Oxidative Coupling of Methane in Dense Ceramic Membrane Reactor with High Yields

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Oxidative coupling of methane (OCM) was studied with dense tubular $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ *(BYS) membranes at various temperatures (870–930°C). BYS powders were synthesized by a citrate method. Tubular-shaped dense membranes of BYS in the fluorite-type FCC phase structure were fabricated by cold isostatic pressing with green machining. The best one-pass* C_2 $(C_2H_4 + C_2H_6)$ *yield achieved for OCM in the BYS dead-end membrane reactor was 35% at a* C_2 *selectivity of 54% at 900°C. At the same* C_2 *yield, the membrane reactor mode gives* C_2 *selectivity of over 200% higher than the cofeed mode in the same membrane reactor under similar conditions. The oxygen permeation fluxes through tubular BYS membrane reactors under OCM reaction conditions are approximately 1.5 to 3.5 times higher than those under oxygen permeation conditions with He as the purge. After 6 days of OCM, BYS membrane remained in good integrity with minor phase segregation observed at the reaction side of the membrane.*

Introduction

Natural gas, containing primarily ($>95\%$) methane, is a natural resource that rivals liquid petroleum in abundance (Lunsford, 2000). With inevitable depletion of liquid petroleum and a concomitant increase in natural gas reserves, it is expected that methane will eventually become a major resource for chemicals and liquid fuels. Both direct and indirect routes have been studied for converting methane to chemicals and liquids. The indirect route relies on the production of synthesis gas (H_2 and CO mixture) by steam reforming or partial oxidative reaction of methane, followed by a conversion of the synthesis gas to higher hydrocarbons by the Fischer Tropsch process. The representative method in the direct route is oxidative coupling of methane (OCM) to ethane and ethylene, a feedstock for synthesis of liquid fuels or a large number of synthetic materials.

In OCM, CH_4 and O_2 react over a catalyst, mostly oxides, at elevated temperatures to form C_2 products (ethane and ethylene). However, the reaction often leads to the formation of the thermodynamically more favored CO_2. Extensive research in the 1980s and early 1990s was reported on a variety of catalysts that could kinetically control the reaction for enhancing the C_2 selectivity and yield after the pioneering work of Keller and Bhasin (1982). It is generally agreed that OCM on an oxide catalyst follows a unique heterogeneous-homogeneous reaction mechanism: methyl radicals are generated on the solid surface and coupled to form C_2 in the gas phase. The CO_2 is formed by oxidizing carbon containing species mostly in the gas phase, and possibly also on the catalyst surface. The inherent problem with the OCM is that oxygen required for OCM can react with CH_4 and C_2 product to form CO_2 and a higher selectivity is always compromised with a lower activity (or conversion). Therefore, per-pass C_2 yield on all catalysts reported was limited to about 25% (Lunsford, 2000). This is lower than the economically attractive C_2 yield threshold (30%).

The research progress on OCM catalysis has lagged since the beginning of the 1990s due to the failure on obtaining a higher C_2 yield on all catalysts reported. However, the past decade has seen substantial efforts in developing new reactor configurations, such as a simulated countercurrent moving-bed reactor (Tonkovich et al., 1993) and a gas recycled electrocatalytic reactor (Jiang et al., 1994), for OCM with the aim of obtaining a C_2 yield higher than 30%. These processes couple a separation unit with the reactor, allowing OCM re-

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action to take place at a high selectivity and low conversion. High overall, not per-pass, C_2 yields (> 30%) were achieved, but the conversion of the methane per pass was actually kept very low. The use of a separation unit in the reactor and recycling of a large amount of the reactants or products make the process more complicated and economically less attractive. In another configuration oxygen was distributed along the reactor to maintain low oxygen concentration in the reactor (Choudray et al., 1989; Reyes et al., 1993). Low local oxygen concentration in the reactor should favor the desired reaction and, thus, improve the selectivity at a given conversion. However, the requirement of a low oxygen concentration in the gas phase did not allow attaining substantial conversion levels to obtain high yields. A special configuration uses membrane reactors with a dense and catalytically active inorganic membrane that is semipermeable only to oxygen.

Membrane reactors have the potential to advance the process industry by enhancing selectivity and yield, reducing energy consumption, improving operation safety, and miniaturizing the reactor system. Membrane reactors have traditionally been studied as a means of improving the yield of the reactions of limited conversion by removing one of the products from the reactor. OCM represents a large group of chemical reactions with a selectivity, not conversion, problem. Thus, studies on OCM in inorganic membrane reactors may not only lead to a breakthrough in obtaining a higher C_2 yield for the important OCM reaction, but also improve our understanding of the reaction mechanism. For example, membrane reactors may shed light on the homogeneous-heterogeneous reaction mechanism of OCM, which has been an area of debate. In addition to that OCM studies on inorganic membrane reactors may also improve our understanding of the new type of membrane reactors for the large number of partial oxidative reactions.

Over the past decade, several groups studied OCM in membrane reactors made of either a catalytically inert porous or dense membrane tube (packed with a regular OCM catalyst) which serves as an oxygen distributor (Coronas et al., 1994; Tonkovich et al., 1996; Lu et al., 2000) or a catalytically active membrane which changes the OCM reaction mechanism and minimizes the presence of the gas-phase oxygen in the methane stream (Nozaki et al., 1994; ten Elshof et al., 1995; Xu and Thomson, 1997; Zeng et al., 1998; Shao et al., 2001; Zeng and Lin, 1999). However, in these studies per-pass C_2 yields obtained were around 3–15%. The inability to obtain a higher C_2 yield for OCM in these membrane reactors is due to problems inherent to the membrane reactors studied, such as poor membrane surface catalytic properties and unfavorable reactor configuration. To obtain a high C_2 yield for OCM, we designed a new membrane reactor with a large permeation surface area to volume ratio. The OCM experiments are performed under the conditions that the oxygen consumption rate matches the oxygen permeation rate to minimize the presence of oxygen in the gas phase.

The new membrane reactor that we report here is made of a catalytically active fluorite structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (abbreviated as BYS) membrane tube. δ-Phase Bi_2O_3 based materials are catalytically active and selective for OCM. However, under a reducing environment, these materials undergo reduction and phase changes, and, thus, lose their catalytic properties for OCM. In our search for a better catalyst we found that doping a given amount of Y and Sm into the structure stabilized the δ-phase under a reducing environment at a wider temperature range. We recently found that BYS is highly oxygen permeable, catalytically active and selective for OCM, and chemically and mechanically stable under OCM conditions (Zeng and Lin, 2001). In this article we will report on the performance of the membrane reactor that achieves per-pass C_2 yields exceeding the economic breakthrough value of 30%.

Experimental Studies

Preparation and characterization of dead-end tubular BYS membranes

The $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) powder was prepared using the citrate method. In this method, stoichiometric amounts of $Bi(NO_3)_3 5H_2O$ (98% Fischer), $Y(NO_3)_3 6H_2O$ (99.5%, Alfa), and $Sm(NO_3)_3 6H_2O$ (99.5%, Alfa) were first fully dissolved in a 10 vol. % nitric acid solution, followed by the addition of citric acid. The obtained solution was heated while stirring to 100°C. After the system was isothermally refluxed and stirred for about 3 h, water was evaporated until a gel-like material was formed. This gel-like substance was then self-ignited at 400°C and calcined at 600°C for 5 h. The obtained powder was ground in an agate mortar before being used for the processing of dead-end tubular membranes.

Dead-end tubular BYS membranes were prepared by cold isostatic pressing (CIP) with the green machining method. The BYS powder was first pressed into cylindrical rods of 3–5 cm high, 6–8 mm diameter. Carbide bits of 4.2–4 mm diameter were used to drill the rods into dead-end geometry. Dead-end tubes were then sintered at 1,050°C for 20 h and annealed at 850 and 600°C for 2 h. The phase structure of the membrane samples was characterized by XRD (Philips Analytical Xpert, CuKα) with a 2θ scan from 20 to 70° with steps of 0.05°. Fresh BYS membrane was ground to fine powder for XRD analysis. XRD analysis was also conducted with a slit size of 1 mm for X-ray beam on the inner and outer surfaces of a membrane piece taken from the middle section of a BYS membrane after being used in the membrane reactor for OCM reaction for 6 days at 900°C. The membrane surface compositions after OCM were analyzed by energy dispersive X-ray (EDX, Oxford ISIS).

Membrane reactor setup and OCM experiments

The experiments were carried out in a laboratory membrane reactor. Before the OCM experiments, the dead-end BYS membrane tube was sealed onto the mullite tube (13 mm OD, 5 mm ID, Coors Ceramics Co.) in which a dense alumina tube (3.3 mm OD, Alfa) passes through. The whole system was sited in a quartz tube (15 mm ID, Custom Glassblowing of Louisville), which served as the shell side in the reactor operation, as shown in Figure 1. The 4 mm step in the mullite tube serves as a holder for both the seal material and the membrane. The sealing material consisted of: 45 wt. % BYS powder (unsintered) used to prepare the membrane, 25 wt. % $SrCe_{0.95}Tb_{0.05}O_3$, 10 wt. % Pyrex glass, 10 wt. % $NaAlO_2$ and 10 wt. % B_2O_3. To seal the BYS membrane onto the mullite tube, first the contact faces of mullite and the BYS tube were cleaned and wetted with water. A uni-

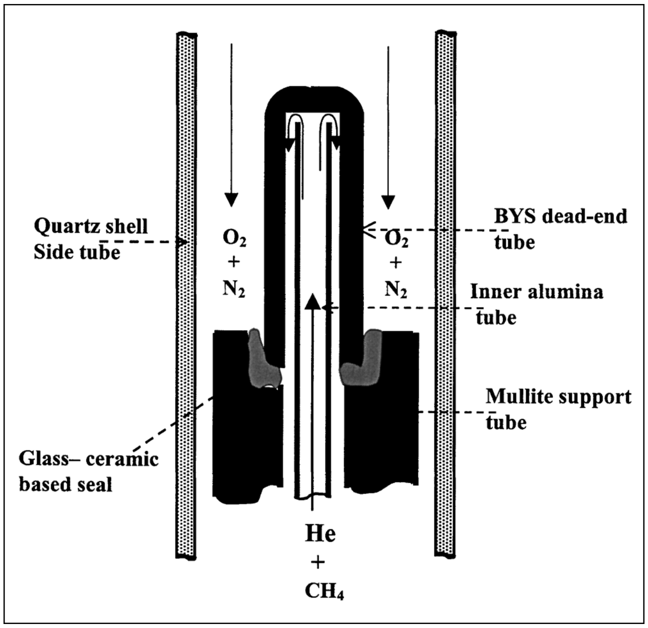

Figure 1. Dead-end tubular membrane.

form seal paste layer was put around the contact face of the support tube held in a vertical position outside the permeation/reaction system. After the seal was dried in a room atmosphere for 2 h, the support tube with the membrane was installed into the permeation/reaction system, as shown in Figure 2. The membrane reactor was surrounded by a clamshell type furnace allowing a maximum temperature of 1,000°C (see Figure 3). The sealant remained intact for as long as one week under OCM conditions.

Two different types of OCM experiments were carried out in the BYS dead-end tubular membrane reactor: membrane mode and co-feed mode. The membrane dimensions and experimental conditions for OCM are summarized in Table 1. In the membrane mode, nitrogen/oxygen mixture and methane/helium mixtures were respectively introduced to both sides of the membrane, as illustrated in Figure 1. OCM experiments in the BYS membrane reactor were conducted at different temperatures (930–870°C), CH_4-He feed flow rates (3–15 cm^3/min), oxygen partial pressure in the shell side (5.1–51 kPa), and CH_4 partial pressure in the tube side (1.6 to 10.1 kPa).

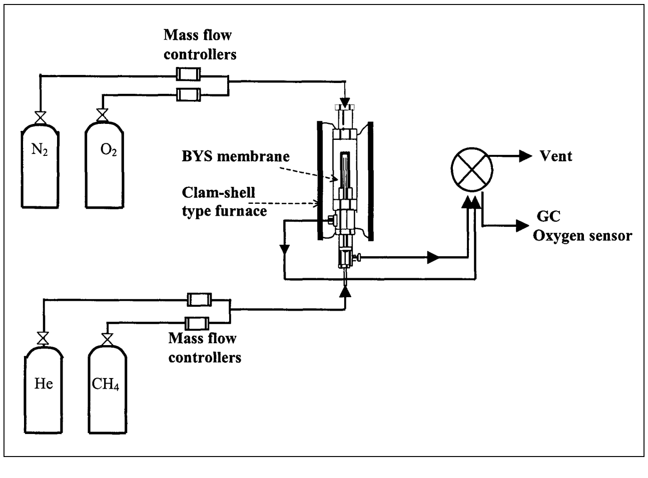

Figure 2. Membrane reactor system.

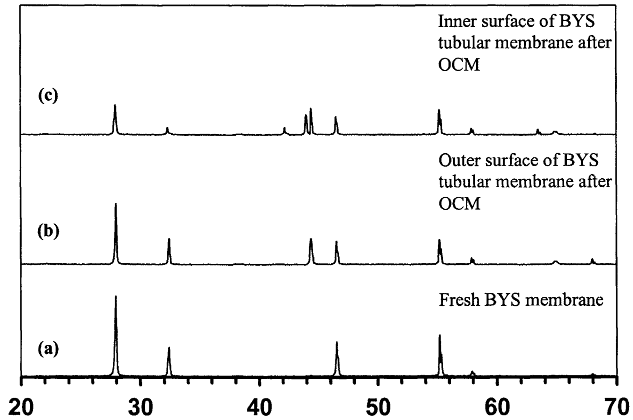

Figure 3. XRD pattern of the BYS membrane:

(x) $Bi_{0.62}Sm_{0.38}O_{1.5}$ phase peaks; (a) before OCM; (b) outside BYS tube after OCM; (c) inside BYS tube after OCM.

The cofeed mode refers to the co-feeding of the reactants: CH_4-O_2 diluted with He into the tube side and N_2 to the shell side. The tube side flow rate and P_{CH4} were kept at 10 mL/min and 10.1 kPa, respectively. Under similar conditions, the calculated oxygen fluxes in membrane mode were 0.08–0.2 mL/min. It was not possible to keep the CH_4/O_2 ratios in the cofeed mode predetermined from the values of oxygen fluxes in the membrane mode due to the mass-flow controller limitations. In order to make a fair comparison between co-feed and membrane modes, we looked at points where the C_2 yields were comparable in two modes. The flow rate of oxygen inlet in the co-feed mode was kept at approximately ten times the value of the oxygen permeation flow rate in the membrane mode under similar conditions. The co-feed mode experiments were conducted at different temperatures (930–870°C) and CH_4/O_2 ratios (0.75–1.3).

The effluents from the reactors were intermittently sampled by a 6-port rotary valve (Valco Instruments), and analyzed by a GC (Perkin Elmer 8500, 80/100 Carbosphere col-

Table 1. BYS Membrane Reactor Dimension and OCM Reaction Conditions

Parameters	Value
BYS Membrane inner dia.	3.8 mm
BYS Membrane outer dia.	6.25 mm
BYS Inner tube length	29 mm
BYS memb. inner surface area	3.1 cm^2
Cross-sectional area of downstream side	2.8 mm^2
Cross-sectional area of upstream side	144 mm^2
Membrane surface to reaction vol. ratio	27 1/cm
Reaction temperature	870–930 °C
Downstream CH_4-He feed flow rate	3–15 cm^3/min
Upstream air feed flow rate	40 cm^3/min
P_{CH_4} in feed (methane side)	1.4–7.2 kPa
P_{O_2} in feed (oxygen side)	5.1–51 kPa

umn) that could detect oxygen with a concentration as low as 200 ppm (Zeng and Lin, 2001). Oxygen concentrations in both the shell and tube side chambers were also monitored by an yttria stabilized zirconia oxygen sensor (6000 Oxygen Analyzer, from Illinois Instruments). Gas leakage through the sealant, if it occurred, could be detected by monitoring nitrogen concentration in the tube side. OCM reactions were performed in the membrane reactor with the feeds of O_2/N_2 and CH_4/He mixtures. The methane conversion was calculated by

$$C = 1 - \frac{Y_{\mathrm{CH}_4}}{\sum n_i Y_i} \tag{1}$$

where n_i is the number of carbon atoms in the molecule of the carbon containing product i, and Y is molar fractions in the effluent of the reaction chamber. The selectivity for the carbon containing product i is the percentage of reacted methane that forms product i and was calculated by

$$S_i = \frac{n_i Y_i}{\sum n_i Y_i - Y_{\mathrm{CH}_4}} \tag{2}$$

The C_2 yield is the percentage of total methane that forms ethane and ethylene, which was calculated from the product of methane conversion and C_2 selectivity.

Results and Discussion

The BYS membranes prepared had an fcc fluorite structure, as confirmed by XRD data shown in Figure 3a, with a lattice constant of a = 0.555 nm. The BYS membrane exhibited yellowish color and had a real density of 8.0 g/cm^3. Helium permeation test showed that the membranes were hermetic to helium (permeance lower than 1×10^{-10} mols^{-1}m^{-2}Pa^{-1} based on the helium permeation setup detection limit).

Figure 4 shows the effect of shell side oxygen partial pressure on C_2 selectivity, conversion, yield, and C_2H_4/C_2H_6. In order to reach high activity and selectivity in a membrane reactor, oxygen transport rate needs to be matched to the OCM reaction rate. Oxygen flux is dependent on the membrane thickness (when bulk transfer controls), temperature, and partial oxygen pressure gradient. It is very difficult to control and measure the oxygen partial pressure in the methane side due to the complex reactions taking place. Thus, we studied the effect of P_{O_2} by changing the oxygen content in the oxygen rich side of the membrane. The oxygen partial pressure was varied between 5.1 and 51 kPa with a fixed shell side flow rate ($F_{N_2} + F_{O_2}$) of 30 mL/min. Temperature was varied between 870–930°C.

As shown in Figure 4a, C_2 selectivity decreases slowly as the shell side P_{O_2} is increased. The decrease in selectivity gets sharpened with temperature. C_2 selectivity decreases by 11% at 870°C, 21% at 900°C and 33% at 930°C when P_{O_2} is increased from 5.1 to 51 kPa. The steeper decline in selectivity at higher temperatures indicates that the nonselective, gas-phase reactions play a more significant role than those at lower temperatures. Selectivity is highest at lower temperatures and at lower P_{O_2}. Conversely, methane conversion rate is higher at higher temperatures and increases with P_{O_2}. By regressing the data shown in Figure 4b using the power equation ($R = K[P_{O_2}]^n$), the apparent reaction order (N) of

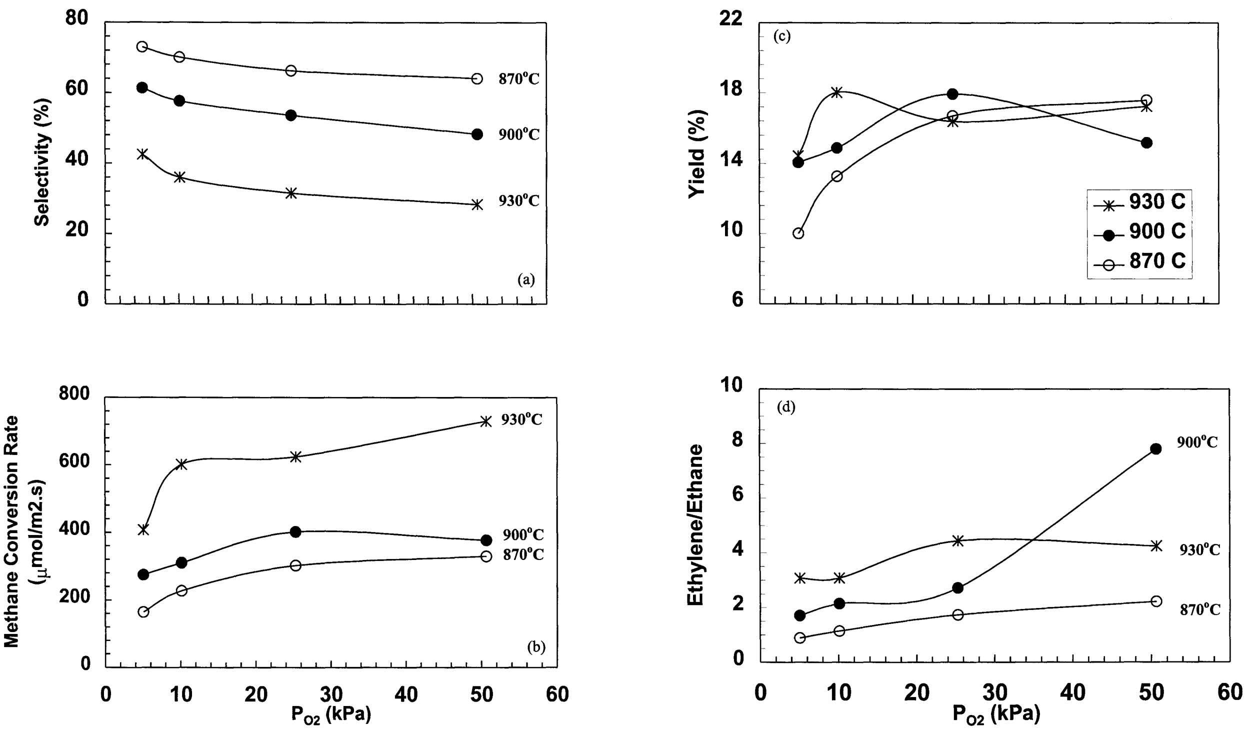

Figure 4. OCM in the BYS membrane reactor at different P_{O_2} in the membrane mode.

Conditions: T = 870–900°C; P_{O_2} = 5.1–51 kPa; F_{shell} = 40 mL/min; F_{tube} = 5 mL/min; P_{CH_4} = 10.1 kPa.

methane conversion with respect to P_{O_2} is around 0.20–0.27 over 870–930°C. The reaction on the BYS membrane surface exposed to O_2-N_2 is expressed by (in Kroger Vink notations) (Wang and Lin, 1995)

$$1/4O_2 + 1/2V_O^{\bullet\bullet} \Leftrightarrow 1/2O_O^x + h^\bullet \tag{a}$$

During OCM, the reactions on the surface exposed to methane can be listed as

$$CH_4(g) \Leftrightarrow CH_4(s) \tag{b}$$

$$CH_4(s) + 1/2O_O^x + h^\bullet \rightarrow {}^\bullet CH_3 + 1/2H_2O + \tfrac{1}{2}V_O^{\bullet\bullet} \tag{c}$$

$$2 \cdot CH_3 \rightarrow C_2H_6 \tag{d}$$

$$2O_O^x + 4h^\bullet \rightarrow O_2 + 2V_O^{\bullet\bullet} \tag{e}$$

The ethylene and carbon oxides are believed to form through the oxidation of intermediate specie, ethane, and these are irreversible and fast reactions. Thus, the net oxygen flux through the interface at the methane side is determined by adsorption-desorption equilibrium of methane onto the solid phase as well as the supply of electron holes from the other side of the membrane (reactions b, c). In other words, the conversion rate of methane is determined by the concentration of methane in the gas phase and the concentration of electron hole in the solid phase: $R_{CH_4} = -k[CH_4][p]$, where $[p]$ is the electron hole concentration and is roughly proportional to $P_{O_2}^{1/4}$. The observed apparent reaction order of methane conversion with respect to P_{O_2} is around 0.20–0.27. The C_2 yield however is essentially independent of the shell side P_{O_2}.

At the membrane surface exposed to methane, oxygen ions are consumed by reactions (c) and (e). Since the gaseous oxygen formed in reaction (e) can further react with methyl radicals and C_2s, a high oxygen flux increases the activity, but does not necessarily improve selectivity. As can be seen from Figure 4b, the methane conversion rate increases almost by 100% while selectivity decreases by 11% to by 33% as P_{O_2} is increased from 5.1 to 51 kPa.

The effect of tube side flow rate at various temperatures is shown in Figures 5a–5d. C_2 selectivity benefits from higher flow rates, possibly because intermediate products (C_2s) do not have the chance to get further oxidized by being flushed out of the reactor chamber faster. It is possible that higher flow rates create a better mass-transfer environment in the reactor. Ethylene to ethane ratio first increases when the tube side flow rate is increased from 3 to 5 mL/min and then it decreases with increasing flow rate. Methane residence time becomes shorter as the flow rate increases, thus making ethane less likely to be further oxidized into ethylene compared to longer residence times. As the flow rate decreases, conversion increases because of the higher contact time of methane with the surface, but selectivity decreases possibly due to the competitive nature of OCM and complete oxidation reactions.

At lower methane contact time, it is also possible that more molecular oxygen have gotten into the gas phase in the membrane. The methane concentration possibly is higher, because a smaller fraction of methane is reacted at higher flow rates

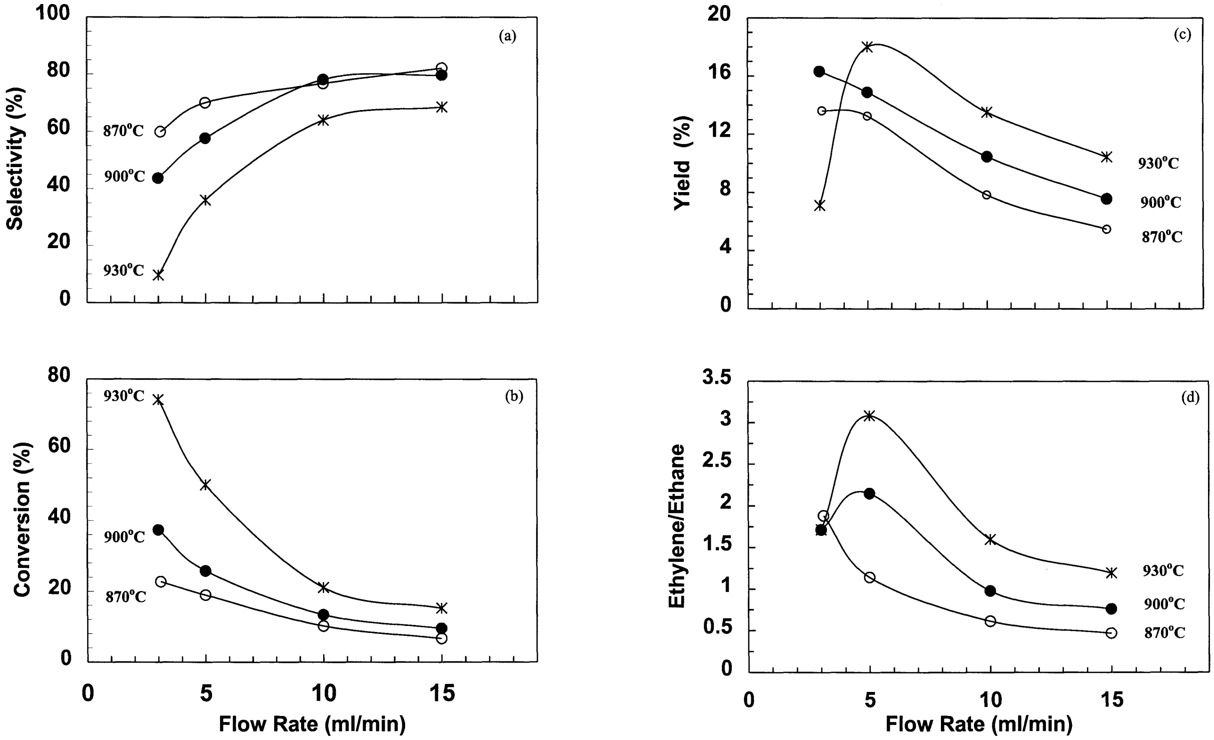

Figure 5. OCM in the BYS membrane reactor at different tube side flow rates in the membrane mode.

Conditions: $T = 870–900°C$, $P_{O_2} = 10.1$ kPa; $F_{shell} = 40$ mL/min; $F_{tube} = 3–15$ mL/min; $P_{CH_4} = 10.1$ kPa.

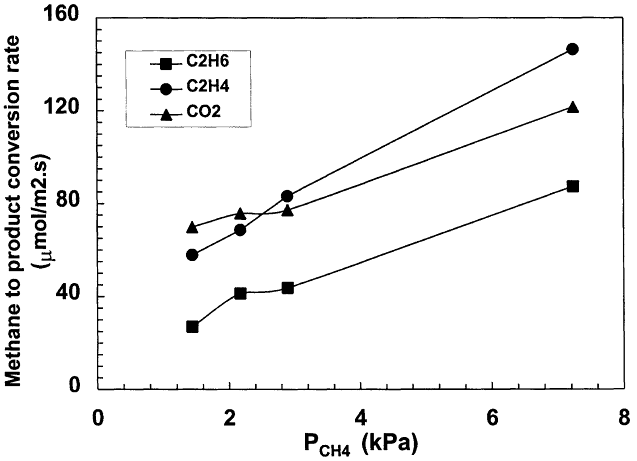

Figure 6. Methane to product conversion rate in the BYS membrane reactor at different P_{CH_4} in the membrane mode.

Conditions: T = 870–900°C; P_{O_2} = 25 kPa; F_{shell} = 40 mL/min; F_{tube} = 7 mL/min; P_{CH_4} = 1.4–7.2 kPa.

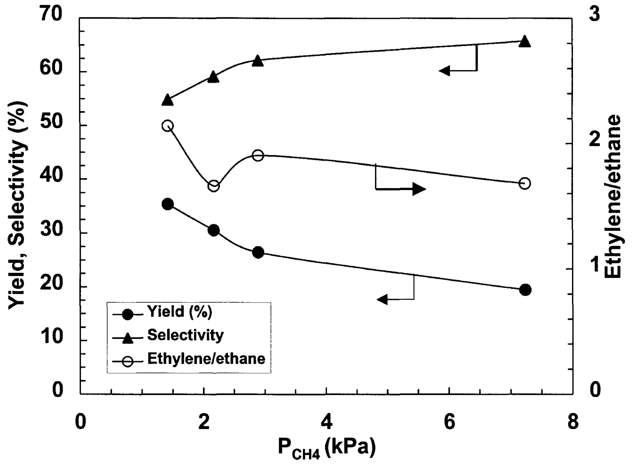

Figure 7. OCM in the BYS membrane reactor at different P_{CH_4} in the membrane mode.

Conditions: T = 870–900°C; P_{O_2} = 25 kPa; F_{shell} = 40 mL/min; F_{tube} = 7 mL/min; P_{CH_4} = 1.4–7.2 kPa.

resulting in a higher selectivity. When the flow rate is reduced, more methane is converted to C_2 products by the OCM reaction, although in the meantime more total oxidation reactions may take place. When the flow rate is higher than 5–10 mL/min (10 mL/min for temperatures of 870°C and 900°C), the amount of C_2 produced is larger than CO_2. So, the yield increases with a decrease in selectivity. At 930°C, when the flow rate is smaller than 5 mL/min, the yield decreases sharply due possibly to the increase in total oxidation reactions, resulting in a much lower selectivity. The presence of more molecular oxygen in the gas phase lowers the selectivity for OCM in the membrane reactor. Ethylene to ethane ratio increases with increasing temperature.

The optimum C_2 yield is obtained at 900°C in a large feed flow rate range. The effect of methane partial pressure on OCM is studied at 900°C, and C_2 and CO_2 formation rates as a function of P_{CH_4} are shown in Figure 6. The C_2 formation rate with respect to P_{CH_4} at 900°C is of 0.5–1st order. Figure 7 shows the OCM results at different tube side P_{CH_4} with other experimental parameters fixed under the optimum conditions (listed in Table 1). As shown, the C_2 selectivity increases and yield decreases with increasing P_{CH_4}. In a dense tubular membrane reactor, oxygen is fed differentially to the entire reactor length by permeation. Methane molecules can react as long as there is enough oxygen for the reaction. As shown in Figure 7, selectivity increases first with increasing methane partial pressure, and then reaches asymptotically to 65%. Since the oxygen supply across the membrane is practically constant, the reaction rate is controlled by the oxygen supply. As the oxygen supply decreases, deep oxidation reactions do not take place leading to higher selectivity, but lower methane conversion. C_2 yield higher than 30%, with C_2 selectivity higher than 50%, and C_2H_4/C_2H_6 of about 2 is obtained at P_{CH_4} lower than 2 kPa. The oxygen permeation flux under this condition is 4×10^{-8} mol/cm^2·s. These high C_2 yield results have been reproduced on three different BYS membrane reactors and as shown in Figure 8, the agreement between three different runs is very good.

These are the highest per pass C_2 yields ever reported for OCM on a membrane reactor. Table 2 compares the results of OCM on membrane reactors made of a perovskite type ceramic membrane $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$ (LSCF) disk and BYS disk (both with a diameter of about 2 cm), and a BYS tube of geometry given in Table 1. The BYS-disk membrane gives a much higher C_2 selectivity than the LSCF-disk membrane under similar conditions. This is because the BYS surface is catalytically much more selective and active for OCM than the LSCF (Zeng et al., 1998; Zeng and Lin, 2000). Changing the BYS membrane reactor geometry from disk to tubular further improves C_2 selectivity and methane conver-

Table 2. OCM in Dense Ceramic Membrane Reactors of Different Membrane Material and Reactor Geometries (at 900°C)

Membrane Materials	LSCF* Disk	BYS** Disk	BYS Tube
Memb. react. surf. area	3.7 cm^2	3.5 cm^2	3.6 cm^2
P_{CH_4} in feed, methane side	0.05 atm	0.1 atm	0.04 atm
P_{O_2} in feed, oxygen side	0.21 atm	0.21 atm	0.21 atm
Methane feed flow rate	~ 5 cm^3/min	~ 10 cm^3/min	~ 4 cm^3/min
Methane conversion	24%	15%	50%
C_2 selectivity	36%	69%	60%
C_2 yield	9%	10%	30%
J_{O_2}	2.1×10^{-7} mol/s·cm^2	4.3×10^{7} mol/s·cm^2	0.04×10^{7} mol/s·cm^2

*LSCF—$La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$.
**BYS-$Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$.

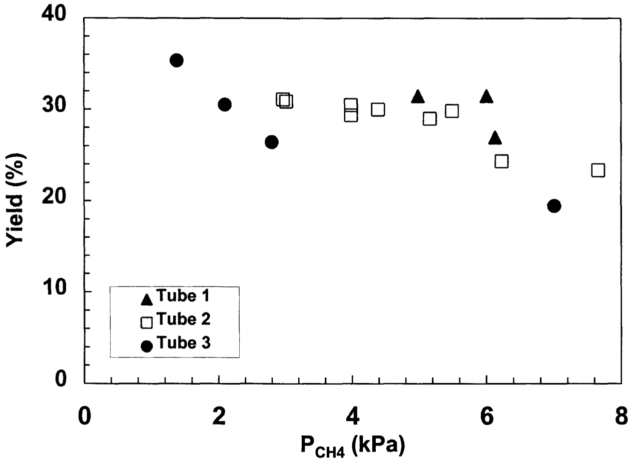

Figure 8. OCM in three different BYS membrane reactor at different P_{CH_4} in the membrane mode.

Conditions: Reaction surface area/reaction volume = 2.7–2.9 (1/mm); F_{tube} = 6–7 mL/min; F_{tube} = 30–40 mL/min; P_{O_2} = 10–20 kPa, T = 900°C.

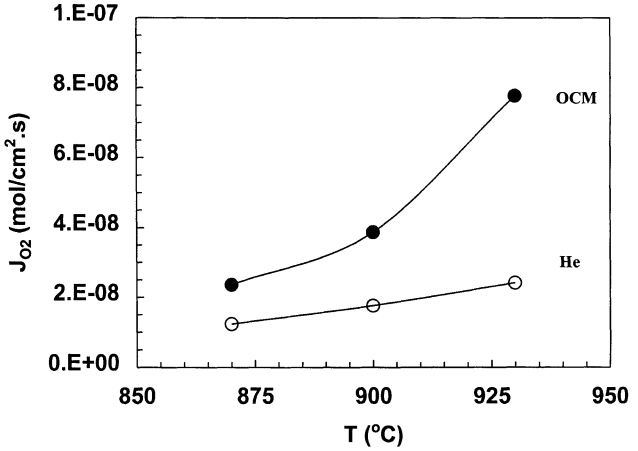

Figure 9. Oxygen fluxes in: OCM reaction (O_2-N_2/CH_4-He) vs. oxygen permeation experiments (O_2-N_2/He).

Conditions: in OCM P_{O_2} = 25 kPa, F_{shell} = 40 mL/min, P_{CH_4} = 10.1 kPa; in oxygen permeation P_{O_2} = 17.2 kPa, F_{shell} = 40 mL/min.

sion due to a smaller reaction volume to surface area ratio of the tubular geometry.

Figure 9 compares oxygen permeation fluxes through the BYS membrane during OCM (O_2-N_2/CH_4-He) with those under similar conditions with helium ($P_{O_2} = 6 \times 10^{-2}$ kPa) as purge gas in the tube side (O_2-N_2/He). The oxygen permeation flux in O_2-N_2/CH_4-He is 1.5–3.5 times that in O_2-N_2/He. Oxygen permeation through the 1–2 mm thick ionic conducting BYS membrane is controlled by electronic conduction in the bulk membrane phase, with oxygen permeation flux J_{O_2} (mol/cm^2·s) related to the upstream and downstream oxygen partial pressures P'_{O_2} and P''_{O_2} (in atm) by (Zeng and Lin, 2001)

$$J_{O_2} = 37.3\left(P'^{0.27}_{O_2} - P''^{0.27}_{O_2}\right) \qquad (3)$$

If the same permeation mechanism applies to oxygen permeation during OCM, the above equation would indicate that oxygen permeation flux with (O_2-N_2/CH_4-He) should be only less than 50% higher than that with (O_2-N_2/He). The larger-than-the-expected increase in oxygen permeation flux with O_2-N_2/CH_4-He as compared to that in O_2-N_2/He indicates a contribution of n-type electron transport during OCM reaction. In this case, an additional term $k_n(P''^{1/4}_{O_2} - P'^{1/4}_{O_2})$] appears on the righthand side of Eq. 3. Although the electronic transport in the Bi_2O_3 based ceramics is primarily of a p-type in a large P_{O_2} range, n-type electronic transport may appear in oxide at low oxygen partial pressure such as in CH_4. The presence of the n-type electrons can cause a reduced selectivity for the formation of methyl radicals (Zhang et al., 1994). Use of a thinner BYS membrane could enhance oxygen permeance and raise the oxygen potential of the membrane surface exposed to methane. This could be an effective way to keep the p-type electron-transport mechanism, and, therefore, good OCM selectivity, of the BYS membrane surface. Improvement in membrane reactor design, such as using hollow-fiber BYS membrane reactor, would also be effective in further improving C_2 yield for OCM.

Cofeed OCM reaction experiments were conducted in the same membrane reactor to examine the effect of the membrane reactor on OCM. Figure 10 compares C_2 selectivity, conversion, and yield for OCM in the membrane reactor operated in the membrane reactor mode (with O_2-N_2 fed to the shell side and CH_4-He to the tube side) and cofeed mode (with N_2 to the shell side and CH_4-O_2-He in the tube side). In order to compare these two modes on the same basis, cofeed mode conditions were chosen such that it would give similar C_2 yields. The oxygen to methane ratio in the feed in the cofeed mode is about ten times the ratio of oxygen permeating into the tube side to the methane feed flow rate in the membrane mode under similar conditions. P_{CH_4} in all these experiments were kept at 10.1 kPa. Two set of results obtained in the membrane mode are used to do the comparison.

At 870°C, the cofeed and membrane modes give similar C_2 yields. However, the C_2 selectivity of the cofeed mode is much smaller than those of the membrane mode. In 870–930°C, the membrane reactor mode gives a significantly higher C_2 selectivity (70–80%) with a lower C_2 conversion (5–20%) as compared to the co-feed mode. The higher selectivity obtained in membrane mode also reflects the importance of the heterogeneous step in OCM. If the OCM reaction mechanism consisted of only homogeneous steps, the membrane reactor operation would not enhance the selectivity as it did in this study. Membrane reactors may also be used to study OCM reaction mechanistically.

The C_2 yield at 900°C in the membrane mode is almost twice as high as that obtained in the co-feed mode when the tube side flow rate in both modes are the same, that is, 10 mL/min. The ethylene to ethane ratio of about 1.5 was obtained in both operation modes at 900°C. In the co-feed mode, O_2 and CH_4 approach the inner BYS membrane surface and methyl radicals are formed and diffuse back into the gas phase in the tube side for coupling. Gas phase O_2 in the tube side at high P_{O_2} could completely oxidize the carbon containing species (CH_4, $CH_3^\bullet$, C_2H_4, C_2H_6) in the tube side gas phase,

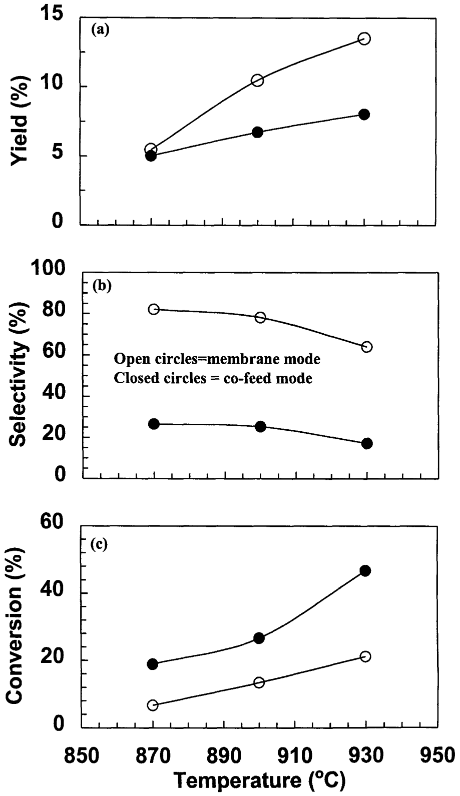

Figure 10. OCM in the BYS membrane reactor operated in: membrane vs. cofeed modes.

The open circles represent the results when the tube side flow rate is 10 mL/min and $P_{CH_4} = 10.1$ kPa; closed circles represent the results when the tube side flow rate was kept at 15 mL/min and $P_{CH_4} = 10.1$ kPa, in membrane mode. Dense circles represent the cofeed mode results: $F_{tube} = 10$ mL/min; $P_{CH_4} = 10.1$ kPa; $CH_4/O_2 = 0.75$ at 930°C; $CH_4/O_2 = 1$ at 930°C, $CH_4/O_2 = 1.3$ at 870°C.

lowering the C_2 selectivity. In the membrane mode, by feeding oxygen from the shell side, gas-phase complete oxidation reactions are minimized, resulting in a much higher C_2 selectivity than when O_2 is co-fed with CH_4. The C_2 selectivity in the membrane mode is less than 100%, indicating that the BYS surface is not 100% selective for formation of methyl radicals. Some of the carbon containing species are also oxidized by the lattice oxygen on the BYS membrane surface.

XRD patterns of the inner and outer surfaces of the BYS tube after OCM reaction are compared with that of powder sample of fresh BYS in Figure 3. The membrane was quenched under OCM conditions at room temperature. The data shows that the outer surface (air side) of the BYS tube after OCM reaction remains in the fcc fluorite structure. The inner surface (methane side) of the BYS membrane after OCM still remains mainly in the fluorite structure, with a small amount of impurity phase identified as $Bi_{0.62}Sm_{0.38}O_{1.5}$ (JCPDs45-0620). The element composition of the outer surface (air side) and inner surface (methane side) of the BYS tube measured by EDX are listed in the first and second rows of Table 3. The mathematical average of the element compositions in both surfaces is given in the third row of Table 3. The results show that the inner surface is bismuth rich and outer surface is yttrium rich. These average element compositions (mathematical average of the two compositions in both surface) are very close to the stoichiometric compositions of $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$, as given in the fourth row of Table 3. This indicates that the enrichment of an element on one surface is accompanied with a depletion of the same element to the same extent on the other surface.

Table 3. EDX Analysis of Inner and Outer Surfaces of BYS Tube After OCM Reaction Experiments for 5 Days at 900°C

Membrane	Bi Atomic %	Y Atomic %	Sm Atomic %
Inner surface (methane side)	79.6	13.3	7.2
Outer surface (air side)	68.2	22.4	9.4
Mathematical averaged	73.9	17.8	8.3
Stoichiometry	75	15	10

Among the oxides of the three metal elements in BYS, bismuth oxide and yttrium oxide is respectively least and most thermodynamically stable. Thus, under the reducing condition, bismuth ion on the inner membrane surface (methane side) is more likely reduced to bismuth element which may not be XRD-detectable under the present conditions. This reduction is accompanied with the formation of bismuth-samarium-oxide ($Bi_{0.62}Sm_{0.38}O_{1.5}$) and yttrium ion. The latter migrate towards the other surface of the membrane, enriching yttrium content in the fluorite structured BYS solid solution on the outer surface of the BYS membrane. It is important to note that the inner membrane surface remains catalytically active and selective for OCM despite a substantial change in the element compositions.

Conclusions

The fluorite structured BYS dead end tubes were successfully synthesized by citrate method and processed by CIP with green machining. The dead end tubes were used in a membrane reactor for OCM. The oxygen partial fluxes through the dead end BYS membranes under air/helium conditions are in the range of 0.7×10^{-8}–4×10^{-8} mol/cm$^2 \cdot$s at 870–930°C. The oxygen permeation fluxes through tubular BYS membrane reactors under OCM reaction conditions are approximately 1.5 to 3.5 times higher than those under oxygen permeation conditions with He as the purge.

The best single-pass C_2 ($C_2H_4 + C_2H_6$) yield achieved for oxidative coupling of methane in the BYS dead-end membrane reactor was 35% at a C_2 selectivity of 54% at 900°C. At the same C_2 yield, the membrane reactor mode gives C_2 selectivity of over 200% higher than the co-feed mode in the same membrane reactor under similar conditions. High C_2 yields were obtained at very low methane partial pressures. The results are reproduced in three different membrane reactors. The OCM reaction results in migration of bismuth and yttrium, respectively, towards membrane surface exposed to methane and air and formation of a small amount of impurity phases on the membrane surfaces. These changes do not seem to have an effect on the membrane surface catalytic properties for OCM.

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