



## Interface Reaction Between $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ Membrane and Ni-Based Catalyst†

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The interface reaction between  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (BCFNO) membrane and Ni-based catalyst materials were studied by analyzing the different catalyst materials, such as  $\text{Al}_2\text{O}_3$ , MgO, YSZ and  $\text{TiO}_2$ . XRD and SEM characterization of the BCFNO membrane show that the  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  easily react with BCFNO membrane and form a new phase. The MgO also reacts with BCFNO membrane in long time running, while the reaction is relatively small. However, the YSZ does not react with BCFNO. This provided a way to choose the suitable catalyst materials for membrane reactor during the long time running operation.

**Keywords:** BCFNO membrane, Catalyst, Interface reaction, Membrane reactor.

### INTRODUCTION

In recent years, mixed ionic and electronic conducting (MIEC) membrane have attracted much interest due to their application to separate pure oxygen from the air to produce syngas gas from the catalytic membrane reactor, such as partial oxidation of methane (POM)<sup>1-3</sup>. The coupling of the mixed ionic and electronic conducting membrane with partial oxidation of methane reaction could allow for the separation of oxygen and catalytic oxidation in one process, thereby eliminating a costly oxygen separation plant that is needed in the partial oxidation of methane units, resulting in significantly reduced cost. In addition, the heat produced by partial oxidation of methane could be used to sustain the temperature needed for oxygen permeation of membrane<sup>4,5</sup>.

The technical innovation in this research field was strongly dependent on the development of the mixed conductors, having the potential for high oxygen permeability and stability under reducing atmosphere. Among the MIEC membrane, perovskite type ceramic membrane are founded that have considerably the highest oxygen permeability due to their highest ionic and electronic conductivity. Such as  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (SCFO) was found to exhibit the largest oxygen permeation flux of about  $1 \times 10^6$  mol/s  $\text{cm}^2$  at 900 °C, while, it has very limited chemical and structural stability in a reductive condition<sup>6</sup>.

For building a membrane reactor, the oxygen permeation fluxes are not the only parameter, the membrane stability are

also very important, such as the chemical and thermal stability at high temperatures, to withstand the harsh operating conditions<sup>7-9</sup>. In recent years, a new age in ceramic membrane reactors has opened up and a group of new materials such as  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (BCFNO) membrane has been regarded as one of the most promising oxygen permeation membranes, which could achieve a very high oxygen permeation flux, around 20 mL/( $\text{cm}^2$  min) at 900 °C and a 300 h successful operation in the partial oxidation of methane reaction<sup>10,11</sup>.

However, the chemical stability remains unattractive for reaction between membrane and catalyst under methane reforming conditions. In the partial oxidation of methane process, the catalyst is coated directly onto the oxygen-permeable membrane. It is thus important that the catalyst employed for the reaction is chemically stable in contact with the membrane in order to prevent the formation of a new crystalline layer that may reduce the oxygen permeability. At the previous investigation of the Coke oven gas (COG) reforming, the author found that the Ni/ $\text{Al}_2\text{O}_3$  catalyst was reactive to  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$  (LSFGO),  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (BCFNO) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  membrane during the long time test. The results showed in Fig. 1. The product formed at the boundary as result of reaction between the catalyst and mixed conductor leads to block the oxygen permeation with mixed conductor from the membrane to the gas phase. The phenomenon may cause several serious problems for long life operation in the partial oxidation of methane process. In the

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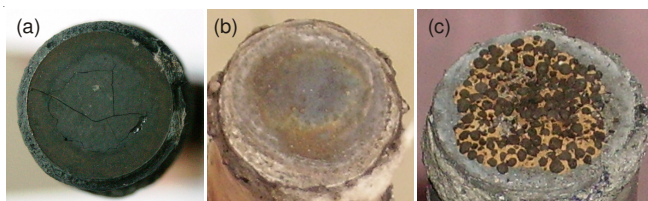


Fig. 1. Photos of membrane after long time running for partial oxidation of methane (a)  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.7}\text{Ga}_{0.3}\text{O}_{3-\delta}$  (b)  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (c)  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

present study, we selected  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (BCFNO) as a representative material to study the interface reaction of the catalyst and membrane after long time reaction in high temperature. The purpose of this paper is to understand the relationship between membrane and catalyst and provide a way for choose suitable catalyst material in oxygen permeation membrane reactor.

## EXPERIMENTAL

The  $\text{BaCO}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\gamma\text{-Al}_2\text{O}_3$ , YSZ, MgO and  $\text{TiO}_2$  were purchased from Sinopharm Chemical Reagent Co., Ltd. All those reagents are analytic grade. Powder samples of  $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$  (abbreviated BCFNO) were prepared by the conventional solid state reaction process. Detail information for the preparation of BCFNO oxide powder can be found in reference<sup>12</sup>. Briefly, stoichiometric amount of  $\text{BaCO}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were mixed and ground in an agate mortar. After milling, the suspension was separated from the milling balls and dried overnight in ambient air. The precursor powder was calcined at  $1100^\circ\text{C}$  in stagnant air for 20 h with heating and cooling rates of  $2^\circ\text{C}/\text{min}$ .

The powders were pressed under 48 Mpa to discoid membranes, which were sintered at temperatures  $1150^\circ\text{C}$  for 20 h with heating rates of  $1^\circ\text{C}/\text{min}$ . The final diameter of the membranes was 16 mm and the thickness of 1.0 mm. The densities of the sintered membranes were determined by Archimedes method using ethanol. Only those membranes which have relative densities higher than 92 % were used for permeation studies.

The changes of the morphology of the membranes were observed using a scanning electron microscope (SEM, JEOL JSM-6700F). Their compositions before and after the reaction were determined using an energy-dispersive X-ray spectroscopy (EDXS, OXFORD INCA). X-Ray diffraction (XRD, Rigaku D/Max-2550) was used to characterize the phase evolution of the membranes and catalysts.

## RESULTS AND DISCUSSION

In previous research<sup>13-15</sup>, we reported a new process for hydrogen production from Coke oven gas, in which one side of MIEC membrane exposed to Air and the other side to Coke oven gas. The disc-shape membrane reactor was constructed from BCFNO and partial oxidation of methane in Coke oven gas was carried out. In the BCFNO membrane reactor, the  $\text{CH}_4$  conversion of 95 % and an oxygen permeation flux as high as  $16.3 \text{ mL}/\text{min}^{-1} \text{ cm}^{-2}$  were achieved. The operating time as long as 100 h was obtained in the membrane reactor<sup>13</sup>. However, we found that there exist the reaction between the NiO/MgO solid solution catalyst and BCFNO membrane.

The author also found the CoO/MgO solid solution catalyst reacted with the BCFNO membrane besides the NiO/MgO solid solution catalyst (Fig. 2). In order to investigate the membrane surface reaction, the membrane after reforming was analyzed by the SEM and EDS, the result is shown in Fig. 3. An obvious small particles distribution on surface of BCFNO membrane were observed. Further more, EDS analysis revealed that the small particles were mainly CoO/MgO solid solution (Table-1). We also find the catalyst built by the  $\text{TiO}_2$  and hydrocalcite easily react with the BCFNO membrane material.

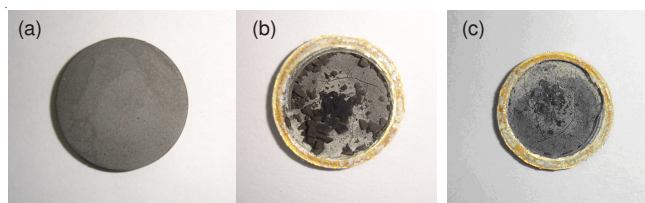


Fig. 2. Photos of the BCFNO membrane after 100 h reforming test (a) original membrane (b) after test (c) take away catalyst

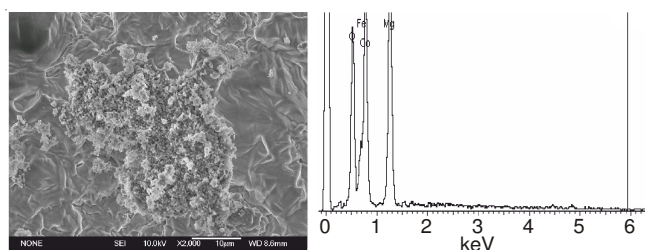


Fig. 3. SEM and EDS for the surface of reaction side in BCFNO membrane

TABLE-1  
STOICHIOMETRY OF METAL IONS ON THE  
REACTION SIDE OF BCFNO MEMBRANE

Element (At %)	Co	Fe	Mg	O
Surface of reaction side	28.68	1.76	35.7	33.82

These catalysts have been surveyed with respect to compatibility with the BCFNO membrane.  $\gamma\text{-Al}_2\text{O}_3$ , YSZ, MgO and  $\text{TiO}_2$  were examined as candidates for catalyst supports. The BCFNO membrane disc was placed in alumina crucible filled with  $\gamma\text{-Al}_2\text{O}_3$ , YSZ, MgO and  $\text{TiO}_2$  powder support, respectively. Then put them in baking oven of  $100^\circ\text{C}$  for 2 h, aiming to evaporate water. After evaporating, they were sintered in a SiC muffle oven under a temperature of  $900^\circ\text{C}$  for 50 h, with a heating rate of  $10^\circ\text{C}/\text{min}$ . After thermal treatment, the morphologies of BCFNO membrane surface were characterized by the SEM (Fig. 4).

Fig. 4 shows that the above catalyst support had a different reaction to BCFNO membrane. Fig. 4(a) shows many small particles appeared on the surface of membrane unlike the clean surface features suggesting that  $\gamma\text{-Al}_2\text{O}_3$  easily reacted to BCFNO membrane. The MgO can also react with BCFNO membrane but not serious. Fig. 4(b) showed that there are exist the many white regions on the surface of BCFNO membrane which were determined by EDS to be carbonate. Fig. 4(c) however shows a very clear path of eroded region and large amount of big bulges are observed at wall structure of BCFNO membrane being sintered by  $\text{TiO}_2$ . This is attributed to the

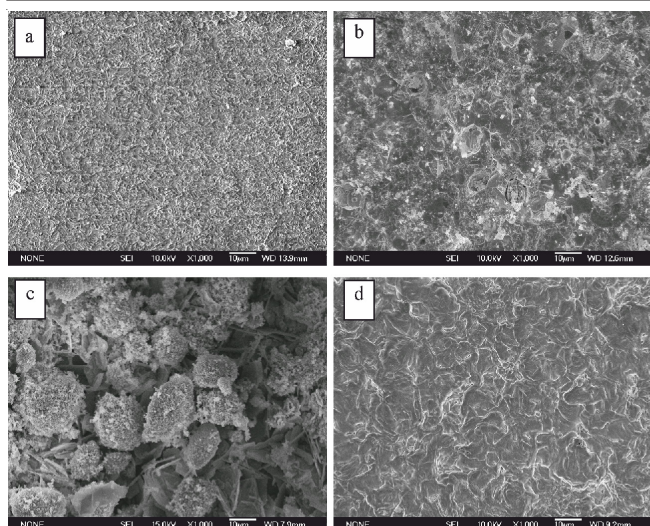


Fig. 4. SEM micrographs of the BCFNO after treating in different catalyst support (a)  $\gamma$ - $\text{Al}_2\text{O}_3$  (b) MgO (c)  $\text{TiO}_2$  (d) YSZ

extensive surface reaction which took place on the membrane as a result of  $\text{TiO}_2$ . However, the external surface of the BCFNO membrane in Fig. 4(d) shows that sintering in YSZ supports could still maintain the clear perovskite crystal morphology.

In order to further investigate the reaction between catalyst support and BCFNO membrane, the author continued to study the several common catalyst support mixing with BCFNO membrane powder and reaction for a long time in higher temperature. The experimental procedure is as follows: powders of the MgO,  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , YSZ catalyst supports and BCFNO were mixed in alumina crucible and sintered in air at  $1000^\circ\text{C}$  for 48 h.

Fig. 5(a) shows a  $\text{BaAl}_2\text{O}_4$  spinel structure was formed in the  $\text{Al}_2\text{O}_3$  by reaction with Ba, the  $\text{BaAl}_2\text{O}_4$  obtained by solid-phase reaction between  $\text{Al}_2\text{O}_3$  and Ba. However, from the XRD patterns of MgO and BCFNO after high temperature treatment (Fig. 5(b)), we can see the original BCFNO phase structure still exists, indicating that the BCFNO is not all reactive to MgO support. Through the concrete analysis, we found the BCFNO membrane material after the reaction contained MgO,  $\text{BaNbO}_3$  and  $\text{BaCoO}_{2.93}$ . In Fig. 5(C) patterns, detected a large number of  $\text{BaTiO}_3$  and  $\text{TiO}_2$  phases, the original BCFNO perovskite structure was completely destroyed, not detected the original perovskite phase. However, the YSZ were not reactive to BCFNO, In Fig. 5(d), the original BCFNO phase structure still exists, indicating that YSZ support almost no response to BCFNO membrane in high temperature treatment. These results correspond well with the SEM results, shown in Fig. 4 for these samples.

In summary, The  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and MgO were reactive to BCFNO, though the XRD changes for MgO was relatively small. The YSZ were not reactive to BCFNO. Therefore, YSZ is more suitable as a catalyst support.

## Conclusion

This paper presented the interface reaction between the Ni-based catalyst and BCFNO membrane, then analyzed the reaction between  $\text{Al}_2\text{O}_3$ , MgO,  $\text{TiO}_2$  and YSZ catalyst supports and BCFNO membrane characterized by SEM and XRD. All

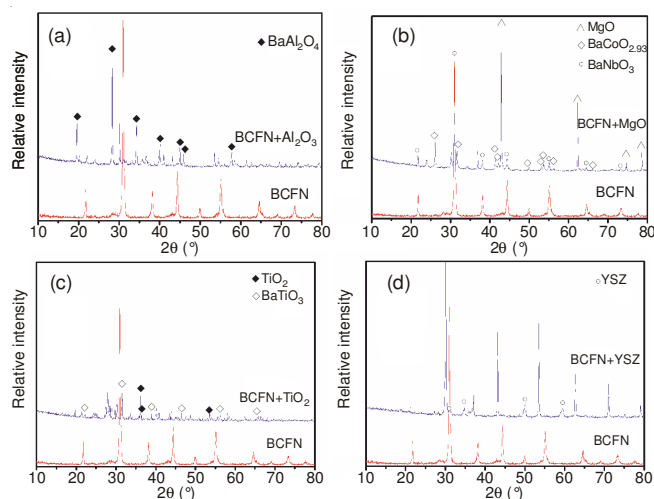


Fig. 5. XRD patterns of the BCFNO after treating in different catalyst support (a)  $\gamma$ - $\text{Al}_2\text{O}_3$  (b) MgO (c)  $\text{TiO}_2$  (d) YSZ support

these results showed that the  $\text{TiO}_2$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  were easily reactive to BCFNO membrane. The YSZ support was not reactive to BCFNO. Compared to the  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and MgO support, YSZ is more suitable as a catalyst support.

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