Performance Study of Heptane Reforming in the Dense Ceramic Membrane Reactors

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Heptane reforming was investigated in three dense ceramic membrane reactors, where the membranes were modified differently with reforming catalyst. Each reactor displayed distinctive catalytic behavior. The reactor with a bare membrane showed low catalytic activity and low oxygen permeation flux (J_{O2}), but gave stable performance. The left two membranes reactors modified with catalyst both displayed shift processes at the preliminary stage of membrane reaction, not only in J_{O2} but also in the selectivity of all products. Moreover, the membrane reactor with more catalyst gave higher performance in the case of J_{O2} and CO selectivity. The observed shift phenomena are due to the activation of catalyst on the membrane surface, and the different amounts of catalyst produce different impaction on the membrane reactions. On the basis of the results in three membrane reactors, a reaction pathway of hydrocarbon reforming in dense ceramic membrane reactor is proposed. Being some different from combustion and reforming mechanism (CRR), hydrocarbon reforming in dense ceramic membrane reactor has its own characteristics. © 2007 American Institute of Chemical Engineers *AIChE J,* 54: 242–248, 2008

Keywords: dense ceramic membrane, membrane reactor, hydrocarbon reforming, syngas, reaction pathway

Introduction

Dense ceramic membranes for oxygen permeation are fabricated from multicomponent metallic oxides and possess oxygen-ionic conductivity and electronic conductivity. At high temperature (>1023 K), the membrane carries oxygen ions from one side to the other via oxygen vacancies.[1,2] The greatly promising application of dense ceramic membranes is syngas (CO + H_2) production in the membrane reactors by reforming or partial oxidation of hydrocarbons.[3–13] This technology combined oxygen production from air with hydrocarbon reforming in a membrane reactor, which could potentially save the capital cost of syngas production by 30%.[7] Since syngas is a feedstock for a wide range of different chemical processes, dense ceramic membranes represent a technical platform that has numerous applications, such as gas-to-liquids, hydrogen, clean fuels and so on.[11] Great efforts have been made to develop this technology. Nowadays, Air products and its partners did well and began to fabricate commercial-scale wafers.[11]

Up to now, a large number of studies have focused on the performances of perovskite-type oxide as well as reforming or partial oxidation of hydrocarbons to syngas in the membrane reactors. In the most case, combustion and reforming mechanism (CRR) is considered as the reaction mechanism in the membrane reactor. Xiong and coworkers[14,15] reported disk-shaped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) membrane reactor with Ni-based reforming catalyst for the partial oxidation of methane (POM) and observed that, after the tests, the catalyst bed was composed of three different color layers, where different Ni-based species are detected. It was similar to what Lunsford and coworkers[16] observed in a fixed-bed

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reactor and thus CRR mechanism was proposed. Wang et al.[5,17] investigated BSCFO tubular membrane reactors and also observed different Ni-based species along the radial direction after tests. On the basis of the above observations and the influence of methane concentrations on POM, CRR mechanism was also suggested. Kharton et al.[8] investigated methane oxidation in $La_{0.3}Sr_{0.7}Co_{0.8}Ga_{0.2}O_{3-\delta}$ membrane reactor and proposed CRR mechanism. Although CRR mechanism was proposed in the most cases, these conclusions are just based on catalyst states after reactions and there were not any particular investigations on reaction pathway. Therefore, there is a need to investigate reforming reaction in detail in the membrane reactor to reveal the pathway of hydrocarbon reforming and confirm the reforming mechanism.

Generally, the reaction area in a membrane reactor can be divided into three parts, i.e. the membrane, the catalyst, and the interface between membrane and catalyst. If the reactions in each part are clear, it is likely to elucidate to the whole process of membrane reaction. Therefore, three dense ceramic membrane reactors modified differently by catalyst were designed and perovskite-type BSCFO membrane was selected, which demonstrated good performance in POM.[14,15]

Experimental

BSCFO membrane[14,15] and LiLaNiO/γ-Al_2O_3 catalyst[18–20] developed in our group were used for study. BSCFO oxide powder was synthesized as the method described in the literature[21] and reforming catalyst LiLaNiO/γ-Al_2O_3 with 10 wt % Ni was prepared by the usual impregnation method.[19] A disk-type ceramic membrane, two quartz tubes, and a gold ring assemble the membrane reactor, as shown in Figure 1. Gold ring is soft at around 1333 K and touched closely with the membrane and the quartz tubes under the pressure by a spring. The thickness of BSCFO membrane was 1.4 mm and its effective area exposed to reactions was 1.0 cm^2.

The first membrane reactor only had a bare membrane without any catalyst (Figure 1A); the second one possessed a modified membrane, which was gained through a pretreatment with a small quantity of catalyst powder at 1313 K (Figure 1B); besides a modified membrane, the third one had 400 mg catalyst on the membrane (Figure 1C), which formed a catalyst bed.

Liquid hydrocarbons, such as naphtha, gasoline, diesel oil, and kerosene could be on-board hydrogen sources in the near future[22] and heptane was selected as a typical component of them. Steam was brought into the reactor by helium and its amount was controlled by helium flow rate and water temperature. After being vaporized and mixed uniformly, feed was introduced into the membrane reactor and reacted with oxygen permeating from air. An on-line HP4890 GC chromatograph was used to analyze the products. Since reaction temperatures were around 1123 K, heptane converted completely by cracking or reacting with water and oxygen. Chromatograph did not detect any propane, propylene, or any other heavy hydrocarbons. The selectivity of CO, CO_2, CH_4, C_2H_4, and J_{O2} are defined as follows:

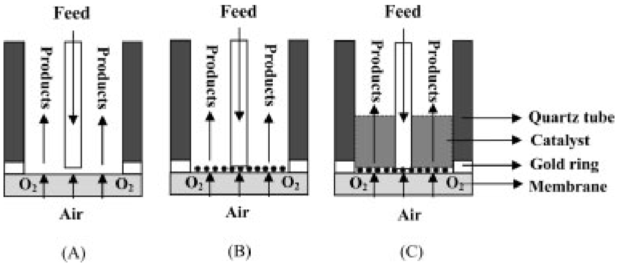


Figure 1. The configurations of three dense ceramic membrane reactors.

$$\text{CO,Selectivity} = \frac{F_{CO}}{F_{CO} + F_{CO_2} + F_{CH_4} + 2(F_{C_2H_4} + F_{C_2H_6})}$$

$$CO_2\text{, Selectivity} = \frac{F_{CO_2}}{F_{CO} + F_{CO_2} + F_{CH_4} + 2(F_{C_2H_4} + F_{C_2H_6})}$$

$$CH_4\text{, Selectivity} = \frac{F_{CH_4}}{F_{CO} + F_{CO_2} + F_{CH_4} + 2(F_{C_2H_4} + F_{C_2H_6})}$$

$$C_2H_4\text{, Selectivity} = \frac{2 \times F_{C_2H_4}}{F_{CO} + F_{CO_2} + F_{CH_4} + 2(F_{C_2H_4} + F_{C_2H_6})}$$

$$J_{O2}\text{, permeation} = \frac{F_{CO} + 2 \times F_{CO_2} + 2 \times F_{O_2}(\text{unreacted}) - F_{H_2O}(\text{reacted})}{2 \times S(\text{effective area})}$$

After the tests, reactor temperature dropped rapidly to room temperature in helium atmosphere. SEM and XRD analysis was used to characterize the used membranes and catalyst.

Results and Discussion

Reforming in the reactor with a bare membrane

To decouple the role of catalyst from membrane reactions, catalytic behavior of BSCFO membrane reactor without any catalyst (Figure 1A) was investigated first at T = 1123 K, V_{air} = 200 ml min^{-1} (air flow rate), W/C = 0.90 (molar ratio of water/carbon) and results are shown in Figure 2. In 200-min test, the reaction keeps stable, but J_{O2} is low, only 2.8 ml cm^{-2} min^{-1}, which is moderately higher than the results under air/helium gradient (J_{O2} = 1.2 ml cm^{-2} min^{-1}) at the same temperature.[15] Since insufficient oxygen and low catalytic activity of membrane surface, a great deal of C_2H_4 is detected in the products, which is mainly the thermal cracking product of heptane. Meanwhile, around 25% hydrocarbons converted into CO, CO_2, H_2, and H_2O. The results indicate that the membrane surface possesses catalytic activity for hydrocarbon oxidation, but low. In addition, much unreacted gas-phase oxygen is detected in the products.

As we know, oxygen permeation process through dense ceramic membrane involves a series of individual step in the form of oxygen ions. There are different kinds of intermediate oxygen species ($O_{2\ ad}$, O, O^-, O_2^-, O_2^{2-}, O^{2-}) on the membrane surface.[23] Therefore, the membranes surface possesses catalytic activity for oxidation reactions, like oxidative coupling of methane to C_2 (OCM).[24] U. Balachandran et al.[3]

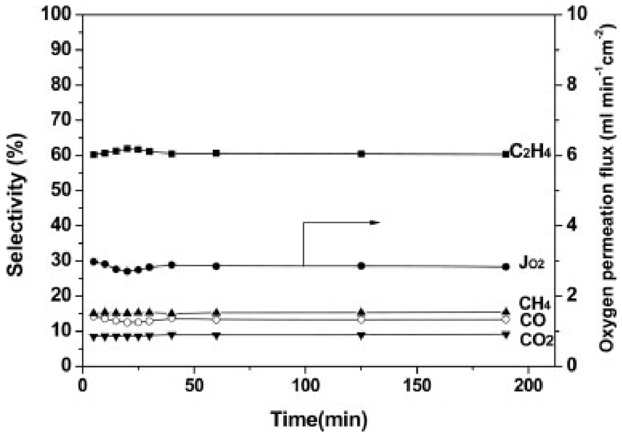


Figure 2. The preliminary stage of reforming reactions in the bare membrane reactor without any catalyst T = 1123 K, V_{air} = 200 ml min^{-1}, W/C = 0.90, He/C = 3.4.

investigated Perovskites LaSrFeCoO for POM and observed that, if there was no catalyst on the membrane, all of oxygen permeating through the membrane formed CO_2 and H_2O with methane on the membrane surface. However, in this case, main products on BSCFO membrane surface are CO and CO_2, as shown in Figure 2. The difference is due to the different catalytic performance of membrane.[25] If active oxygen species cannot react with hydrocarbons in time on the membrane surface, they will recombine into gas-phase oxygen quickly.

Since H_2 and CO are generated, lattice oxygen of membrane could lose. Once partial lattice oxygen is lost, the lattice would collapse and the membrane material would decompose. Figure 3 shows the SEM micrographs of the used membrane (Figure 1A) from top view after 12-h membrane reaction. It can be found that the boundaries of ceramic grains can still be distinguished and the structure of membrane is intact. Main reason is the good structure reversibility of BSCFO material, which makes membrane stable in a strongly reducing atmosphere.[15] Although the membrane surface material is reduced by reducing gas, the lost lattice oxygen can be refilled by oxygen permeating from other side of membrane. As a result, membrane material keeps stable in reforming reaction.

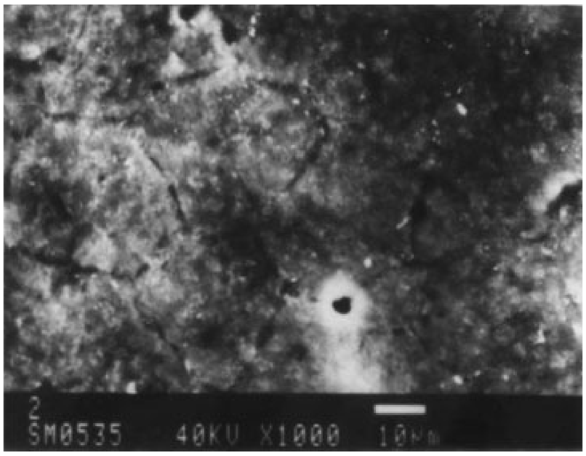


Figure 3. The SEM micrographs of used BSCFO membrane from top view.

Figure 4 demonstrates the effect of temperature on the reforming reactions in the membrane reactor without catalyst. It can be seen that J_{O2} increased gradually from 2.6 to 6.7 ml cm^{-2} min^{-1} with the increase of reaction temperature from 1073 to 1223 K, and accordingly C_2H_4 selectivity decreases. It is obviously that the selectivity to CO and CO_2 rises rapidly, but CO_2 selectivity is always higher than that of CO when the reaction temperature is >1123 K. BSCFO bare membrane surface favored the total oxidation of hydrocarbons at high temperature.

Reforming in the reactor with a modified membrane

The tests were performed at the same reaction conditions as in the reactor with a bare membrane, i.e. T = 1123 K, V_{air} = 200 ml min^{-1}, W/C = 0.90. The reactor configuration is shown in Figure 1B. Its membrane surface is modified with reforming catalyst LiLaNiO/γ-Al_2O_3 as follows: 10 mg fresh catalyst powder was packed on the membrane surface and pretreated with membrane at 1313 K for 5 h, and then temperature dropped to reaction temperatures. Before the introduction of feed, high helium flow blew away the redundant catalyst powder. Figure 5 shows SEM micrographs of BSCFO membrane surface after the modification. It can be seen that small catalyst particles fused over the membrane surface.

Figure 6 shows the time dependence of J_{O2} and the selectivity of products in the reactor with a modified membrane. It is quite different from the results in the membrane reactor without catalyst, where the membrane reaction is stable. In this case, the membrane reactions keep stable only at the beginning of reaction and at time-on-stream (TOS) of 60 min a shift takes place. Within the subsequent 70 min, J_{O2} increases gradually from 3.5 to 6.5 ml cm^{-2} min^{-1} and the selectivity to CO and CO_2 increases from 12 to 40% and 21 to 24%, respectively. Meanwhile, C_2H_4 selectivity drops

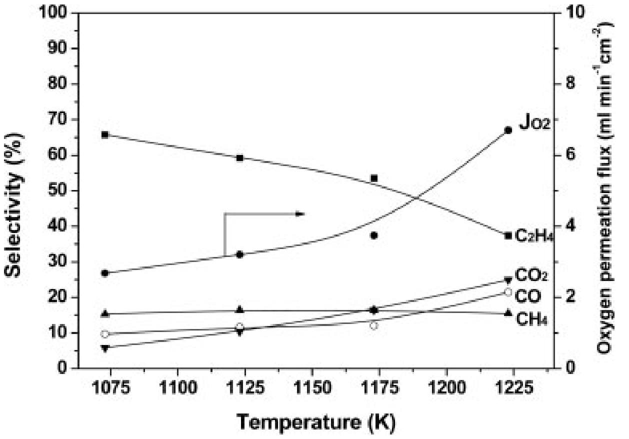
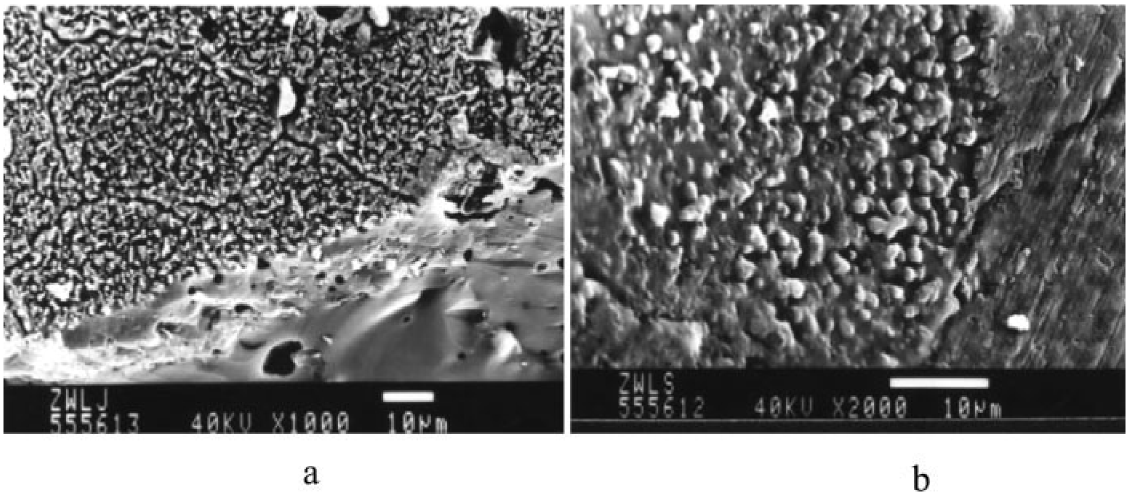


Figure 4. The effect of temperature on the selectivity and J_{O2} in the bare membrane reactor without catalyst V_{air} = 200 ml min^{-1}, W/C = 0.90, He/C = 3.4.



a

b

Figure 5. The SEM micrographs of modified BSCFO membrane surface from top view after 5 h at 1313 K with 10 mg catalyst powder a: ×1000, b: ×2000.

from 48.0 to 22%. At TOS of 130 min, the membrane reaction reaches a steady state and around 70% hydrocarbons converted.

The observed shift process in J_{O2} and the selectivity of products is ascribed to the reduction of catalyst attached on the membrane surface. The catalyst used in this study is fresh and its active component is $NiAlO_4$, which is the active center of total oxidation reaction. This is the reason why CO_2 selectivity (48%) is higher than that of CO(12%) at the beginning of membrane reactions. Along with the test, $NiAlO_4$ is reduced gradually into Ni^0 which is the active center of partial oxidation of hydrocarbons, so that more H_2 and CO are formed and leads to more catalyst to be reduced. Therefore, an autocatalysis process is formed and reaction rate accelerates. In Figure 6, it is can be seen that, in the shift stage, the rising rate of CO is higher than that of CO_2. This proves the initiation process of the modified membrane is the reduction of active component from $NiAlO_4$ to Ni^0. When the reaction reaches stable, J_{O2} is 6.5 ml cm^{-2} min^{-1}, which is higher than that in the bare membrane reactor (2.8 ml cm^{-2} min^{-1}). It can be seen that LiLaNiO/γ-Al_2O_3 catalyst plays an important role in membrane reforming. Liu et al.[26] considered that the conductivity (ionic and electronic) of membrane materials determined the mass and charge transportation rate of membrane, while catalytic activity controls the rate of the interfacial electrochemical reactions. The catalytic activity of the membrane surface or interfaces between membrane and catalyst has a significant effect on oxygen permeation. Therefore, in order to form a higher oxygen gradient pressure between both sides of membrane, some catalyst contacting closely to membrane surface is necessary to deplete oxygen on the immediate membrane surface. In this case, a small amount of gas-phase oxygen is still detected.

To further study the catalytic performance of BSCFO membrane modified by reforming catalyst, the temperature dependences of J_{O2} and the selectivity of products are investigated and the results are shown in Figure 7. With the increase of reaction temperature, the changing trends of J_{O2}

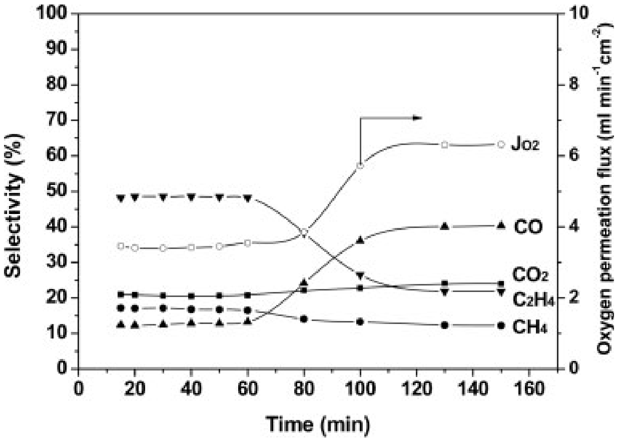


Figure 6. The preliminary stage of reforming reaction in the modified membrane reactor *T* = 1123 K, V_{air} = 200 ml min^{-1}, W/C = 0.90, He/C = 3.4.

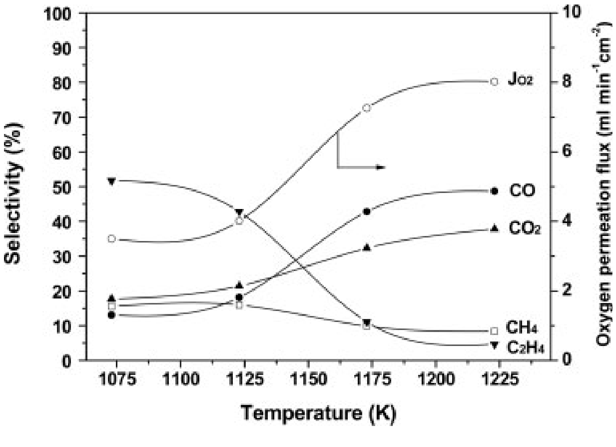


Figure 7. The effect of temperature on the selectivity and J_{O2} in the modified membrane reactor V_{air} = 200 ml min^{-1}, W/C = 0.90, He/C = 3.4.

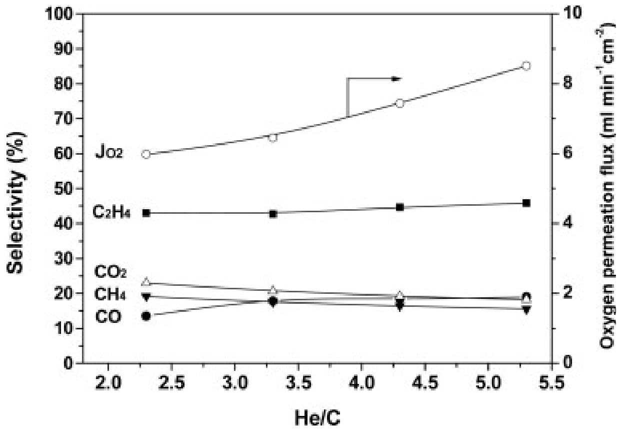


Figure 8. The effect of He/C on the selectivity and J_{O2} in the modified membrane reactor T = 1123 K, V_{air} = 200 ml min^{-1}, W/C = 0.90.

and the selectivity of all compositions are similar to the results in the reactor with bare membrane. However, it is interesting to observe that, in the reactor with a bare membrane, CO_2 increasing rate is larger than that of CO when temperature is >1123 K, but in the reactor with modified membrane, the result is opposite. The observed phenomenon is attributed to the different catalytic conditions in two cases. In the reactor with bare membrane, membrane surface is the catalytic medium and hydrocarbons react directly with lattice oxygen on it. As pointed by Gellings and Bouwmeester[27] and Irusta et al.[28] the catalytic properties of oxygen supplied by conducting oxides include either total or partial oxidation reactions and the surface properties of dense membranes have important catalytic effects on it. Delivering active oxygen species on the membrane surface are often very selective for oxidation reactions,[25] as it was discussed earlier that total oxidation reaction of hydrocarbons is dominant reaction on the surface of BSCFO membrane. However, on the modified membrane surface, catalyst covers the most of membrane surface and thus hydrocarbons react with oxygen mainly on the catalyst, not on the bare membrane surface. Since the reduced LiLaNiO/γ-Al_2O_3 is the partial oxidation catalyst, CO increasing rate is larger than that of CO_2 with the increase of reaction temperature. In addition, oxygen could spill directly over to Ni particles and react with hydrocarbons to syngas[15] because of the catalyst particles fused on the membrane surface. Figure 8 shows the effect of He/C on reforming reaction. It can be seen that J_{O2} and CO selectivity rises with the increase of He/C for the reduced catalyst.

Reforming in the membrane reactor with 400 mg catalyst

Figure 9 shows the time dependence of J_{O2} and the selectivity of compositions in the membrane reactor with 400 mg LiLaNiO/γ-Al_2O_3 catalyst. Compared with Figures 4 and 6, the profiles of Figure 9 change greatly. J_{O2} has a great increase, from 7.0 to 10.0 ml cm^{-2} min^{-1}, nine times larger than the value under air/helium gradient at the same temperature. Meanwhile, C_2H_4 and gas-phase oxygen disappear in products.

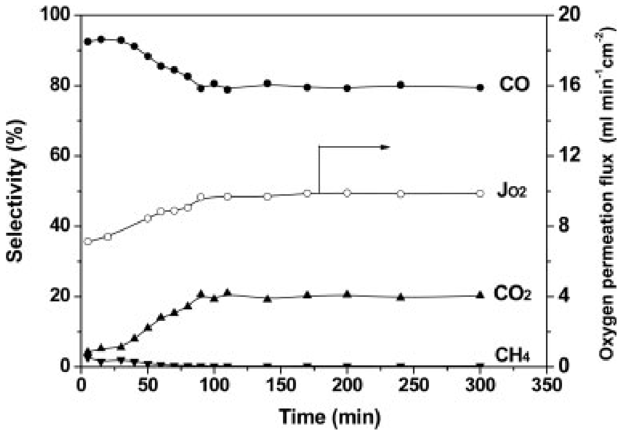


Figure 9. The preliminary stage of reforming reactions in the membrane reactor with 400 mg catalyst T = 1123 K, V_{air} = 200 ml min^{-1}, W/C = 0.40, He/C = 1.7.

Since 400 mg LiLaNiO/γ-Al_2O_3 catalyst forms a catalyst bed on the membrane, unreacted hydrocarbons have more chance to further reform with gas-phase oxygen and produced CO_2 and H_2O, so that in this case CO selectivity is always higher than that of CO_2 even at the beginning of reaction, and the changing selectivity to CO, CO_2 with the reduction of reforming catalyst in the modified membrane reactor does not show here. This also causes the depletion of gas-phase oxygen so that higher oxygen gradient pressure is formed, which leads to higher J_{O2}. Therefore, in this case, oxygen flux is high even at the beginning of reaction. Since oxygen supplied by membrane is more than the amount needed for the conversion of all hydrocarbons to syngas, excessive oxygen results in the reoxidation of CO and thus the selectivity to CO drops. As discussed earlier that around 70% hydrocarbons convert into CO and CO_2 on the modified

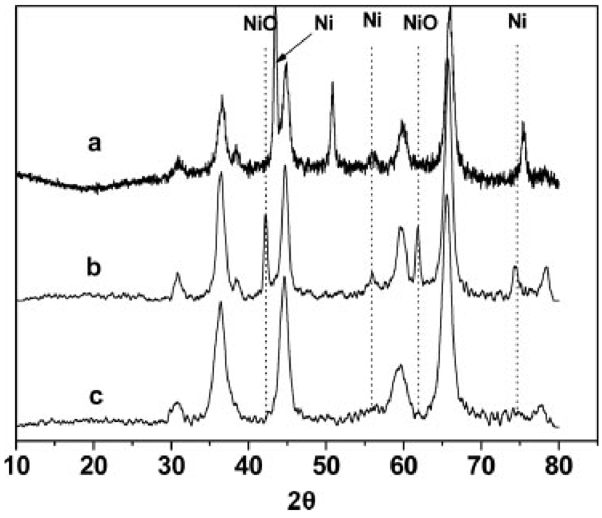


Figure 10. XRD patterns of used LiLaNiO/γ-Al_2O_3 catalyst in different zones (a) reduced fresh catalyst; (b) used catalyst in the black zone; (c) used catalyst in the blue zone.

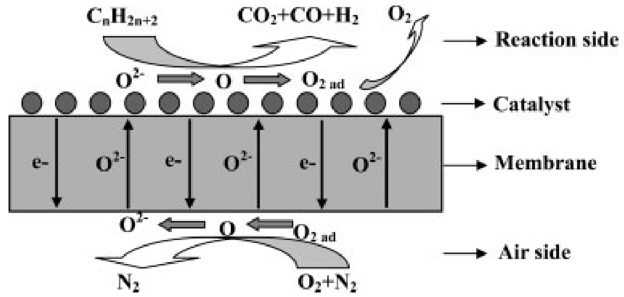


Figure 11. The schematic of hydrocarbon reforming in the dense ceramic membrane reactor.

membrane surface, the dominant reaction in 400 mg catalyst bed is the reforming of left hydrocarbons with CO_2, H_2O to syngas, not the combustion of hydrocarbons with gas-phase oxygen from membrane, though there is a small amount of gas-phase oxygen in the reactant.

As we know, membrane materials need some time to adjust their structures to the membrane reactions at the preliminary stage of reactions. Some are quick[14,29] and some are very slow.[30] In our previous works,[14] it took more than 20 h to initiate BSCFO membrane reaction in POM, but in this case, it only takes 130 minters. The same dense ceramic membranes demonstrate so different results. Main reason is the opposite feeding directions in two tests. In POM,[14] feed was introduced first through the catalyst bed, so that the catalyst is activated from the top of catalyst bed, and then moves downward slowly, and finally reaches the membrane surface. Just at this moment, reaction rate accelerates and J_{O2} increased dramatically because oxygen is depleted completely over the reduced catalyst. However, in this case, feed is introduced through the inner quartz tube and reacts directly with oxygen on the membrane surface. Such a model avoids the activation of whole catalyst bed. This indicates that, besides the own performance of membrane material, the reaction conditions are other important factors to the initiation of membrane reactions.

After reaction, membrane reactor cooled down rapidly to room temperature in the helium atmosphere. It was found that the catalyst bed was separated into two parts, a very thin blue layer closed to the membrane surface and a thick black layer on top of the blue layer. Different nickel species are found in two catalysts zones, as shown in Figure 10: $NiAl_2O_4$ in blue layer and NiO and Ni^0 in black layer. This phenomenon is similar to what Wang et al. observed in the tubular membrane reactor[5,17] and Dong et al. observed in the disk-type membrane reactor.[14] They considered that, in the blue layer, total oxidation reactions take place and, in the black catalyst bed, reforming reactions of CO_2 and H_2O with hydrocarbons occur. However, we consider that the very thin blue catalyst layer is not the real catalyst during reaction. It is the reoxidized products of the reduced catalyst during the cooling process after membrane reaction, namely the conversion of black Ni^0 catalyst to blue $NiAl_2O_4$ catalyst after test. Despite air stops, some oxygen can still permeate continuously through the membrane under the low oxygen gradient pressure and oxidize Ni^0 to $NiAl_2O_4$ during the cooling of the reactor. On the other hand, if the catalyst keeps $NiAl_2O_4$ state during the reaction, there would not be a shift process at the preliminary stage.

On the basis of the results in three different membrane reactors, a reaction pathway of hydrocarbon reforming in a dense ceramic membrane reactor is proposed and the schematic of reaction process is shown in Figure 11. In this case, most of hydrocarbons react directly with active oxygen species on the modified membrane surface first and produce CO, CO_2, H_2O, and H_2. Unreacted active oxygen species recombine into gas-phase oxygen quickly and diffuse away the membrane surface. Subsequently, unreacted hydrocarbons reform with CO_2, H_2O and a small amount of gas-phase oxygen in the catalyst bed. This reaction pathway is some different from CRR mechanism.

Conclusion

Three dense ceramic BSCFO membrane reactors pretreated by different modification methods are used for the investigation of hydrocarbon reforming. It is found that the different treatments of catalyst have obvious effects on the reforming reactions in the dense ceramic membrane reactor.

1. The reforming reaction in the membrane reactor without catalyst is stable, but J_{O2} is low. The bare membrane possesses limited catalytic activity for hydrocarbon reforming and around 25% hydrocarbons converted into CO, CO_2, H_2, and H_2O. The reactions on the bare membrane surface favor the total oxidation for CO_2.
2. The membrane reactors modified with catalyst display very different catalytic behaviors from the results in the bare membrane reactor. Shift process at the preliminary stage of membrane reaction is ascribed to the activation of catalyst fused on the membrane surface. Around 70% hydrocarbons directly converted into CO, CO_2, H_2, and H_2O with active oxygen on the modified membrane surface, but CO and H_2 are the main products. Therefore, the reactions in catalyst bed are mainly the reforming of left hydrocarbons with CO_2 and H_2O to CO and H_2, not the combustion reaction. It is some different from CRR mechanism.
3. In this case, the initiation time of BSCFO membrane reactor with 400 mg reforming catalyst is only 130 min, which is different from the result in POM (20 h). This indicates that reaction conditions are other important factors which can affect the initiation of membrane besides the own performance of membrane material.

Literature Cited

1. Saracco G, Versteeg GF, Swaaij WPM. Current hurdles to the success of high-temperature membrane reactors. *J Membr Sci*. 1994;95:105–123.
2. Bouwmeester HJM, Burggraaf AJ. Dense ceramic membranes for oxygen separation. In: Burggraaf AJ, Cot L, editor. *Fundamentals of Inorganic Membrane Science and Technology*. Amsterdam: Elsevier, 1996:435–528.
3. Balachandran U, Dusek JT, Mieville RL, Poeppel RB, Kleefisch MS, Pei S, Kobylinski TP, Udovich CA, Bose AC. Dense ceramic membranes for partial oxidation of methane to syngas. *Appl Catal, A*. 1995;133:19–29.
4. Tsai CY, Dixon AG, Moser WR, Ma YH. Dense perovskite membrane reactor for partial oxidation of methane to syngas. *AIChE J*. 1997;43:2741–2748.

5. Wang H, Tablet C, Schiestel T, Werth S, Caro J. Partial oxidation of methane to syngas in a perovskite hollow fiber membrane reactor. *Catal Commun*. 2006;7:909–914.
6. Ikeguchi M, Mimura T, Sekine Y, Kikuchi E, Matsukata M. Reaction and oxygen permeation studies in $Sm_{0.4}Ba_{0.6}Fe_{0.8}Co_{0.2}O_{3-\delta}$ membrane reactor for partial oxidation of methane to syngas. *Appl Catal, A*. 2005;290:212–220.
7. Chen CM, Dyer PN, Gerdes KF, Lowe CM, Akhave SR, Rowley DR, Åsen KI, Eriksen EH. An integrated ITM syngas/Fischer-Tropsch process for GTL conversion. *Stud Surf Sci Catal*. 2001;136:45–50.
8. Kharton VV, Sobyanin VA, Belyaev VD. Methane oxidation on the surface of mixed-conducting $La_{0.3}Sr_{0.7}Co_{0.8}Ga_{0.2}O_{3-\delta}$. *Catal Commun*. 2004;5:311–316.
9. Gu XH, Jin WQ, Chen CL, Xu NP, Shi J, Ma YH. YSZ-$SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ Membranes for the partial oxidation of methane to Syngas. *AIChE J*. 2002;48:2051–2060.
10. Bouwmeester HJM. Dense ceramic membranes for methane conversion. *Catal Today*. 2003;82:141–150.
11. Christopher MC, Douglas LB, Michael FC, Edward PF, William LS, Dale MT. ITM syngas ceramic membrane technology for synthesis gas production. *Stud Surf Sci Catal*. 2004;147:55–60.
12. Zhu W, Xiong G, Han W, Yang W. Catalytic partial oxidation of gasoline to syngas in a dense membrane reactor. *Catal Today*. 2004;93–95:257–261.
13. Zhu W, Han W, Xiong G. Mixed reforming of heptane to syngas in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ membrane reactor. *Catal Today*. 2005; 104:149–154.
14. Dong H, Shao Z, Xiong G. Investigation on POM reaction in a new perovskite membrane reactor. *Catal Today*. 2001;67:3–13.
15. Shao Z, Dong H, Xiong G. Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion. *J Membr Sci*. 2001;183:181–192.
16. Dissanayake D, Rosynek MP, Kharas KCC, Lunsford JH. Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/Al_2O_3 catalyst. *J Catal*. 1991;132:117–127.
17. Wang H, Cong Y, Yang W. Investigation on the partial oxidation of methane to syngas in a tubular $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane reactor. *Catal Today*. 2003;82:157–166.
18. Liu SL, Xiong GX. Partial oxidation of ethane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide. *Catal Lett*. 1999;63:167–171.
19. Liu SL, Xiong GL, Sheng SS. Partial oxidation of methane and ethane to synthesis gas over a LiLaNiO/r-Al_2O_3 catalyst. *Appl Catal A*. 2000;198:261–266.
20. Ran R, Xiong GX, Sheng SS. Catalytic partial oxidation of *n*-heptane for hydrogen production. *Catal Lett*. 2003;88:55–59.
21. Shao ZP, Xiong GX, Cong Y, Dong H, Tong JH. Investigation of the permeation behavior and stability of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ oxygen membrane. *J Membr Sci*. 2000;172:177–188.
22. Wang Y, Wu D. The experimental research for production of hydrogen from n-octane through partially oxidizing and steam reforming method. *Int J Hydrogen Energy*. 2001;26:795–800.
23. Steele B. *Compte Rendu de l'Acade'mie des Sciences*. Paris, tome 1. Se'rie II c. 1998:533.
24. Wang H, Cong Y, Yang W. Oxidative coupling of methane in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ tubular membrane reactors. *Catal Today*. 2005;104:160–167.
25. Julbe A, Farrusseng D, Guizard C. Limitations and potentials of oxygen transport dense and porous ceramic membranes for oxidation reactions. *Catal Today*. 2005;104:102–113.
26. Liu M, Shen Y, Ludlow J, Josh A, Krist K. In Proceedings of International Gas Research Conference (Thompson HA, editor), Orlando, FL, 1992:183–192.
27. Gellings J, Bouwmeester HJM. Solid state aspects of oxidation catalysis. *Catal Today*. 2000;58:1–53.
28. Irusta S, Pina MP, Menendez M, Santamaria J. Development and application of perovskite-based catalytic membrane reactors. *Catal Lett*. 1998;54:69–78.
29. Tong J, Yang W, Cai R, Zhu B, Lin L. Novel and ideal zirconium-based dense membrane reactors for partial oxidation of methane to syngas. *Catal Lett*. 2002;78:129–137.
30. Tsai CY, Dixon AG, Moser WR, Ma YH. Ceramics processing. *AIChE J*. 1997;43:2741–2750.
31. Vernon PDF, Green MLH, Cheetham AK, Ashcroft AT. Partial oxidation of methane to synthesis gas. *Catal Lett*. 1990;6:181–186.

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