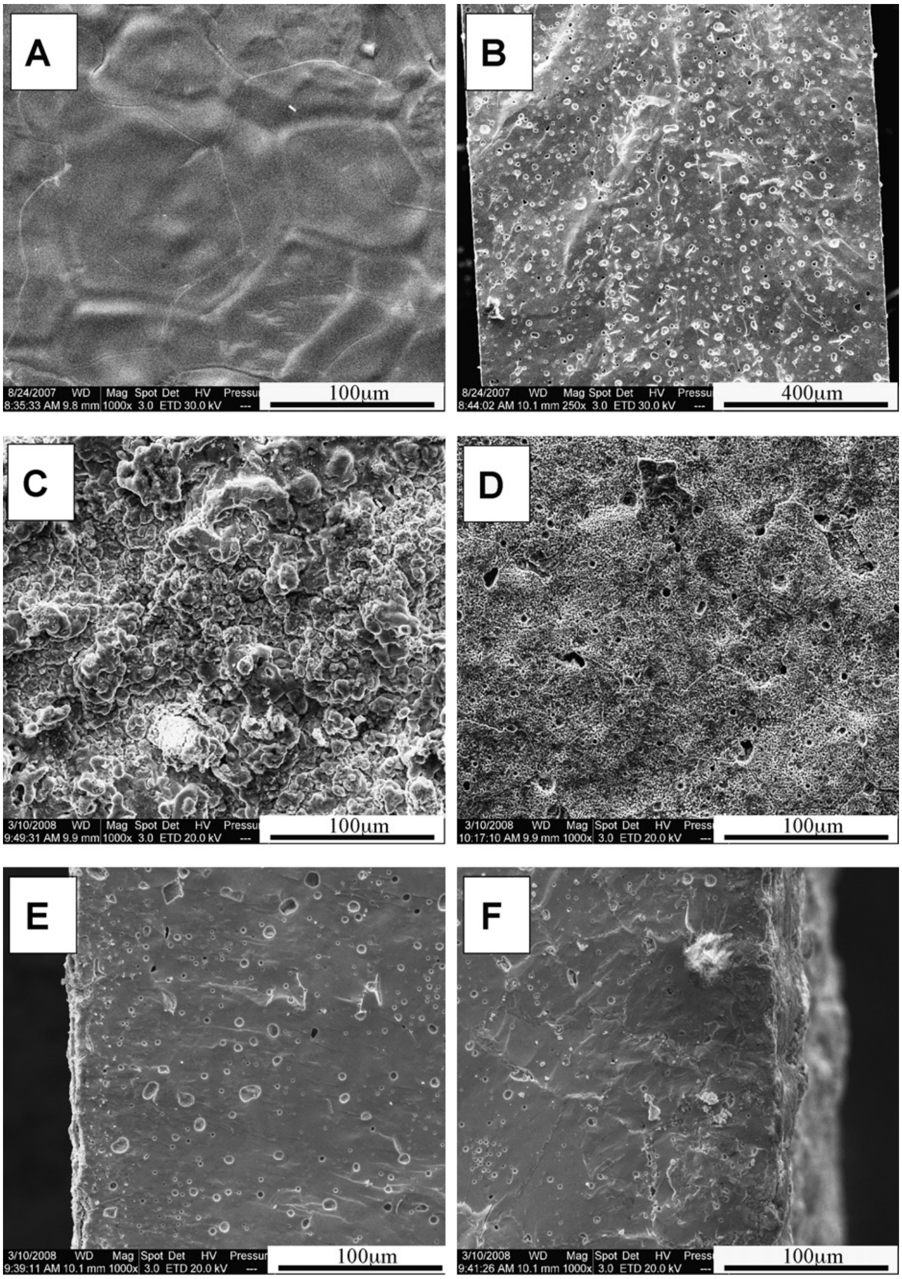

Fig. 8. SEM pictures of the fresh membrane and the used membrane (A) and (B) were the surface and cross-section of fresh membrane, respectively; (C) the surface of syngas side of the used membrane (the catalyst was removed ultrasonically); (D) the surface of air side of the used membrane and (E) and (F) were the cross-section of near the syngas side and near the air side, respectively.

4. Conclusions

$BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane materials were synthesized by an EDTA and citrate acid complexing method. POM in $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor was investigated in detail. In the POM reaction, $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor showed high oxygen permeation flux which was eight times than that of conventional permeation without reaction. At the same time, high conversion of CH_4 and selectivity to CO were obtained. $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor operated stably for more than 1000 h without any degradation of reaction performance. Although SEM characterization of used membrane shows a little change on the micrograph of two sides, the $BaCe_{0.1}Co_{0.4}Fe_{0.5}O_{3-\delta}$ membrane reactor still can survive the long-term operation.

Acknowledgements

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