Partial oxidation of ethane to syngas in an oxygen-permeable membrane reactor

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Abstract

A perovskite-type oxide of Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCFO) with mixed electronic and oxygen ionic conductivity at high temperatures was used as an oxygen-permeable membrane. A tubular membrane of BSCFO made by extrusion method has been used in the membrane reactor to exclusively transport oxygen for the partial oxidation of ethane (POE) to syngas with catalyst of LiLaNiO2−δ-Al2O3 at temperatures of 800–900 ◦C. After only 30 min POE reaction in the membrane reactor, the oxygen permeation flux reached at 8.2 ml cm−2 min−1. After that, the oxygen permeation flux increased slowly and it took 12 h to reach at 11.0 ml cm−2 min−1. SEM and EDS analysis showed that Sr and Ba segregations occurred on the used membrane surface exposed to air while Co slightly enriched on the membrane surface exposed to ethane. The oxygen permeation flux increased with increasing of concentration of C2H6, which was attributed to increasing of the driving force resulting from the more reducing conditions produced with an increase of concentration of C2H6 in the feed gas. The tubular membrane reactor was successfully operated for POE reaction at 875 ◦C for more than 100 h without failure, with ethane conversion of ∼100%, CO selectivity of >91% and oxygen permeation fluxes of 10–11 ml cm−2 min−1.

Keywords: Partial oxidation of ethane; Membrane reactor; Oxygen separation; Perovskite; Syngas

1. Introduction

Nature gas is predominantly composed of CH4. It also contains 5–30% C2H6, C3H8 and C4H10. Generally, C2H6 is the second most abundant component in nature gas [1]. For catalytic conversion of nature gas, a lot of research work was related to the catalytic conversion of methane to syngas [2,3], but only a few work has been devoted to catalytic conversion of ethane [4,5]. There are two ways to convert ethane to useful products. One way is thermal or oxidative dehydrogenation of ethane to ethylene [6], and another way is partial oxidation of ethane (POE) to syngas (CO + H2) [7]. The thermal dehydrogenation of ethane exhibits a high selectivity to ethylene (∼80%) with a fairly high conversion (∼60%), which represent the main process for commercial olefin production. The oxidative dehydrogenation of ethane to ethylene over oxide catalyst, such as V2O5/SiO2, has also shown very high selectivity (∼100%) at low conversion (<1%) [8]. Since these processes are operated under severely fuel-rich conditions, carbon deposition, and deactivation, consequently, can be the major problem [9].

For POE to syngas, Schmids and co-workers [4,7] got CO selectivity of up to 70% at ethane conversion...
of about 95% by using a supported Rh catalyst. In our group, we used supported Ni-based catalyst for POE to syngas in fixed-bed reactor and got CO selectivity of ∼94% at ethane conversion of ∼100% [10]. However, the big problems of POE to syngas are (1) the reaction needs expensive pure oxygen as oxidant in order to get rid of unwanted N2 in the products; (2) it is hard to control the complete oxidation of ethane reacted with O2 to CO2 and H2O in gas phase in free radical chain reactions which can cause flames and explosion. These problems can be solved by using recently developed dense oxygen-permeable ceramic membrane reactor [11–13], in which POE to syngas and the oxygen separation from air will be carried out in a single unit, thus it will significantly reduce the capital cost and effectively control, by the gradual oxygen supply through a membrane (as shown in Fig. 1), the hot spots in the catalyst bed caused by the complete oxidation reaction in gas phase.

Several researchers [14–16] have reported the oxygen-permeable ceramic membrane reactor for partial oxidation of methane (POM) to syngas, in which O2 from air transported through an oxygen-permeable dense ceramic membrane by diffusion induced by an oxygen partial pressure gradient across the membrane. For commercial applications, the membrane should not only have high oxygen permeation flux, but also have sufficient chemical stability and mechanical integrity in reaction conditions at elevated temperature. Recently, we have developed some novel oxygen-permeable membranes with perovskite structure based on Ba system, such as Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCFO) [17–20] and Ba0.5Zn0.5Co0.5Fe0.5O3−δ (BZCFO) [21,22], and applied these membrane reactors to POM to syngas at 800–900 °C [19,21]. These materials exhibit high oxygen permeability and high chemical stability even in highly reductive methane atmosphere on the one side of the membrane and highly oxidizing air environment on the other side of the membrane. The BSCFO membrane reactor had been successfully operated in the POM for 500 h at 875 °C, and the membrane reactor based on BZCFO had been steadily operated in the POM for more than 2200 h. On the other hand, we also developed a good catalyst based on LiLaNiO/H9253/Al2O3 for POE to syngas in conventional reactor [5,10]. The present paper will extend our membrane reactor to POE to syngas with the catalyst of LiLaNiO/H9253/Al2O3. The Ba0.5Sr0.5Co0.8Fe0.2O3−δ tubular membrane will be used in the membrane reactor.

2. Experimental

2.1. Preparation of tubular membrane

BSCFO oxide powder was synthesized by a combined citrate and EDTA complexing method. Detail information for the preparation of BSCFO oxide powder was present in our previous paper [17]. The membrane tube was prepared by extrusion method. Firstly, the calcined ceramic powder was mixed with several additives, such as a solvent, a dispersant, a binder and a plasticizer to make a formulation (slip) with enough plasticity to be easily formed into tube while retaining satisfactory strength in the green state. Secondly, the slip was extruded through a die at a high pressure to produce the tube-shape membrane. Thirdly, extruded tube-shape membrane was heated at 5 °C/h in the temperature range of 100–450 °C to facilitate the removal
of the gaseous species formed during the decomposition of the organic additives, then the heating rate was increased to 1 °C min⁻¹ and sintered at 1100–1200 °C in air for 3–5 h. Finally the sintered tube was cooled down to room temperature with the cooling rate of 2 °C min⁻¹. The sintered tubular membrane has an outer diameter of about 8 mm, an inner diameter of about 5 mm, and length up to 30 cm.

2.2. Preparation of catalyst

LiLaNiO/γ-Al₂O₃ catalyst with 10 wt% nickel loading was prepared by impregnation method [10], i.e. impregnating γ-Al₂O₃ supports with appropriate amounts of LiNO₃, Ni(NO₃)₂ and La(NO₃)₃ for 24 h, then dried at 100 °C under open environment, and calcined in air at 550–800 °C for 4 h.

2.3. Set-up of tubular membrane reactor

A shell-and-tube reactor was used in this work for POE to syngas. The configuration is shown in Fig. 2. Each end of the membrane tube was connected with a quartz tube (Ø = 17 mm) with a ceramic binder in its groove, which serves as the tube side of the shell-and-tube reactor. Another quartz tube (Ø = 29 mm) served as the shell side of the shell-and-tube reactor. The catalyst was packed in the membrane tube and well contacted with the membrane. A tubular furnace was used to heat the reactor and controlled by a microprocessor temperature controller (model AI-708) with ±1 K of the set points. The temperature was measured by a K-type thermocouple encased near the tube.

Ethane mixed with helium was fed to the tube side, while air was fed to the shell side. The inlet gas flow rate was controlled by a mass flow controller (models D07-7A/ZM). Both the shell side and the tube side of the reactor were maintained at atmospheric pressure.

2.4. Analysis of products

The inlet ethane concentration and the product gases were analyzed by on-line gas chromatography (GC). The on-line GC (HP6890) was equipped with two automatic valves, i.e. a sampling valve and a bypassing valve, and the HP Chemstation for data collection and analysis. A serial/bypass configuration was arranged for two isothermal columns (80 °C), i.e. porapak Q and molecular sieve 13X. The mixture of products (H₂, O₂, N₂, CH₄, CO, CO₂, C₂H₄ and C₂H₆) was injected to the porapak Q column by the sampling valve, in which the mixture of H₂, O₂, N₂ and CO was eluted earlier than CH₄, CO₂, C₂H₄ and C₂H₆, then quickly entered the serial-arranged molecular sieve 13X column. Before the mixture of H₂, O₂, N₂ and CO was eluted from the molecular sieve 13X column, the bypassing valve was activated to dead-end the 13X column and direct the eluted gases (CH₄, CO₂, C₂H₄ and C₂H₆) from the porapak Q column to the thermal conductivity detector. Once CH₄, CO₂, C₂H₄ and C₂H₆ had eluted from the porapak Q, the bypassing valve was activated again, and the H₂, O₂, N₂ and CO were eluted from the molecular sieve column 13X to the detector. An external standard method was used for product analysis. Multiple-point calibration curves were created, and recalibrated routinely with standard gas mixture (O₂, N₂, CH₄, CO, CO₂, C₂H₄ and C₂H₆) for long-term studies. The quantity of H₂O was calculated based on hydrogen atomic balance. The oxygen permeation rate was calculated from the measured outlet flow rate and the mole fractions of oxygen-containing products, such as CO, CO₂, O₂ and H₂O. The carbon balance during all of the experiments was within 5%.
The separation of O₂ and N₂ is crucial for leakage checking on the membrane tube and the sealing. The oxygen leakage could be calculated from the nitrogen leakage. In the reaction experiments, the oxygen leakage accounted for 0.3% of the total oxygen flux.

3. Results and discussions

As we know, gas-phase reaction will result in the complete oxidation of ethane to CO₂ and H₂O, thus decrease the selectivity of POE to syngas. So, it is very important to know the effect of gas-phase reaction on POE to syngas. Table 1 showed the conversion of C₂H₆ and selectivity of CO and H₂ in BSCFO membrane reactor without catalyst at reaction conditions of the flow rate of 60 ml min⁻¹ (50% ethane + 50% He) and temperatures between 800 and 900 °C. The results showed that a large amount of ethane was, at this case, completely oxidized to CO₂ and H₂O, thus caused a great decrease of the selectivity of CO and H₂ (<40%). At this case, some unreacted gas-phase O₂ was indeed detected in the products. Compared to non-reactive condition (J_O₂ = 1.2 ml cm⁻² min⁻¹, air/He, at 850 °C), the oxygen permeation fluxes of the tubular membrane increased greatly to 6–10 ml cm⁻² min⁻¹ at reactive conditions. In order to eliminate the effect of gas-phase reaction of ethane with O₂, a catalyst well contacted with the surface of the membrane was needed to efficiently catalyze the POE reaction before the permeated O₂ diffusing into gas phase.

Fig. 3 showed the oxygen permeation flux of the membrane and the catalytic performance of POE.
to syngas in the tubular membrane reactor with LiLaNiO/\text{H9253} (0.52 g). The results showed that the oxygen permeation flux of the membrane was only 1.22 ml cm$^{-2}$ min$^{-1}$ before ethane was introduced to the membrane reactor, but it quickly reached at 8.2 ml cm$^{-2}$ min$^{-1}$ after ethane was introduced to the reactor only about 30 min, which means the catalyst is completely reduced within 30 min. After 30 min, the oxygen permeation flux of the membrane increased slowly to $\sim$11.0 ml cm$^{-2}$ min$^{-1}$ in about 12 h and was kept constant at 11.0 ml cm$^{-2}$ min$^{-1}$. It should be pointed out that no gas-phase oxygen was detected, in this case, at the present of catalyst in the membrane reactor. Accordingly, the selectivity of CO was very high ($\sim$80%) even at beginning, and increased slowly to $\sim$90% within 12 h. After 12 h, all of C$_2$H$_4$ was completely converted to syngas, and there was no C$_2$H$_4$ detected in the downstream.

In membrane reactor, the initial stage of reaction is very interesting and important. In our experiment, the catalyst is not pre-reduced, so the initial stage is divided into two periods. One is the activation period of the catalyst ($<30$ min). The other one is the adjustment period of the structure and composition of the membrane (30 min to 12 h). The activation process of the catalyst in the membrane reactor is different from that in the fixed-bed reactor. In the fixed-bed reactor, the ratio of ethane to oxygen can be easily controlled at an optimum value to activate the catalyst.

In the membrane reactor, the ratio of ethane to oxygen varies with the state of the catalyst, owing to the oxygen permeation flux of the membrane reactor controlled by the oxygen partial pressure gradient across the membrane. The oxygen partial pressure near the membrane surface, which determined the oxygen permeation flux of the membrane, is determined by the degree of the permeated oxygen consumed by the reaction near the membrane. Once the catalytic active centers are formed, the reaction will be accelerated greatly. So the oxygen permeation fluxes increased sharply from 1.22 to 8.2 ml cm$^{-2}$ min$^{-1}$ in the activation period of catalyst ($<30$ min). In the adjustment period of the structure and composition of the membrane (30 min to 12 h), the oxygen permeation flux only has a slight increase from 8.2 to $\sim$11 ml cm$^{-2}$ min$^{-1}$ due to gradual adjustment.

In our previous studies [19], we found that more than 10 h were needed for the activation of catalyst for partial oxidation of methane to syngas in the disk-type BSCFO membrane reactor, which is much longer than that of POE reaction. Generally speaking, ethane is much more active than methane, so ethane can activate the catalyst more easily and faster than methane, thus lead to shorter activation period of catalyst for POE (30 min) than for POM (10 h). These results are also consistent with the results in fixed-bed reactor. In the fixed-bed reactor, it takes about 1 h to activate the fresh catalyst for POM while it only takes 10 min for POE. The activation of catalyst in fixed reactor is faster than that in membrane reactor for both POM and POE. The reason is that the ratio of CH$_4$/O$_2$ or C$_2$H$_6$/O$_2$ can be kept at a constant and an optimum value in fixed reactor, while the ratio of CH$_4$/O$_2$ or C$_2$H$_6$/O$_2$ varies with time and reach at an optimum value slowly in membrane reactor.

In the adjustment period of the structure and composition of the membrane (30 min to 12 h), the oxygen permeation flux only has a slight increase from 8.2 to 11.0 ml cm$^{-2}$ min$^{-1}$. Similar phenomena was also reported by Tsai et al. [23] for POM reaction in a La$_{0.2}$Ba$_{0.8}$Fe$_{0.1}$Co$_{0.1}$O$_{x-y}$ (LBCFO) membrane reactor with 5% Ni/Al$_2$O$_3$ catalyst, it took 500 h to reach at steady state. They found that the surface segregation and decomposition might have eventually contributed to the slower increase in the oxygen permeation flux. In our case, we characterized the fresh membrane tube and the used membrane tube after 100 h POE reaction by SEM, XRD and EDS. The SEM pictures of the membrane tubes are shown in Fig. 4. For the fresh membrane, ceramic grains with clear grain boundaries are visible as shown in Fig. 4a. For the used membrane, the surface exposed to ethane became to be highly porous as shown in Fig. 4c and the thickness of the porous layer is $\sim$60 $\mu$m as shown in Fig. 4d. XRD analysis of the surface indicated the presence of SrCO$_3$ and BaCO$_3$. Elshof et al. [24] also found the presence of SrCO$_3$ on the membrane surface after the oxidative coupling of methane in a disk-shaped La$_{0.2}$Sr$_{0.8}$Co$_{0.1}$Fe$_{0.1}$O$_{x-y}$ membrane reactor. They contributed the formation of SrCO$_3$ to Sr reacted with the deposited carbon on the membrane surface.

EDS analysis of the surface exposed to air is similar to the fresh membrane, but the grains became smaller and the grain boundaries became to be blurr, as shown in Fig. 4e, but still in dense shown in Fig. 4f. EDS analysis showed an enrichment in Sr and Ba.
on the surface of the used membrane exposed to air, as shown in Table 2. This indicated that Sr and Ba segregations occurred on the used membrane surface exposed to air. Although the segregation mechanism was not clear by now, it might be mainly attributed to the charge compensation mechanism due to oxygen anion dissociation on the surface exposed to air and migration from the air-side to the reducing-side surface. EDS analysis for the fresh membrane and the used membrane showed that the composition change is obvious on the membrane surface exposed to ethane. Compared to fresh membrane \((\text{Co}/(\text{Co} + \text{Fe}) = 0.80)\), a slightly higher \((\text{Co}/(\text{Co} + \text{Fe}) = 0.85)\) was found on the reducing-side. This indicated that the Co content increased compared to Fe content in the reducing-side. Tsai et al. [23] also found that the Co content increased on the reducing-side on the membrane surface after partial oxidation of methane in a...
Table 2
EDS results of fresh membrane and the used membrane after POE for 100 h

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>Fe</th>
<th>Cr</th>
<th>Sr</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh membrane</td>
<td>58.79</td>
<td>4.25</td>
<td>16.87</td>
<td>9.72</td>
<td>10.37</td>
</tr>
<tr>
<td>Glomerations on the surface exposed to air of the used membrane</td>
<td>59.9</td>
<td>2.31</td>
<td>9.39</td>
<td>14.86</td>
<td>13.54</td>
</tr>
</tbody>
</table>

LBCFO membrane reactor. The composition on the used membrane surface exposed to air was similar to the fresh membrane. Apparently, the membrane surface exposed to ethane was affected by the reducing atmosphere. Different element segregations took place on the different membrane surfaces indicating that the structure and composition of the membrane changed with the reaction proceeding. The changes of the structure and composition of the membrane lead to the changes of the oxygen permeation flux of the membrane. Therefore, the oxygen permeation fluxes of the membrane for POE gradually increased from 8.2 to 11.0 ml cm⁻² min⁻¹ within 12 h can be interpreted as follows. When the catalyst was packed in the membrane reactor, the gas-phase oxygen was consumed quickly and completely by POE reaction. The membrane surface was transformed into a structure that was more favorable to oxygen transport. Sr and Ba segregation on the surface exposed to air lead to the surface oxygen exchange rate increase, which result in the increase of the oxygen permeation flux. Until the structure was fully developed, the oxygen permeation flux kept stable value. In order to exactly understand the effect of other parameters on the catalytic performance of POE in the membrane reactor, the data should be collected after 12 h experiment. Fig. 5 showed the temperature effect on the catalytic performance of POE in the membrane reactor. The results showed that the oxygen flux of the membrane gradually increased from 7.4 to 11.7 ml cm⁻² min⁻¹ with the increasing of reaction temperatures from 800 to 900 °C, which can be attributed to the increase of the diffusion rate of oxygen vacancy via bulk lattice and the rate of surface exchange. In the membrane...
Table 3  Effects of ethane concentrations on oxygen permeation fluxes, C₂H₆ conversion and the selectivity of CH₄, CO₂, CO and C₂H₄ and the ratio of C₂H₆/O₂ at 850°C

<table>
<thead>
<tr>
<th>C₂H₆ concentration (%)</th>
<th>C₂H₆ conversion (%)</th>
<th>Products selectivity (%)</th>
<th>Λₒ (ml/cm² min⁻¹)</th>
<th>C₂H₆/O₂ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.31</td>
<td>100</td>
<td>57.06 41.64 1.24 0.06</td>
<td>4.32</td>
<td>0.44</td>
</tr>
<tr>
<td>19.88</td>
<td>100</td>
<td>71.98 26.20 1.34 0.08</td>
<td>6.71</td>
<td>0.58</td>
</tr>
<tr>
<td>40.21</td>
<td>99.94</td>
<td>89.01 7.18 3.51 0.3</td>
<td>9.01</td>
<td>0.87</td>
</tr>
<tr>
<td>50.29</td>
<td>99.78</td>
<td>96.88 2.24 6.18 0.7</td>
<td>9.78</td>
<td>1.01</td>
</tr>
<tr>
<td>60.18</td>
<td>99.51</td>
<td>81.68 1.48 14.86 1.98</td>
<td>10.27</td>
<td>1.18</td>
</tr>
<tr>
<td>80.28</td>
<td>96.29</td>
<td>67.03 1.40 21.67 9.90</td>
<td>10.9</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Reaction conditions: the membrane surface area is 3.562 cm², the total flow rate of He and C₂H₆ in tube side is kept constant at 60.11 ml min⁻¹, the air flow rate in shell side is 300 ml min⁻¹.

Fig. 6. Long-term test of tubular membrane reactor for POE reaction with LiLaNiO/γ-Al₂O₃ catalyst at 875°C. Reaction conditions: the membrane surface area is 3.562 cm², the flow rate of 50% He + 50% C₂H₆ in tube side is kept constant at 70.22 ml min⁻¹, the air flow rate in shell side is 300 ml min⁻¹.

The reactor, the oxygen permeation flux of the membrane directly affects the reaction performance. With the increase of the temperatures, the selectivity of CO increased rapidly, but the selectivity of C₂H₄ decreased on the contrary. At lower temperature (<875°C), the oxygen permeated is not high enough to completely convert C₂H₆ and C₂H₄ produced via thermal dehydrogenation of C₂H₆, so there is a lot of C₂H₄, which result in lower CO selectivity. At higher temperature (>875°C), the oxygen permeated is high enough to convert all of the C₂ to CO, so there is no C₂ detected in the downstream, and the selectivity of CO reached at the highest value, i.e. >90%.

Table 3 showed the effect of ethane concentrations on the reaction performance of POE and the oxygen permeation flux of the membrane at 850°C. Different ethane concentrations were adjusted by the ratios of C₂H₆/He when the total flow rate was kept at 60.11 ml min⁻¹. With increasing of ethane concentrations, the oxygen permeation flux of the membrane increased from 4.32 to 10.9 ml cm⁻² min⁻¹ due to more oxygen consumed by C₂H₆, and the selectivity of
Fig. 6 showed a 100 h long-time POE reaction in the reactor, long-term stability test is very important. As shown in Table 3, the highest CO selectivity (90.88%) was achieved, with a conversion of ethane reaching 50%, then decreased due to the increases of CO and thermal dehydrogenation product, C2H4. It was found that the optimum ratio of C2H6/O2 is 1.01, at which the CO selectivity is the highest (90.88%), as shown in Table 3. For practical application of POE in the membrane reactor, long-term stability test is very important. Fig. 6 showed 100 h long-time POE reaction in the membrane reactor. The reaction was performed at 875°C with the diluted ethane at the flow rate of 70.22 ml min⁻¹. Air feed rate was kept at 300 ml min⁻¹. It can be seen in Fig. 6, the conversion of ethane was ~100%, the selectivity CO was higher than 91%, and the oxygen permeation flux was 10–11 ml cm⁻² min⁻¹. During the 100 h run, the oxygen permeation flux and the catalytic performance of POE were kept at a stable state. We have studied POM reaction in BSCFO membrane reactor with LiLaNiO/H9253-Al2O3 for about 500 h [19]. Combined both results, we can conclude that BSCFO membrane reactor has excellent performance not only for POM but also for POE with the catalyst of LiLaNiO/H9253-Al2O3.

4. Conclusion

(1) BSCFO oxide has been synthesized by a combined and EDTA complexion method, and a dense BSCFO tubular membrane was successfully prepared by extrusion method.

(2) The membrane tube was used in a membrane reactor for POE reaction with the catalyst of LiLaNiO/H9253-Al2O3. The activation of catalyst for POE (only 30 min) in membrane reactor is much faster than that for POM (about 10 h) in the disk-type membrane reactor. After the activation of the catalyst, the oxygen permeation flux increased from 8.2 to 11.0 ml cm⁻² min⁻¹ slowly. The gradual increase of oxygen permeation flux is attributed to the membrane structure adjustment and composition change in the reaction process.

(3) There is an optimum value at C2H6/O2 ratio of 1.01, where the CO selectivity is higher than 90% and C2H4 conversion approach to 100%.

(4) The tubular membrane reactor can be operated steadily for 100 h at 875°C with ~100% C2H6 conversion and higher than 91% CO selectivity.

Acknowledgements

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