ELSEVIER

Catalysis Today 56 (2000) 297–305

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Oxidative coupling of methane using oxygen-permeable dense membrane reactors

Yaping Lu [a,1], Anthony G. Dixon [a,*], William R. Moser [a], Yi Hua Ma [a], Uthamalingam Balachandran [b]

[a] *Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, MA 01609, USA*
[b] *Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA*

Abstract

Oxidative coupling of methane was studied with La/MgO catalyst and a distributed oxygen feed through mixed-conducting dense membrane tubes in a shell-and-tube reactor configuration. A $SrFeCo_{0.5}O_3$ membrane was tested, and a blank run confirmed that it acted as a total oxidation catalyst, with no C_2 products. Attempts to coat the inside of the membrane tube with a non-combustion material $BaCe_{0.6}Sm_{0.4}O_3$ were only partially successful, giving 7% yield to C_2 products. The oxygen flux through the coated tube was reduced to 30% of its original value.

A membrane tube was fabricated from a non-combustion oxygen-permeating material, $BaCe_{0.8}Gd_{0.2}O_3$, and it was confirmed that this was not a total oxidation catalyst. Yields to C_2 products of up to 16.5% were obtained, higher than those in comparable fixed bed studies. The C_2 yield obtained is the highest reported in the literature for oxidative coupling of methane in dense membrane reactors.

The flux of oxygen through both dense membranes increased under reaction conditions, by a factor of four, over the non-reaction flux measured in permeation experiments. Changes in surface morphology were observed for the side of the membrane in contact with the reducing atmosphere. Similar phenomena have been observed in previous studies.

Keywords: Methane; Oxidation; Membrane

1. Introduction

Direct conversion of methane to C_{2+} hydrocarbons has been one of the most active research subjects in the catalysis field in the past 15 years, since the publication of the first systematic screening of metal oxides for methane oxidative coupling to ethane and ethylene by Keller and Bhasin [1]. The major challenge to the commercialization of the oxidative coupling of methane (OCM) process is that the C_2 yield is still not high enough. Higher C_2 hydrocarbon yield can be realized by either increasing methane conversion, C_2 selectivity, or both. However, higher methane conversion usually leads to lower C_2 selectivity.

Compared to a conventional co-feed reactor, reactors with distributed feed of oxygen through a membrane or multiple injection feed points could reduce the oxygen partial pressure and thus result in higher C_2 selectivity. The first experimental study showing the beneficial effect of distributed oxygen feed on

* Corresponding author. Tel.: +1-508-831-5350; fax: +1-508-831-5853.
E-mail address: agdixon@wpi.edu (A.G. Dixon).
[1] Currently with The BOC Group Technical Center, 100 Mountain Avenue, Murray Hill, NJ 07974, USA.

0920-5861/00/$ – see front matter
PII: S0920-5861(99)00287-4

methane conversion and C_2 hydrocarbon selectivity was done by Choudahary et al. [2] in four tubular reactors connected in series with La/MgO as the catalyst. For a fixed overall methane to oxygen ratio, the C_2 yield increased as the number of oxygen feed points increased. In addition to achieving higher C_2 hydrocarbon yield, the controlled delivery of oxygen could mitigate thermal hot-spots for the highly exothermic reactions of methane oxidative coupling. It could also achieve higher methane conversion, by operating the reactor at a relatively higher overall oxygen to methane ratio than that of a conventional co-feed reactor. The conventional reactor is limited by the local oxygen concentration imposed by the explosion limit.

Ceramic materials can exhibit both electronic and ionic conductivities. The dense membrane reactors made of these materials allow selective passage of oxygen gas to the reaction zone, thus, a cheaper oxygen source such as air, rather than pure oxygen, can be used without contaminating the product by nitrogen and nitrogen oxides. Lin and Zeng [3–4] studied the catalytic properties of oxygen semi-permeable perovskite-type and yttria-doped bismuth ceramic membrane materials for oxidative coupling of methane. Xu and Thomson [5] investigated the OCM in a La-Ba-Co-Fe-O perovskite membrane reactor. Although they did not report methane conversion, higher C_2 selectivities (up to 50%) were achieved in the membrane reactor than the packed-bed reactor. Fujimoto and his co-workers [6–13] studied oxidative coupling of methane by using dense membrane reactors. Although the C_2 selectivity data they reported were very high (>90%), the methane conversions were too low (about 0.5%). Using a proton-hole mixed conductor ($Sr_{0.95}Yb_{0.05}CeO_{3-\delta}$) as a membrane reactor, Iwahara and his co-workers [14–15] and Chiang et al. [16–17] carried out methane coupling reactions. The formation of C_2 hydrocarbons was enhanced by the permeation of hydrogen and the removal of hydrogen by reacting with oxygen on the side opposite to the methane-feeding side of the membrane. Although there were no carbon oxides formed, the conversion was less than 1% due to the equilibrium limitation and low activity of the catalyst they used.

Anshits et al. [18–19] investigated the methane coupling reaction with oxygen feed passing through a silver membrane. At methane conversions of 0.03 and 3%, the C_2 selectivities were 92 and 42%, respectively. A ceramic membrane reported by Hazbun [20] was comprised of an impervious outer layer of mixed conducting zirconia (10% yttria, 89% ZrO_2, and 1% TiO_2) and a porous inner layer of magnesia stabilized zirconia (87% ZrO_2 and 13% MgO) with catalyst inside. With Li/MgO as the catalyst, the C_2 selectivity and yield were $50 \sim 60\%$ and $20 \sim 25\%$, respectively. Guo et al. [21] investigated the effects of oxygen flux, temperature and feed concentration on the performance of the oxidative coupling of methane using 1 wt.% Sr/La_2O_3-Bi_2O_3-Ag-YSZ solid oxide membrane reactor, and C_2 yields up to 5% were achieved at C_2 selectivity of 80%. Elshof et al. [22] used an ionic electronic mixed-conducting perovskite-type oxide $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ as a dense membrane for oxygen supply in a reactor for methane coupling. C_2 selectivities up to 70% were achieved. Still, the methane conversion was low (only 1–3%).

In the present study, the oxidative coupling of methane was studied with oxygen-permeable dense membrane reactors. The first dense membrane was a non-perovskite material with both oxygen ion and electrical conductivities. A perovskite oxide material ($BaCe_{1-x}Sm_xO_3$) was coated on the inner wall of the dense membrane tube to reduce the total oxidation of hydrocarbons catalyzed by the dense membrane material. The distributed feed of oxygen through the dense membrane tube resulted in higher C_2 yield than that with co-feed of oxygen and methane in the same dense membrane reactor setup. However, the C_2 yield was still lower than the conventional co-feed quartz tube reactor. A second dense membrane made of a non-oxidation catalyst was tried, which gave improved results.

2. Membrane characterization

The first dense membrane tube used in this study was provided by Argonne National Laboratory. The membrane tube geometry was cylindrical with an i.d. of 4.5 mm and an o.d. of 6.5 mm. The length of the tube was between 12 cm to 18 cm. The stoichiometry of the membrane material was $SrFeCo_{0.5}O_{3-\delta}$. Ceramic powder was made by solid state reaction of constituent cation salts [23–24]. Appropriate amounts of $SrCO_3$, $Co(NO_3)_3{\cdot}6H_2O$, and Fe_2O_3 were mixed and milled in isopropanol with ZrO_2 media for 15 h. After

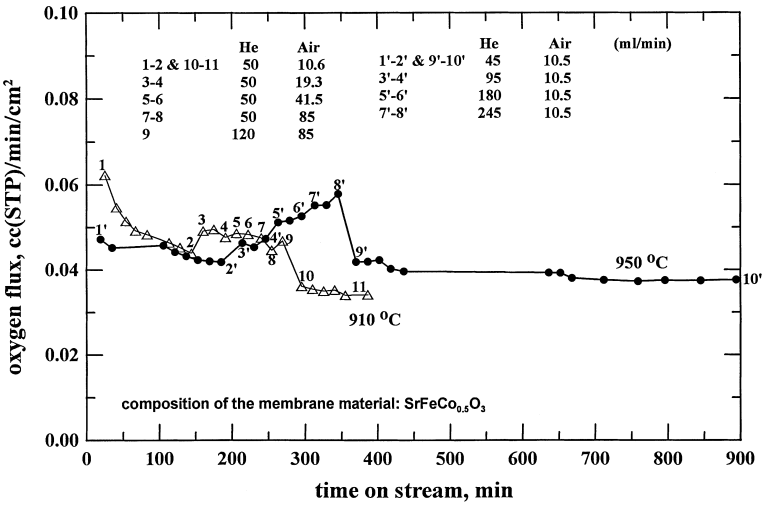

Fig. 1. Oxygen flux through the dense membrane tube (air was fed into the shell side and helium into the tube side).

drying, the mixtures were calcined in air at 850°C for 16 h, with an intermittent grinding. Then the powder was ground in an agate mortar and pestle to an average particle size of about 7 μm. Before the membrane tubes were fabricated by plastic extrusion, the powder was mixed with several organic additives (a solvent, a dispersant, a binder, and a plasticizer) to provide enough plasticity for easy forming into various shapes while retaining satisfactory strength in the green state. The extruded tube was heated slowly in the temperature range of 150–400°C to remove the organics. After that the heating rate was increased to 60°C/h and the tube was sintered at 1200°C in stagnant air for 5–10 h.

2.1. Oxygen flux through the dense membrane tube

The flux of oxygen through the dense membrane tube was measured with air fed in the shell side of the reactor module and helium in the membrane tube. Fig. 1 shows the oxygen fluxes of two membrane tube samples measured at 950°C and 910°C. The helium flow rate was kept at 45 cc/min except in the period from 2′ to 8′ in Fig. 1, during which the helium flow rate was increased from 45 cc/min to 95, 180, and finally 245 cc/min. After that, the helium flow rate was reduced to the original value (45 cc/min). Since an increase in the helium sweep flow rate in the tube side reduced the oxygen partial pressure in the tube side (thus resulting in a higher oxygen partial pressure difference across the membrane), the oxygen flux increased with increasing helium sweep flow rate.

It can be seen from these results that the oxygen flux reached a stable level within about 10 h. The highest oxygen flux observed was only 20% of the reported value of 0.3 cc/min/cm^2 [23]. The results at 910°C in Fig. 1 were obtained with catalyst packing. The oxygen flux observed was consistent with the data at 950°C with no catalyst packing. The oxygen flux increased with an increase in either helium sweep flow rate or the air flow rate.

2.2. Catalytic activity of the dense membrane material

In order to test the catalytic activity of the dense membrane material itself ($SrFeCo_{0.5}O_{3-x}$) under methane coupling conditions, experiments were conducted in a dense membrane reactor with no catalyst packed in the tube side. Methane and helium were fed to the tube side and air to the shell side of the reactor.

Fig. 2 shows the methane conversion as a function of the initial feed ratio of methane to oxygen in the dense membrane reactor without catalyst at 850°C and 1 atm. No detectable C_2 hydrocarbons and oxygen were observed during these runs, and all the methane consumed was converted to carbon dioxide. This indicates that the membrane material was a total oxidation catalyst, and the total oxidation of methane by the

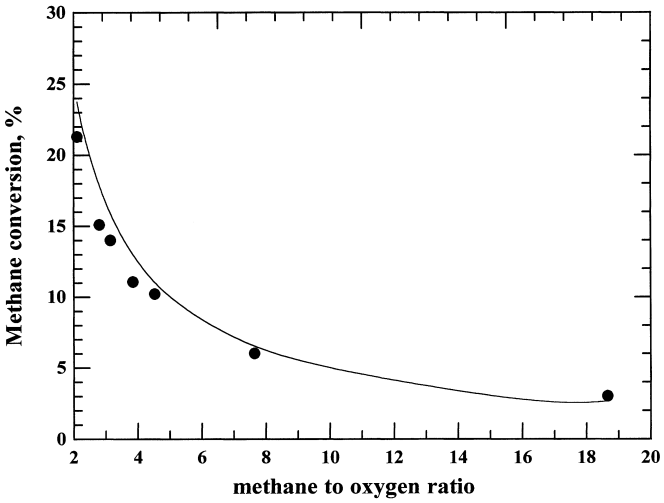

Fig. 2. Methane conversions at different methane to oxygen ratios of a dense membrane reactor without methane coupling catalyst (solid line is calculated by assuming 100% CO_2 selectivity).

dense membrane material dominated the catalytic reaction in this configuration. Once CO_2 was formed, it could not be reduced to C_2 hydrocarbons, in contrast to methane partial oxidation to synthesis gas, where CO_2 formation is the first step in producing CO and H_2.

When reactions took place in the membrane tube, the oxygen flux was found to be about four times higher than that observed under non-reaction conditions. This may have been due to the lower partial pressure of oxygen in the tube side (thus giving a higher oxygen partial pressure difference across the membrane) than that under non-reaction conditions. Balanchandran et al. [23] and Tsai et al. [25] also observed an increase in oxygen flux through dense membranes under reaction conditions.

After the experiment the membrane tube was examined by scanning electron microscopy. The SEM images in the region close to the inner surface, in the middle of the wall thickness, and the region close to the outer surface of the cross section of the membrane wall are shown in Figs. 3–5, respectively. It can be

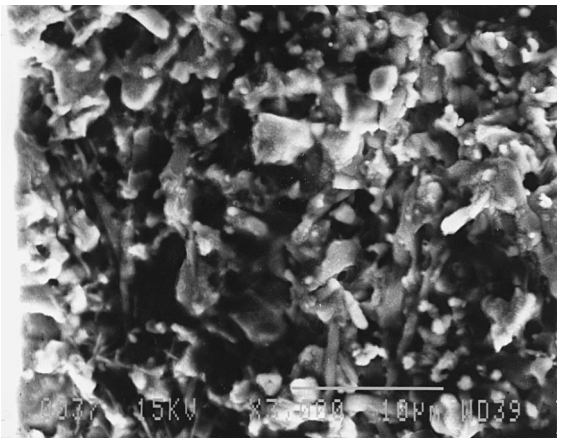

Fig. 3. Cross-section view of the region close to the inner wall of the membrane tube.

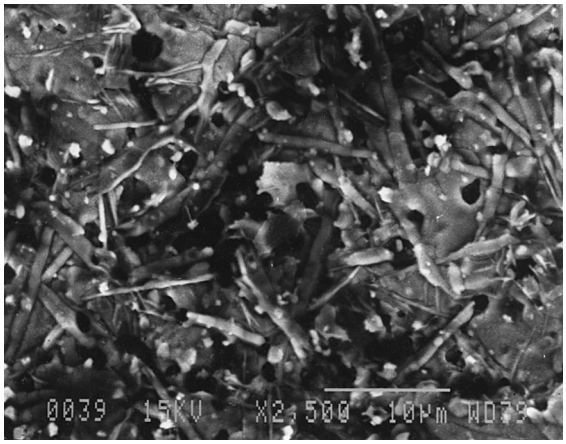

Fig. 4. Cross-section view of the central region of the membrane tube.

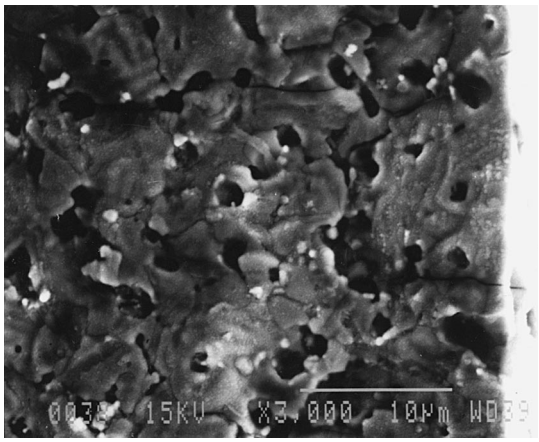

Fig. 5. Cross-section view of the region close to the outside wall of the membrane tube.

seen from these figures that the particle size gradually decreased from the outer surface, which was exposed to an oxidative atmosphere, to the inner surface, which was exposed to a reducing atmosphere. This indicated that the particles of the membrane were broken down to smaller sizes under a reducing atmosphere. Similar results were found in the case of syngas generation using a perovskite membrane, and were discussed in detail by Tsai et al. [26].

3. Experimental studies with catalytic dense membrane reactors

3.1. Membrane reactor module

A shell-and-tube reactor was used to study the oxidative coupling of methane. Fig. 6 shows the membrane reactor module. The membrane tube served as the 'tube', and a quartz tube served as the shell side of the shell-and-tube reactor. Catalyst was packed inside of the dense membrane tube. A quartz tube thermowell (1 mm i.d.) was positioned concentrically in the membrane tube so that a thermocouple could be slid inside the thermowell to monitor the axial temperature profile of the reactor. Methane mixed with helium flowed in the tube side, while air was fed to the shell side. The composition of the products was measured by on-line gas chromatography (HP-5890) with a mass spectrometer analyzer (HP-5971A).

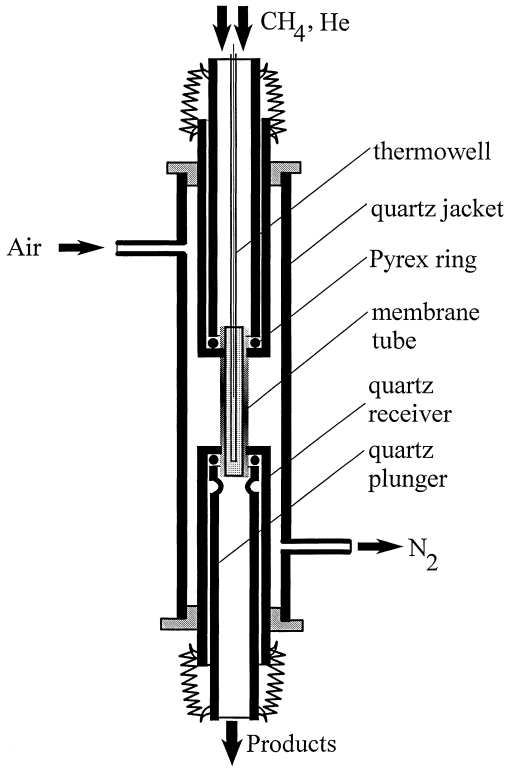

Fig. 6. Schematic of the dense membrane reactor module.

The two ends of the dense membrane tube were connected to quartz tubes. The reactor was heated slowly to about 1000°C to make the seal between the membrane and the quartz tube. At temperatures above 750°C, the dense membrane material allowed uni-directional transfer of oxygen, from the high pressure shell side, to the catalyst packed tube side. Successful sealing was verified when no nitrogen could be detected at the tube side outlet by the GC when air was fed to the shell side of the membrane reactor.

3.2. Catalytic experiments in a packed-bed reactor with La/MgO catalyst

La/MgO was chosen as the OCM catalyst. It was reported that this catalyst showed a significant improvement in C_2 yield by using a distributed oxygen feed reactor over that of a conventional co-feed reactor [2]. La/MgO catalyst was prepared by the precipitation method. $Mg(OH)_2$ was first prepared by precipitation

from aqueous $Mg(NO_3)_2$ solution by adding an excessive amount of 29% ammonia. Then the $Mg(OH)_2$ was dried at 180°C, crushed, and impregnated with $La(NO)_3$ solution. The mixture was dried at 110°C, followed by calcination at 550°C overnight. Then the powder was pelletized, treated at 1000°C for 10 h, and sieved into 30–60 mesh.

1.5 g La/MgO catalyst was loosely packed in the annular space between the thermowell and the membrane tube to avoid breaking due to the thermal expansion of the catalyst during heating. Before running the catalytic membrane reactor, the oxygen flux through the membrane was measured. Also, a catalytic experiment with a conventional packed-bed reactor was conducted as a basis for comparison to the catalytic membrane reactor.

Fig. 7 shows the methane conversion, C_2 selectivity, and C_2 yield at different initial methane to oxygen ratios with La/MgO as the catalyst in the co-feed packed bed reactor. These data were evaluated at a temperature of 790°C, total pressure of 1 atm, oxygen flowrate of 1.6 cc/min and helium (as dilution gas) flowrate of 65 cc/min with 1.5 g La/MgO. As shown in Fig. 7, as the methane to oxygen ratio increased from 1.8 to 11.4, the C_2 selectivity increased from 33.7 to 51.0%,

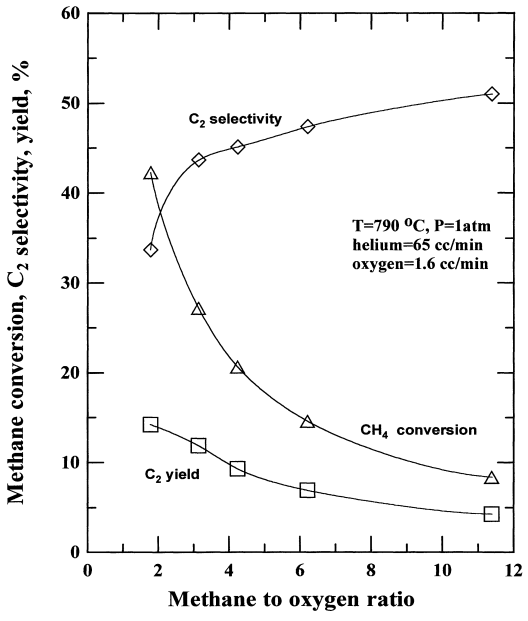

Fig. 7. Methane coupling in a co-feed reactor with La/MgO catalyst.

while the methane conversion and C_2 yield dropped from 42.3 to 8.4% and from 14.2 to 4.3%, respectively. These results were in agreement with the literature for this catalyst.

3.3. Deposition of $BaCe_{0.6}Sm_{0.4}O_3$ on the dense membrane tube

In order to prevent the deep oxidation of methane catalyzed by the contact of methane with the dense membrane material ($SrFeCo_{0.5}O_{3-x}$), the inner surface of the membrane tube was deposited with $BaCe_{0.6}Sm_{0.4}O_3$ by the sol–gel technique. Appropriate amounts of $Ba(C_2H_3O_2)_3$, $Ce(C_2H_3O_2)_3{\cdot}1.5H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, and citric acid were dissolved in ethylene glycol and hydrochloric acid was added into the solution until all the salts were dissolved. Then the solution was heated for about 5 h to form the gel.

Before deposition, the inner surface of the fresh dense membrane tube was pre-treated with a basic solution prepared by dissolving 44 g Na_3PO_4, 65 g Na_2CO_3, and 45 g NaOH in 1000 ml deionized water. Then the inner surface of the dense membrane tube was coated with $BaCe_{0.6}Sm_{0.4}O_3$ by the sol–gel technique. First, the membrane was dip-coated with the sol prepared by the procedure reported earlier. The membrane was heated at a heating rate of 1°C/min to 250°C and was kept at 250°C for 6 h. Then, the temperature of the furnace was raised, at a rate of 1.5°C/min, to 1000°C, where it was kept for 5 h for calcination. The membrane was finally cooled down to room temperature at a cooling rate of 1.5°C/min.

3.4. Oxygen flux through the $BaCe_{0.6}Sm_{0.4}O_3$-coated dense membrane

After the membrane was coated with $BaCe_{0.6}Sm_{0.4}O_3$, the oxygen fluxes through the membrane tube were measured at different temperatures. Air was fed into the shell side and helium fed into the tube side as the purge gas. Fig. 8 shows the oxygen fluxes through the coated dense membrane. The air flow rate was kept at 23 ml/min and helium flow rate at 71 ml/min. The oxygen flux values were only about 30% of those obtained with an uncoated dense membrane tube. When the temperature was increased from 826°C to 913°C, the oxygen flux increased about 45%, which was due

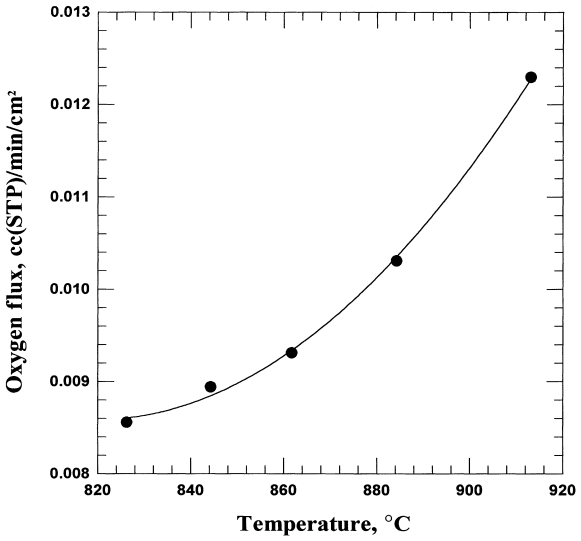

Fig. 8. Oxygen flux through the coated dense membrane tube as a function of temperature.

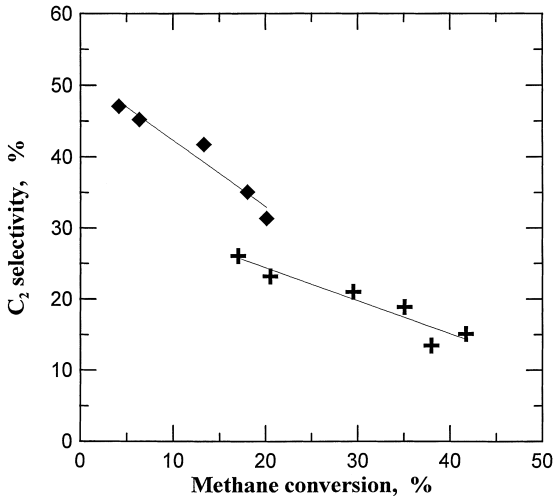

Fig. 9. C_2 selectivity versus methane conversion plots with distributed feed (◆) and co-feed packed-bed (+) dense membrane reactor.

to a higher oxygen defect concentration and defect mobility at higher temperature.

3.5. Experimental results with the $BaCe_{0.6}Sm_{0.4}O_3$-coated dense membrane reactor

After the deposition, the membrane tube was installed into the membrane reactor setup with the La/MgO catalyst packed inside the membrane tube. Fig. 9 shows the C_2 selectivity versus methane conversion plot at 810°C and 1 atm. For comparison, experiments (cross symbols in Fig. 9) were carried out in the same reactor by co-feeding oxygen with methane to the tube side, instead of feeding air to the shell side of the membrane reactor.

Compared to the co-feed mode at a similar methane conversion level, the distributed feed membrane reactor gave higher C_2 selectivity in the low methane conversion region. The C_2 yields obtained in the membrane reactor were about 7%. These were much higher than those reported previously [6–13,22] in dense membrane reactors. However, the C_2 yield was still less than those obtained in the conventional co-feed reactor, as shown in Fig. 7. This may have resulted from incomplete coverage of the inner wall of the membrane tube with the deposited $BaCe_{0.6}Sm_{0.4}O_3$ material, and the limited oxygen flux through the dense membrane.

3.6. Experimental results with a $BaCe_{0.8}Gd_{0.2}O_3$ dense membrane reactor

The oxygen-conducting dense membrane material used in the experiments reported so far was a total oxidation catalyst. Although the reactor performance was improved by coating with $BaCe_{0.6}Sm_{0.4}O_3$ perovskite (which is an oxygen conducting and methane coupling catalyst), the C_2 yield obtained was less than that obtained by the conventional packed-bed reactor, due to the fact that the surface was not completely covered by the coating material. It was, therefore, decided to make a new dense membrane tube from an oxygen-conducting material that was known not to be a total oxidation catalyst. The material selected was $BaCe_{0.8}Gd_{0.2}O_3$ (BCG).

The powder of this material was synthesized by the ethylene glycol method, and the BCG dense membrane tube was made by Argonne National Laboratory by extrusion. The membrane tube was 11 cm long, I.D. = 4.6 mm and O.D. = 6 mm. It was incorporated into the experimental set-up similarly to the previous tube. Oxygen fluxes were measured and found to be close to those of the $SrFeCo_{0.5}O_3$ tube. Details of the material synthesis and characterization will be forthcoming.

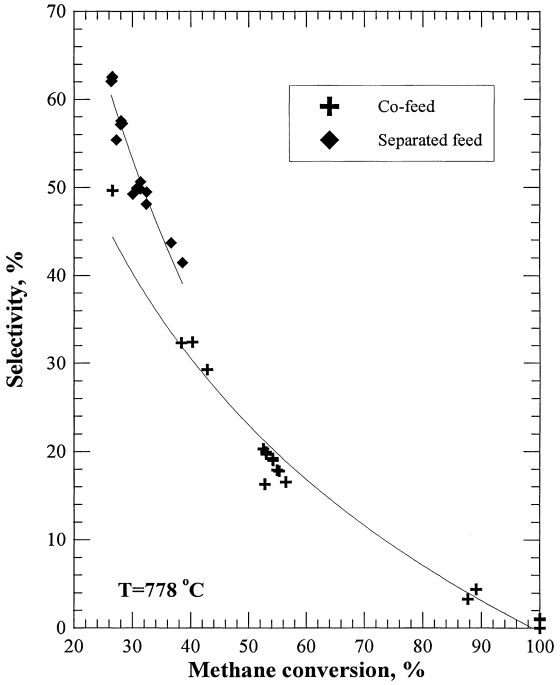

Fig. 10. Comparison of C_2 selectivity between the co-feed and separated-feed BCG membrane reactor.

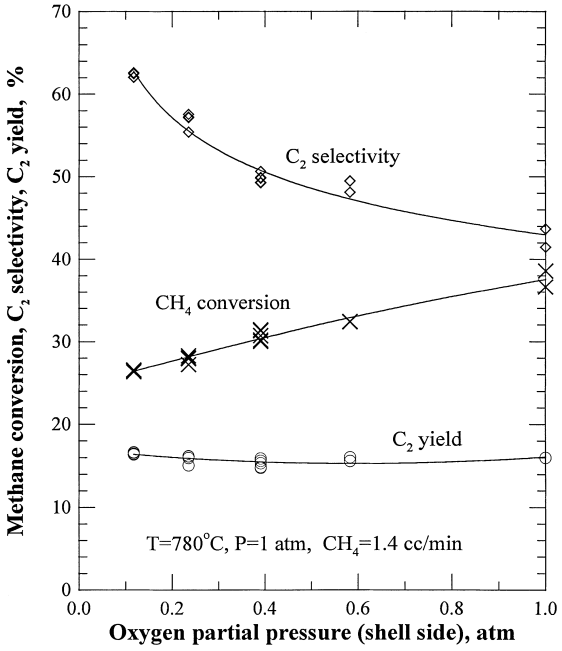

Fig. 11. Effect of oxygen partial pressure in the shell side on the BCG dense membrane reactor performance.

Methane oxidative coupling reactions were carried out in the BCG dense membrane reactor with no catalyst packed in the tube side. A mixture of air and helium was fed from the shell side while a mixture of methane and helium was fed from the top of the reactor into the tube side. For comparison purposes, the reactor module was also run in a co-feed mode by feeding the mixture of methane, oxygen, and helium into the tube side. In both the cases, the product stream was withdrawn from the bottom of the membrane tube side and analyzed by an on-line gas chromatograph.

C_2 yields up to 14% were obtained when the reactor was operated in the co-feed mode, indicating that the BCG membrane was not a total combustion catalyst. Since no detectable C_2 products were observed in the $SrFeCo_{0.5}O_3$ membrane tube without catalyst, the BCG membrane tube was much more active than the $SrFeCo_{0.5}O_3$ membrane tube for methane oxidative coupling.

Fig. 10 shows the C_2 selectivity–methane conversion plots for both membrane and co-feed reactors at 778°C. The methane flow rate was kept at 1.4 cc/min. For the membrane reactor, the methane conversion was changed by changing the oxygen to helium ratio in the shell side, while for the co-feed reactor, the methane conversion was changed by varying the oxygen flow rate in the tube side. For both membrane and co-feed reactor, the C_2 selectivity dropped rapidly as the methane conversion increased. The highest C_2 yield was about 16.5% (observed at a selectivity of 62.5%), which was higher than the highest yield obtained in the $SrFeCo_{0.5}O_3$ dense membrane reactor. The C_2 yield obtained is the highest reported in the literature for OCM in dense membrane reactors. Although the membrane reactor showed slightly higher selectivity than the co-feed reactor at the same methane conversion level, the steep drop in C_2 selectivity as a result of the increase of oxygen partial pressure in the shell side indicated that the non-selective, gas phase reactions still played a significant role.

Fig. 11 shows the BCG dense membrane reactor performance at different shell side oxygen partial pressures. As the oxygen partial pressure in the shell side increased, a decrease in C_2 selectivity and an increase in the methane conversion were observed. The C_2 yield remained unchanged in the entire oxygen partial pressure range used in the experiments.

4. Conclusions

Oxidative coupling of methane was studied with oxygen-permeable dense membrane reactors. A perovskite material ($BaCe_{0.6}Sm_{0.4}O_3$) was coated on the inner wall of the first dense membrane tube to reduce the total oxidation of hydrocarbons catalyzed by the dense membrane material. The distributed feed of oxygen through the dense membrane tube resulted in a higher C_2 yield than that with a co-feed of oxygen and methane in the same dense membrane reactor setup. However, the C_2 yield was still lower than that obtained in the conventional co-feed fixed-bed quartz tube reactor. This was attributed to the interaction of the dense membrane with the reactant mixture, which could not be completely eliminated. Therefore, a dense membrane tube with both the oxygen conducting property and methane coupling activity was prepared. This material was shown to have no total oxidation activity. Higher yields were obtained than with the first tube, and the C_2 yield obtained was the highest reported in the literature for oxidative coupling of methane in dense membrane reactors. The yield, however, was still limited by decreases in selectivity as oxygen partial pressure was increased. It was concluded that gas-phase reactions still played a role in the reactor.

Acknowledgements

Financial support from the US Department of Energy under contract number DE-AC22-92PC92113 is gratefully acknowledged.

References

[1] G.E. Keller, M.M. Bhasin, J. Catal. 73 (1982) 9.
[2] V.R. Choudhary, S.T. Chaudhari, A.M. Rajput, V.H. Rane, J. Chem. Soc. Chem. Commun. 20 (1989) 1526.
[3] Y.S. Lin, Y. Zeng, J. Catal. 164 (1996) 220.
[4] Y. Zeng, Y.S. Lin, Ind. Eng. Chem. Res. 36 (1997) 277.
[5] S. Xu, W. Thomson, AIChE J. 43 (1997) 2731.
[6] K. Omata, S. Hashimoto, H. Tominaga, K. Fujimoto, Appl. Catal. 52 (1989) L1.
[7] K. Fujimoto, K. Asami, K. Omata, S. Hashimoto, Stud. Surf. Sci. Catal. 61 (1991) 525.
[8] T. Nozaki, K. Fujimoto, J. Chem. Soc. Chem. Commun. 17 (1992) 1248.
[9] T. Nozaki, K. Omata, K. Fujimoto, in: T. Inui et al. (Eds.). New Aspects of Spillover Effect in Catalysis, Elsevier, Amsterdam, 1993, p. 377.
[10] T. Nozaki, S. Hashimoto, K. Omata, K. Fujimoto, Ind. Eng. Chem. Res. 32 (1993) 1174.
[11] K. Fujimoto, Jpn. Kokai Tokyo Koho JP 05 238 (1994) 961.
[12] T. Nozaki, K. Fujimoto, AIChE J. 40 (1994) 870.
[13] T. Nozaki, S. Hashimoto, K. Omata, K. Fujimoto, Chem. Eng. Sci. 47 (1992) 2945.
[14] S. Hamakawa, T. Hibino, H. Iwahara, J. Electrochem. Soc. 140 (1993) 459.
[15] S. Hamakawa, T. Hibino, H. Iwahara, J. Electrochem. Soc. 141 (1994) 1720.
[16] P.-H. Chiang, D. Eng, M. Stoukides, J. Electrochem. Soc. 138 (1991) 11.
[17] P.-H. Chiang, D. Eng, M. Stoukides, Solid State Ionics 61 (1993) 99.
[18] A.G. Anshits, A.N. Shigapov, S.N. Vereshchagin, V.N. Shevnin, Kinet. Katal. 30 (1989) 1260.
[19] A.G. Anshits, A.N. Shigapov, S.N. Vereshchagin, V.N. Shevnin, Catal. Today 6 (1990) 593.
[20] E.A. Hazbun, U.S. Patent 4,791,079 (1988).
[21] X.-M. Guo, K. Hidajat, C.-B. Ching, H.-F. Chen, Ind. Eng. Chem. Res. 36 (1997) 3576.
[22] J.E. Elshof, H.J.M. Bouwmeester, H. Verweij, Appl. Catal. A: 130 (1995) 195.
[23] U. Balachandran, J.T. Dusek, R.L. Mieville, R.B. Poeppel, M.S. Kleefisch, S. Pei, T.P. Kobylinski, C.A. Udovich, A.C. Bose, Appl. Catal. A: General 133 (1995) 19.
[24] U. Balachandran, M.S. Kleefisch, T.P. Kobylinski, S.L. Morissette, S. Pei, US Patent, 5,580,497 (1996).
[25] C.-Y. Tsai, A.G. Dixon, W.R. Moser, Y.H. Ma, AIChE J. 43 (1997) 2741.
[26] C.-Y. Tsai, A.G. Dixon, W.R. Moser, Y.H. Ma, M.R. Pascucci, J. Am. Ceram. Soc. 81 (1998) 1437.