Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Catalysis Today 104 (2005) 160–167

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Oxidative coupling of methane in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ tubular membrane reactors

Haihui Wang [a,b], You Cong [a], Weishen Yang [a,*]

[a] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
P.O. Box 110, Dalian 116023, China
[b] University of Hanover, Institute of Physical Chemistry and Electrochemistry,
Callinstr. 3-3A, D-30167 Hanover, Germany

**Abstract**

A dense membrane tube made of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was prepared by plastic extrusion from BSCF oxide synthesized by the complexing EDTA-citrate method. The membrane tube was used in a catalytic membrane reactor for oxidative coupling of methane (OCM) to $C_2$ without an additional catalyst. At high methane concentration (93%), about 62% $C_2$ selectivity was obtained, which is higher than that achieved in a conventional reactor using the BSCF as a catalyst. The dependence of the OCM reaction on temperature and methane concentration indicates that the $C_2$ selectivity in the BSCF membrane reactor is limited by high ion recombination rates. If an active OCM catalyst (La-Sr/CaO) was packed in the membrane tube, $C_2$ selectivity and $CH_4$ conversion increased compared to the blank run. The highest $C_2$ yield in the BSCF membrane reactor in presence of the La-Sr/CaO catalyst was about 15%, similar to that in a packed-bed reactor with the same catalyst under the same conditions. However, the ratio of $C_2H_4/C_2H_6$ in the membrane reactor was much higher than that in the packed-bed reactor, which is an advantage of the membrane reactor.

*Keywords:* Membrane reactor; OCM; Oxygen separation; Methane conversion; Perovskite

## 1. Introduction

During the past years, extensive efforts have been devoted to both direct and indirect conversion of methane [1,2]. The direct conversion approaches involve selective oxidation of methane to methanol and formaldehyde, and oxidative coupling of methane (OCM) to $C_2$ hydrocarbons ($C_2H_6$ and $C_2H_4$) and so on. The indirect conversion requires converting methane to syngas ($CO + H_2$) either by steam reforming or partial oxidation, or by a combination of these two in a first stage, and then conversion of the syngas to a series of important chemicals by Fischer–Tropsch technology. Compared to the indirect conversion, the direct conversion is the more challenge and economic route because it does not require intermediate steps. The OCM to ethane and ethylene is one of the most important routes for direct conversion of natural gas to chemicals, and an enormous number of studies have been performed on this reaction since the pioneering work of Keller and Bhasin [3].

Most reported studies on OCM were carried out in packed-bed reactors in co-feed operation mode, i.e. methane and oxidant ($O_2$) were fed to the reactor together [4–8]. In this operation mode, the $C_2$ selectivity is low because of the total oxidation of the $C_2$ products by gaseous oxygen. Since 1990s, the research on OCM has been shifted from developing new catalysts to exploring new reactor concepts better suited for the OCM reaction mechanism. Lu et al. [9] investigated the OCM reaction in a porous $\gamma$-$Al_2O_3$ membrane reactor using a Mn-W-Na/$SiO_2$ catalyst. $C_2$ yields up to 27.5% were obtained in the membrane reactor. The experimental results clearly demonstrated the benefit of a distributed feed of oxygen along the reactor length for methane oxidative coupling reactions. For oxygen-permeable membranes, oxygen is uniformly transported through the membrane in the form of oxygen ions, so there are many

---

[*] Corresponding author. Tel.: +86 411 84379073; fax: +86 411 84694447.
*E-mail address:* yangws@dicp.ac.cn (W. Yang).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.03.079

oxygen species ($O^-$, $O_2^-$) on the membrane surface. These oxygen species may be more selective for the OCM reaction [10]. Therefore, the $C_2$ selectivity of OCM can be improved in oxygen-permeable membrane reactors. Lin and Zeng [11–13] studied the catalytic properties of oxygen semi-permeable perovskite-type and yttria-doped bismuth ceramic membrane materials for OCM. Lu et al. [14] investigated OCM in a tubular membrane reactor based on the perovskite material $BaCe_{0.8}Gd_{0.2}O_{3-\delta}$. They obtained a $C_2$ yield of about 16% with 62.5% $C_2$ selectivity. They also studied oxidative coupling of methane in a $SrFeCo_{0.5}O_{3-\delta}$ membrane reactor, where the membrane was coated with a non-combusting material $BaCe_{0.6}Sm_{0.4}O_{3-\delta}$ and obtained 7% $C_2$ yield [15]. Elshof et al. [16,17] used $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as membrane reactor material for OCM. They achieved $C_2$ selectivity up to 70%. Xu and Thomson [18] investigated OCM in a La-Ba-Co-Fe-O perovskite membrane reactor. Higher $C_2$ selectivity (up to 50%) was obtained in the membrane reactor compared to a conventional reactor. Akin and Lin [19,20] performed OCM in a tubular dense membrane reactor made of catalytically active $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ with fluorite structure. They obtained a one-pass $C_2$ ($C_2H_4 + C_2H_6$) yield of 35% with a $C_2$ selectivity of 54% at 900 °C, which is the best result for OCM so far. This result shows that oxygen-permeable membrane reactors hold promise for an application of OCM in industry.

Recently, a novel perovskite oxygen-permeable membrane of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was developed in our laboratory [21–25]. The BSCF membrane exhibits higher oxygen flux and higher oxygen vacancy concentration than $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and La-Ba-Co-Fe-O due to substitution of $La^{3+}$ by the lower valence state of $Ba^{2+}$ and $Sr^{2+}$. The higher oxygen vacancy concentration in the BSCF membrane could lead to a higher $C_2$ formation rate. On the other hand, the reported research work on OCM in oxygen-permeable membrane reactors to date mainly used disk-type membrane reactors. In our group, the OCM reaction was primarily studied in disk-type BSCF membrane reactors before [22]. In this paper, we report results on the OCM reaction obtained from a BSCF tubular membrane reactor.

## 2. Experimental

The BSCF oxide material was prepared by a complexation EDTA-citrate method [21]. The membrane tube was made by the plastic extrusion method [26]. The extruded tube was heated with a heating rate of 5 °C/h in the temperature range of 150–400 °C to remove the gaseous species formed during decomposition of the organic additives. Then, the heating rate was increased to 1 °C/min and the tube was sintered at 1100–1200 °C in stagnant air for 3–5 h. The sintered tube has an outside diameter of about 8 mm and inner diameter of about 4.5 mm. The density of the sintered tubular membranes was measured by the Archimedes method with ethanol. Only those membranes that had a relative density higher than 90% of the theoretical value were used for the OCM reaction.

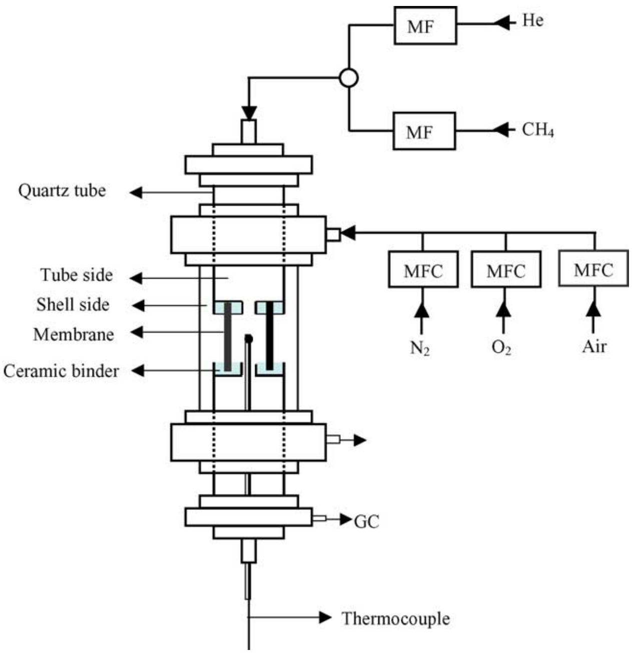

Fig. 1. Experimental set-up for the study of oxygen permeation and OCM using tubular BSCF membranes.

The OCM experiments were performed in the shell-and-tube reactor shown in Fig. 1. The membrane tube was connected to a quartz tube ($\Phi = 17$ mm) with a ceramic glass powder (Keramik-Glasur, UHLIG, Germany). Another quartz tube ($\Phi = 29$ mm) served as shell side tube of the reactor. A thermocouple was put along the axis of the membrane tube to profile the temperature along the reactor. A mixture of methane and helium was fed into the tube, while air (or a mixture of oxygen and nitrogen) was fed to the shell side. Before the mixture of methane and helium was fed to the shell side, pure helium was fed to the shell side to check the sealing efficiency. The products were analyzed by an on-line gas chromatograph (HP6890) with a porapak Q column and a 13X column. The gas chromatograph was equipped with two automatic valves, a sample valve and a bypass valve, and the HP Chemstation computer software was used for data collection and analysis. A serial/bypass configuration was arranged for two isothermal columns (80 °C), porapak Q and molecular sieve 13X. Details of the analytical method can be found in [26]. The oxygen permeation flux during the OCM reaction was calculated from the measured flow rates and the mole fractions of the oxygen-containing product gases, such as CO, $CO_2$, $O_2$ and $H_2O$. The carbon balance during all experiments was within 95%. If air leaked through the membrane or the sealing, the nitrogen signal was subtracted for calculation of the oxygen permeance. Leakage was less than 2% for all samples.

The La-Sr/CaO catalyst was prepared by an impregnation method. In brief, CaO was preheated to 900 °C overnight. A mixed solution of 10% $La(NO_3)_3$ and 20% $Sr(NO_3)_2$ was added slowly to the CaO, while stirring with a glass rod to form a paste. The paste was heated to 800 °C for 6–8 h. Then the powder was pelletized, crushed and sieved into 20–40 mesh. A 0.45 g of a La-Sr/CaO catalyst were loosely packed into the membrane tube. A catalytic experiment with the La-Sr/CaO catalyst in a packed-bed reactor was also conducted as a basis for comparison with the membrane reactor results. A quartz tube ($\Phi = 6$ mm) was used for the packed-bed reactor, 0.45 g of catalyst were packed into the quartz tube. The oxygen amount fed to the packed-bed reactor was equal to the oxygen permeation flux of the membrane at the indicated temperature under OCM conditions.

## 3. Results and discussion

The OCM in the dense BSCF membrane tube without catalyst was investigated at first. After sealing at high temperature, the furnace was cooled down to the indicated temperature, then air (or a mixture of $N_2$ and $O_2$) was fed to the shell side and a mixture of $CH_4$ and helium was introduced to the tube side. The species detected in the products were $C_2H_4$, $C_2H_6$, $H_2O$, $CO_2$, $O_2$ and CO. The OCM reaction in the dense oxygen permeation membrane reactor can be explained by the mechanism shown in Fig. 2. The following reaction occurs on the membrane surface exposed to the air:

$$O_{2g} + 2V_o^{\bullet\bullet} \Leftrightarrow 2O_o^x + 4h^{\bullet} \qquad (A)$$

At high temperature, lattice oxygen ($O_o^x$) and electron holes ($h^{\bullet}$) may be transported through the membrane to the other side of the membrane (surface exposed to methane) and react there with methane. Local charge neutrality is maintained by joint diffusion of oxygen vacancies and electrons on the surface exposed to air. The reactions occurring on the membrane surface exposed to methane may be described by the paths:

$$CH_4(g) \Leftrightarrow CH_4(s) \qquad (B)$$

$$2CH_4(s) + O_o^x + 2h^{\bullet} \Leftrightarrow 2CH_3^{\bullet} + H_2O + V_o^{\bullet\bullet} \qquad (C)$$

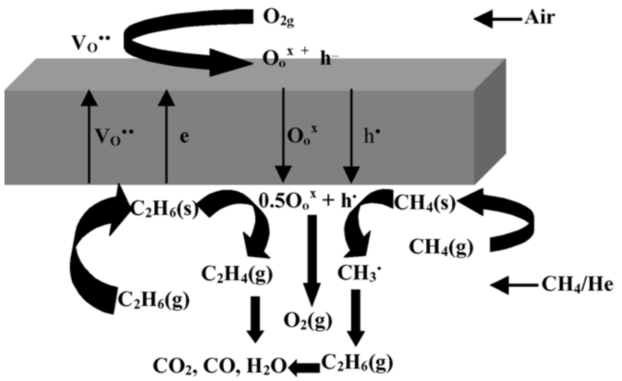

Fig. 2. Possible mechanism of OCM in the BSCF membrane reactor.

$$2CH_3^{\bullet} \rightarrow C_2H_6 \qquad (D)$$

After combining reactions (B)–(D), we can get the following equation:

$$2CH_4(g) + O_o^x + 2h^{\bullet} \rightarrow C_2H_6 + H_2O + V_o^{\bullet\bullet} \qquad (E)$$

Therefore, the ethane formation rate can be expressed as:

$$r_{C_2H_6} = k_E[CH_4]^2P^2 \qquad (1)$$

where $[CH_4]$ is the methane concentration in the gas phase and $P$ is the electron hole concentration on the membrane surface exposed to methane.

Since reaction (D) is a fast irreversible reaction, the reaction constant of reaction (E), $k_E$ is determined by reactions (B) and (C):

$$k_E = k_B \times k_C \qquad (2)$$

where $k_B$ and $k_C$ are the total reaction constants of the reactions (B) and (C), respectively, after they got equilibrated.

Furthermore, the produced ethane can also be converted to ethylene by the following paths:

$$C_2H_6(g) \Leftrightarrow C_2H_6(s) \qquad (F)$$

$$C_2H_6(s) + O_o^x + 2h^{\bullet} \Leftrightarrow C_2H_4 + H_2O + V_o^{\bullet\bullet} \qquad (G)$$

If the reactions (C) and (G) cannot consume all of the lattice oxygen ($O_o^x$) completely, or the reaction rates of (C) and (G) are not fast enough to consume the lattice oxygen in time, the following reaction can occur:

$$2O_o^x + 4h^{\bullet} \rightarrow O_2 + 2V_o^{\bullet\bullet} \qquad (H)$$

Therefore, on the membrane surface exposed to methane lattice oxygen ($O_o^x$) is competitively consumed by three reactions: methane activation (reaction (C)), ethane activation (reaction (G)) and recombination of oxygen ions (reaction (H)). Because the gaseous oxygen produced in reaction (H) could further react with methyl radicals and $C_2$ to form $CO_x$, a high oxygen ion flux can increase OCM activity, but does not necessarily improve the $C_2$ selectivity.

Fig. 3 shows the effect of the oxygen partial pressure in the shell side on the OCM reaction at 850 °C. The flow rate of a mixture of 10% $CH_4$ and 90% He was kept constant at 100.22 ml/min. The total flow rate of $O_2$ and $N_2$ in the shell side was 300 ml/min and different oxygen partial pressures were obtained by adjusting the ratio of $N_2/O_2$. As shown in Fig. 3, with increasing oxygen partial pressure, the oxygen permeation flux increased, which lead to an increase of $CH_4$ conversion and to a moderate decrease of $C_2$ selectivity. This indicates that the non-selective gas phase reactions played an important role in the BSCF membrane reactor. Kao et al. [27] found that lowering the membrane permeability improves the performance. Higher oxygen feed pressure reduced the yield as well as the selectivity to $C_2$ products.

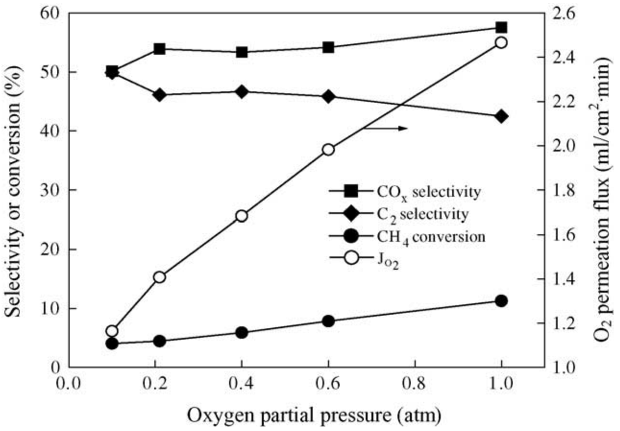

Fig. 3. Influence of the oxygen partial pressure on OCM performance in the tubular BSCF membrane reactor. Flow rate: mixture of 10% $CH_4$ and 90% He = 100.22 ml/min, mixture of $N_2$ and $O_2$ = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 11.17 mm, membrane surface area = 1.599 cm$^2$.

Fig. 4 shows the temperature-dependence of the OCM reaction in the BSCF tubular membrane reactor. A mixture of 10% $CH_4$ and 90% He was fed to the tube side at a flow rate of 100.22 ml/min. As shown in Eq. (1), the ethane formation rate can be improved by increasing the methane concentration and the electron hole concentration on the membrane surface. Since the methane concentration in the gas phase is almost constant during experiments at different temperatures, the reaction rate is mainly determined by the electron hole concentration, i.e. the oxygen permeation rate through the membrane. As shown in previous research [22], the oxygen permeation rate increases with increase of temperature. Therefore, the OCM reactivity on the membrane surface also increases with increase of temperature. As shown in Fig. 4, the $C_2$ formation rate increased with increase of temperature.

Machin et al. [28] pointed out that the surface methyl radical generation reaction (reaction (C)) is temperature-dependent and dramatically slower than the temperature-independent radical coupling reaction (reaction (D)) in the gas phase. Based on their observations it can be inferred that, in the absence of combustion, the $C_2$ formation rate is limited by the generation rate of methyl radicals (reaction (C)) and can be increased by increasing the temperature. In our experiments, a large amount of oxygen was released into the gas phase, which could react with the methyl radicals and $C_2$ species to form $CO_x$, thus lowering the $C_2$ selectivity. So, the $C_2$ selectivity is determined by competition of the combustion and OCM reactions. As shown in Fig. 4, the $C_2$ selectivity increased with increasing temperature in the range below 825 °C. However, for $T > 825$ °C, the $C_2$ selectivity decreased with increasing temperature. This result indicates that the combustion rate increases faster than the OCM rate at temperatures higher than 825 °C. Between 800 and 900 °C, the $C_2$ selectivity was 38–52% and the conversion of methane varied between 2 and 14%. However, the $C_2$ selectivity was only about 20–30% in the packed-bed reactor using BSCF as catalyst (conditions: $CH_4/O_2 = 3:1$, total flow of $CH_4$ and $O_2$ of 100 ml/min, catalyst amount 0.6 g). Compared to the packed-bed reactor, the $C_2$ selectivity obtained in the membrane reactor was higher, so it seems that the membrane reactor was favorable for $C_2$ formation.

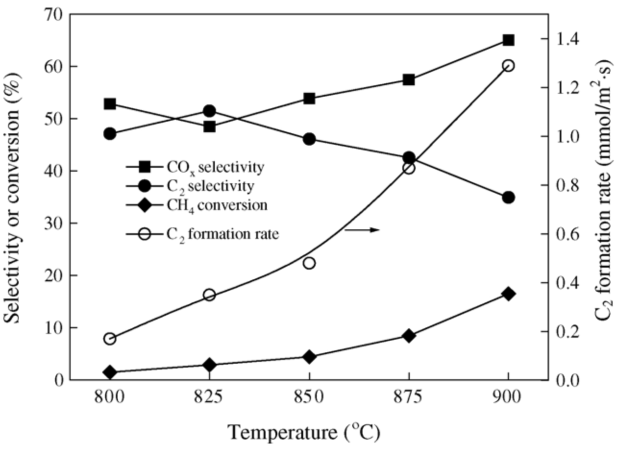

Fig. 4. Influence of temperature on OCM performance in the tubular BSCF membrane reactor. Flow rate: mixture of 10% $CH_4$ and 90% He = 100.22 ml/min, air = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 11.17 mm, membrane surface area = 1.599 cm$^2$.

Fig. 5 shows the effect of the methane concentration on the OCM reaction at 850 °C. The total flow of $CH_4$ and He was 100.22 ml/min, different methane concentrations were achieved by adjusting the ratio of $CH_4$/He. According to Eq. (1), the $C_2H_6$ formation rate can also be enhanced by increasing the methane concentration in the gas phase at constant temperature. As we expected, the $C_2$ formation rate increased with increasing methane concentration (in Fig. 5a). At a methane concentration of 93%, the $C_2$ formation rate reached 1.7 mmol/s m$^2$, which is a much higher value than for the $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) membrane (~0.27 mmol/s m$^2$) and $La_{0.8}Ba_{0.2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LBCF) membrane (~0.02 mmol/s m$^2$) reported by Elshof et al. [16,17]. The higher $C_2$ formation rate of the BSCF membrane was due to the following reason. The substitution of $La^{3+}$ in LSCF and LBCF with lower valence metal ions, such as $Ba^{2+}$ and $Sr^{2+}$, usually leads to an increase of the oxygen vacancy concentration in the membranes. The higher oxygen vacancy concentration not only promotes oxygen ion transport through the membrane, but also increases the activation of methane molecules. Therefore, the BSCF membrane exhibits a better performance for the OCM than the LSCF and the LBCF membranes.

As shown in Fig. 5b, the $C_2$ selectivity enhanced from 47 to 62% when the methane concentration was increased from 10 to 93%. Note that the oxygen concentration detected in the product stream (shown in Fig. 5b) increased, while the $C_2$ selectivity decreased as the $CH_4$ concentration was reduced. This result means that low methane pressures could lower the OCM reaction rate and be beneficial for the recombination rate of oxygen ions. So there is more oxygen

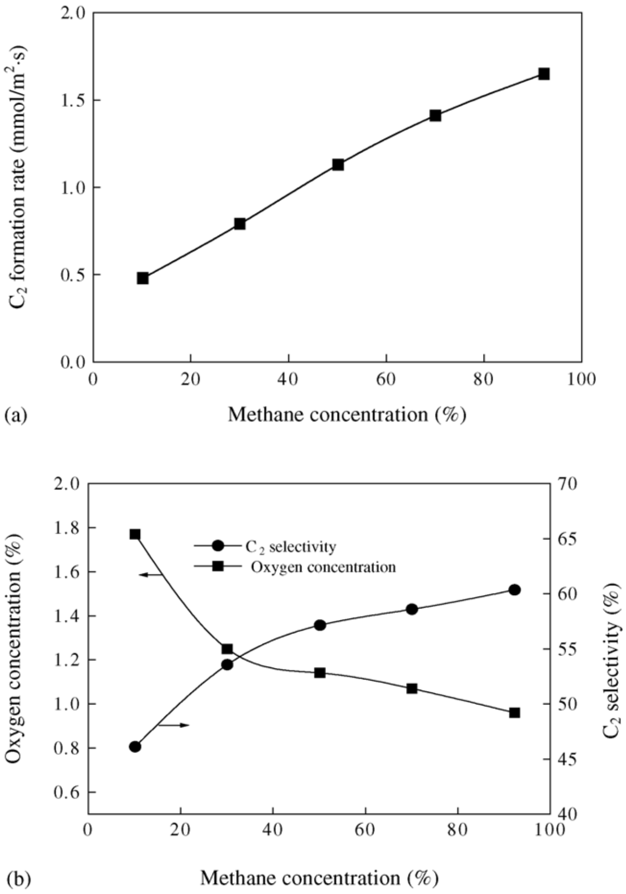

Fig. 5. Dependence of $C_2$ selectivity, $C_2$ formation rate and oxygen concentration in the product stream on methane concentration at 850 °C. Flow rate: mixture of $CH_4$ and He = 100.22 ml/min, air = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 11.17 mm, membrane surface area = 1.599 cm$^2$.

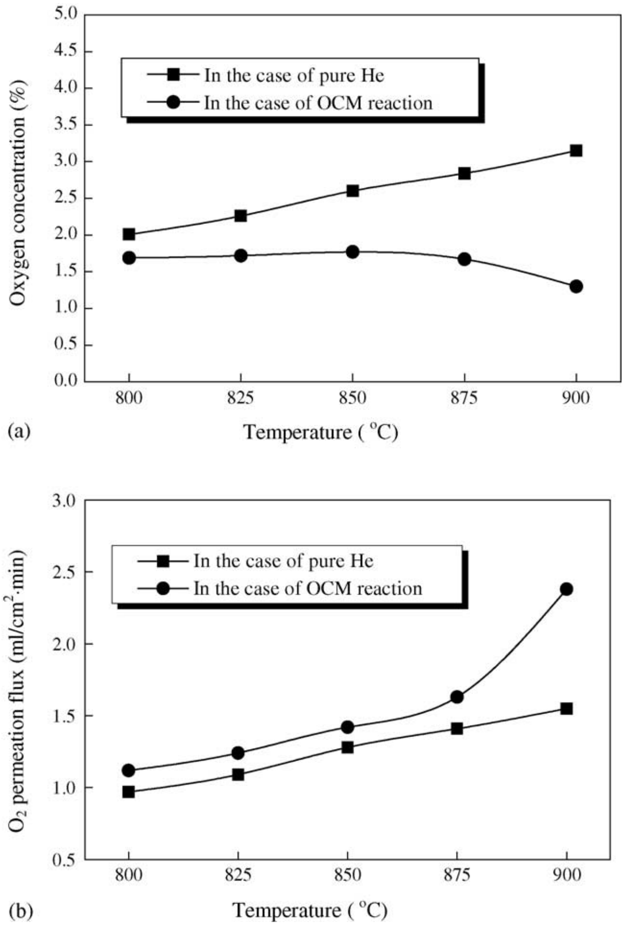

Fig. 6. Dependence of the oxygen concentration in the tube side and the oxygen permeation flux on temperature for OCM conditions and pure He sweep gas. Flow rate: mixture of $CH_4$ and He or pure He = 100.22 ml/min, air = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 11.17 mm, membrane surface area = 1.599 cm$^2$.

in the gas phase, which can combust the $C_2$ products and lower the $C_2$ selectivity.

Xu and Thomson [18] investigated OCM in an oxygen-permeable membrane reactor made of LBCF. They found that the oxygen flux under OCM conditions is higher by a factor of three to four compared to the case of pure helium as sweep gas at 1153 K. They attributed this to surface ion coupling limiting the oxygen ion transport. Zeng and Lin [13] found that the oxygen permeation flux during OCM in a BY25 membrane reactor was larger than that with pure helium as sweep gas. They concluded that the larger oxygen partial pressure gradient in the OCM case leads to a higher oxygen permeation flux. In our experiments, the oxygen permeation flux in the OCM case improved only modestly when compared to that in the pure helium case. These results are consistent with that of Elshof et al. [16] for a LSCF membrane reactor. Fig. 6 shows the temperature-dependence of the oxygen permeation flux and the oxygen partial pressure in the product stream for the cases of OCM and pure helium sweep gas, respectively. As shown in Fig. 6a, the oxygen partial pressure in the product stream in the OCM case is only slightly lower than that in the pure helium case. So the oxygen permeation flux in the OCM case is only slightly improved compared to that in the pure helium case (shown in Fig. 6b). These results could be reasonably understood by considering that the oxygen partial pressure in the membrane tube in the OCM case was in the same range as that in the pure helium case, which leads to the same driving force for oxygen transport. Apparently, a rather large amount of oxygen exits with the product stream, which indicates that the oxygen ion recombination reaction (reaction (H)) rate is by far faster than methane activation (reaction (C)) on the membrane surface. Furthermore, the gaseous oxygen produced accelerates the non-catalytic gas phase methane combustion leading to the decrease of the $C_2$ selectivity. The $C_2$ selectivity and yield might be improved by packing an active OCM catalyst on the membrane surface.

La-Sr/CaO, which is an active catalyst for OCM, was chosen as the catalyst. Compared to the membrane reactor without catalyst, there was no oxygen detected in the product stream. The results of the packed-bed reactor, the membrane reactor without La-Sr/CaO and the membrane reactor with

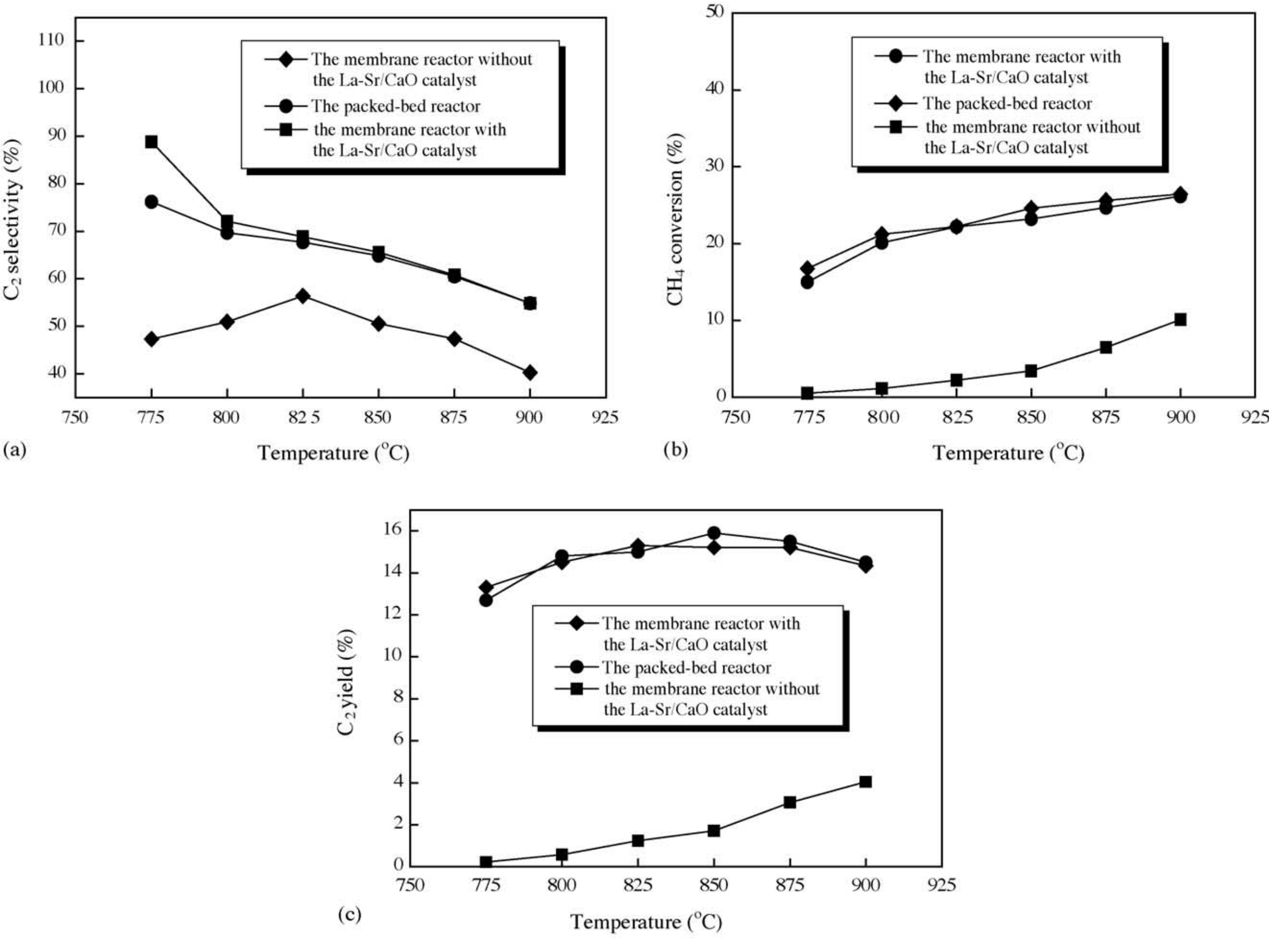

Fig. 7. Comparison of C$_2$ selectivity, CH$_4$ conversion and C$_2$ yield for packed-bed reactor, membrane reactor without catalyst and membrane reactor with La-Sr/CaO catalyst. (a) C$_2$ selectivity, (b) CH$_4$ conversion and (c) C$_2$ yield. Flow rate: CH$_4$ = 20.67 ml/min, He = 79.75 ml/min, air = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 15.94 mm, membrane surface area = 2.282 cm$^2$.

the La-Sr/CaO catalyst are shown in Fig. 7a–c. It can be seen that between 775 and 900 °C 54–88% C$_2$ selectivity and 13–15% C$_2$ yield were achieved in the membrane reactor with the La-Sr/CaO catalyst, while 40–55% C$_2$ selectivity and only 4% C$_2$ yield were obtained in the membrane reactor without the La-Sr/CaO catalyst. The introduction of the La-Sr/CaO catalyst apparently improves the OCM results (C$_2$ selectivity and CH$_4$ conversion). Compared to the packed-bed reactor under the same conditions, the membrane reactor with catalyst gave a higher C$_2$ selectivity at lower temperature ($<$800 °C), while it reached a similar C$_2$ selectivity at higher temperature ($>$800 °C) (shown in Fig. 7a). As shown in Fig. 7c, the C$_2$ yields obtained in the membrane reactor with the La-Sr/CaO catalyst were about 13–15%, which is much higher than those reported previously for dense membrane reactors [16–18]. However, the C$_2$ yield obtained in the membrane reactor with the La-Sr/CaO catalyst was similar to that achieved in the packed-bed reactor under the same conditions. Although C$_2$ yield and C$_2$ selectivity (especially for $T > 800$ °C) in the membrane reactor with the La-Sr/CaO catalyst were not improved compared to those in the packed-bed reactor with the La-Sr/CaO catalyst under the same conditions, the distribution of the C$_2$ products differed greatly in the two reactors.

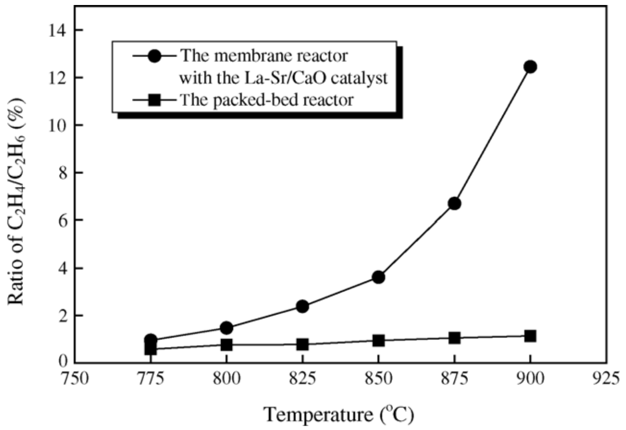

Fig. 8. Comparison of the C$_2$H$_4$/C$_2$H$_6$ ratio obtained in the membrane reactor and in the packed-bed reactor in presence of the La-Sr/CaO catalyst. Flow rate: CH$_4$ = 20.67 ml/min, He = 79.75 ml/min, air = 300 ml/min; outer diameter = 7.96 mm, inner diameter = 4.56 mm, length = 15.94 mm, membrane surface area = 2.282 cm$^2$.

Table 1
Typical values of the $C_2H_4/C_2H_6$ ratio reported for OCM in literature

| Catalyst or membrane | Temperature (°C) | $C_2H_4/C_2H_6$ ratio | References |
|---|---|---|---|
| Li/MgO (co-feed reactor) | 850 | 3.7 | [29] |
| W-Mn-Si (co-feed reactor) | 900 | 2.6 | [30] |
| $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ (membrane reactor) | 850 | 1.4 | [31] |
| BY25 (membrane reactor) | 900 | 4 | [12,13] |
| $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (membrane reactor) | 850 | 1.5 | [32] |
| BSCF (membrane reactor) | 900 | 12.45 | Present work |

Fig. 8 shows the temperature effect on the $C_2H_4/C_2H_6$ ratio in the $C_2$ products. The $C_2H_4/C_2H_6$ ratio in the packed-bed reactor with the La-Sr/CaO catalyst was almost constant at 1.0, but the $C_2H_4/C_2H_6$ ratio in the membrane reactor with the La-Sr/CaO catalyst increased exponentially with increasing temperature and reached a value of 12.0 at 900°C. Since $C_2H_4$ is more valuable than $C_2H_6$, we can say the membrane reactor with catalyst performs better than the packed-bed reactor. It is important to note that the $C_2H_4/C_2H_6$ ratio obtained in our experiments is much higher than those reported in literature, as shown in Table 1.

## 4. Conclusion

When the BSCF membrane tube was employed as a reactor for the OCM reaction without catalyst, the $C_2$ selectivity had 20% increase compared to the packed-bed reactor using BSCF as catalyst. There were large amounts of gaseous oxygen detected in the product stream, which caused the oxygen permeation flux to increase only slightly compared to the pure helium case. A higher oxygen concentration in the product stream also lowered the $C_2$ selectivity, so the highest selectivity was only 62%. The $C_2$ selectivity limitation may be due to the higher oxygen ion recombination rate (i.e. reaction (H) is faster), which is not only competes with the surface methane activation (reaction (C)), but also leads to the formation of gaseous oxygen and subsequent $C_2$ combustion. The $C_2$ formation rate increased with increasing temperature, while the $C_2$ selectivity decreased with increasing temperature at temperatures higher than 825 °C. This indicates that the oxygen ion recombination reaction (reaction (H)) rate increased faster than the methane activation reaction (reaction (C)) above 825 °C. As we expected, not only the $C_2$ formation rate, but also the $C_2$ selectivity increased with increasing methane concentration.

When the BSCF membrane tube was packed with an active OCM catalyst (La-Sr/CaO), both $C_2$ selectivity and $CH_4$ conversion were improved. About 13–15% $C_2$ yield and 54–88% $C_2$ selectivity were obtained. Although the $C_2$ yield in the membrane reactor with the La-Sr/CaO catalyst was similar to that in a packed-bed reactor under the same conditions, the $C_2H_4/C_2H_6$ ratio in the membrane reactor with the La-Sr/CaO catalyst was much higher than that in the packed-bed reactor.

## Acknowledgements

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant No. 50332040). H. Wang greatly thanks the financial support from the Alexander von Humboldt Foundation.

## References

[1] N.D. Spenser, C.J. Pereiva, J. Catal. 116 (1989) 399.
[2] H.D. Gesser, N.R. Hunter, Chem. Rev. 85 (1985) 235.
[3] G.E. Keller, M.M. Bhasin, J. Catal. 73 (1982) 9.
[4] G.T. Baronetti, O.A. Padro, A.A. Scelza, V.C. Castro, Appl. Catal. A 101 (1993) 167.
[5] O.V. Buyevskaya, M. Rothaemel, H.W. Zanthoff, M. Baems, J. Catal. 150 (1994) 71.
[6] V.R. Choudhary, V.H. Rane, R.V. Gadre, J. Catal. 145 (1994) 300.
[7] S. Lacombe, H. Zanthoff, C. Mirodatos, J. Catal. 155 (1995) 106.
[8] Y.S. Lin, Y. Zeng, J. Catal. 164 (1996) 220.
[9] Y.P. Lu, A.G. Dixon, W.R. Moser, Y.H. Ma, Chem. Eng. Sci. 55 (21) (2000) 4901.
[10] J.H. White, E.A. Needham, R.L. Cook, A.F. Sammells, Solid State Ionics 53–56 (1992) 149.
[11] Y. Zeng, Y.S. Lin, AIChE J. 47 (2001) 436.
[12] Y. Zeng, Y.S. Lin, J. Catal. 182 (1999) 30.
[13] Y. Zeng, Y.S. Lin, J. Catal. 193 (2000) 58.
[14] Y.P. Lu, A.G. Dixon, W.R. Roser, Y.H. Ma, U. Balachandran, J. Membr. Sci. 170 (2000) 27.
[15] Y.P. Lu, A.G. Dixon, W.R. Roser, Y.H. Ma, U. Balachandran, Catal. Today 56 (2000) 297.
[16] J.E. Elshof, H.J.M. Bouwmeester, H. Verweij, Appl. Catal. A 130 (1995) 195.
[17] J.E. Elshof, B.A. Hassel, H.J.M. Bouwmeester, Catal. Today 25 (1995) 397.
[18] S.J. Xu, W.J. Thomson, AIChE J. 43 (1997) 2731.
[19] F.T. Akin, Y.S. Lin, AIChE J. 48 (10) (2002) 2298.
[20] F.T. Akin, Y.S. Lin, Catal. Lett. 78 (2002) 239.
[21] Z.P. Shao, W.S. Yang, Y. Cong, H. Dong, J.H. Tong, G.X. Xiong, J. Membr. Sci. 172 (2000) 177.
[22] Z.P. Shao, H. Dong, G.X. Xiong, Y. Cong, W.S. Yang, J. Membr. Sci. 183 (2001) 181.
[23] H.H. Wang, Y. Cong, W.S. Yang, Catal. Today 82 (2003) 157.
[24] H.H. Wang, Y. Cong, W.S. Yang, J. Membr. Sci. 210 (2002) 259.
[25] H.H. Wang, Y. Cong, W.S. Yang, Chem. Commun. 14 (2002) 1468.
[26] H.H. Wang, Y. Cong, W.S. Yang, J. Membr. Sci. 209 (2002) 143.

[27] Y.K. Kao, L. Lei, Y.S. Lin, Catal. Today 82 (2003) 255.

[28] I.P. Machin, D.V. Pereira, F. Rosa, ACS Preprints Symposia 37 (1) (1992) 173.

[29] T. Itoh, J.X. Wang, C.H. Lin, J.H. Lundford, J. Am. Chem. Soc. 107 (1985) 5026.

[30] X.P. Fang, S.B. Li, J.Z. Li, Y.L. Zhe, J. Mol. Catal. 6 (1992) 127.

[31] C.B. Alcock, J.J. Carberry, R. Dashi, N. Gunasekaran, J. Catal. 143 (1993) 533.

[32] K. Omata, O. Yamazaki, K. Tomita, K. Fumjimoto, J. Am. Chem. Soc. Chem. Commun. (1994) 1647.