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Controlled oxidative coupling of methane by ionic conducting ceramic membrane

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Oxidative coupling of methane was performed on a tubular dense membrane reactor made of catalytically active fluorite-structured $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$. Methane and air were separately fed to the tube and shell side of the membrane. The tubular dense membrane reactor gives 35% one-pass C_2 ($C_2H_4 + C_2H_6$) yield for oxidative coupling of methane with a C_2 selectivity of 54% at 900 °C.

KEY WORDS: natural gas conversion; membrane reactor; bismuth oxide; oxygen permeation

1. Introduction

Natural gas, containing primarily (>95%) methane, is an abundant natural resource that rivals liquid petroleum. With depletion of liquid petroleum and increase in the natural gas reserves, it is expected that methane will eventually become a major resource for chemicals and liquid fuels. Two routes have been studied for converting methane to chemicals and liquids. The indirect route relies on production of synthesis gas (H_2 and CO mixture) by steam reforming or partial oxidative reaction of methane, followed by 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.

Oxidative coupling of methane to ethylene and ethane (C_2) is the most desirable approach to directly convert natural gas to valuable chemicals and liquid fuels [1]. Extensive studies were conducted in the past two decades on new catalysts [2,3] or novel chemical reactors [4–8] for this reaction. In oxidative coupling of methane, CH_4 and O_2 react over a catalyst, mostly oxides, at elevated temperatures to form C_2 products (ethane and ethylene). The reaction often leads to the formation of the thermodynamically more favored CO_2. Extensive research was reported in the 1980s and early 1990s on a variety of catalysts to kinetically control the reaction for enhancing the C_2 selectivity and yield after the pioneering work of Keller and Bhasin [2]. The inherent problem with OCM is that the oxygen required for OCM can react with CH_4 and the C_2 products to form CO_2 and a higher selectivity is always compromised with a lower activity (or conversion). As a result, per-pass C_2 yield on all catalysts reported was limited to about 25% [1].

In the past decade substantial efforts were reported on new chemical reactors, such as simulated countercurrent moving-bed reactors [4], gas recycled electrocatalytic reactors [5], and ceramic membrane reactors [6–14], for oxidative coupling of methane. However, per-pass C_2 yield higher than the economically attractive value of 30% has not been accomplished in spite of the intensive studies in this area. Here we report on oxidative coupling of methane on a catalytically active/selective fluorite-type samarium-yttrium-bismuth oxide membrane reactor. In this reactor the membrane separates methane and oxygen streams and allows methane to react selectively with nonstoichiometric oxygen on the catalytically active and selective membrane surface. The membrane reactor also allows *in-situ* separation of oxygen from the air.

2. Experimental

The geometry of the $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) membrane is shown in figure 1. The reactor configuration is similar to what was previously reported [12,14,15]. The physical dimensions of the membranes are given in table 1. To prepare the BYS membrane tubes, BYS powder was first synthesized by the citrate method using bismuth, yttrium and samarium nitrates as the precursors. The citrate-derived BYS powder was calcined at 600 °C for 5 h and then ground in an agate mortar before being used for pressing. BYS rods of about 3 cm in length and 8.5 mm in diameter were prepared by cold isostatic pressing at 138 MPa. These dense rods were then drilled to dead-end tubes by a diamond bit. The dead-end BYS green body tubes were sintered at

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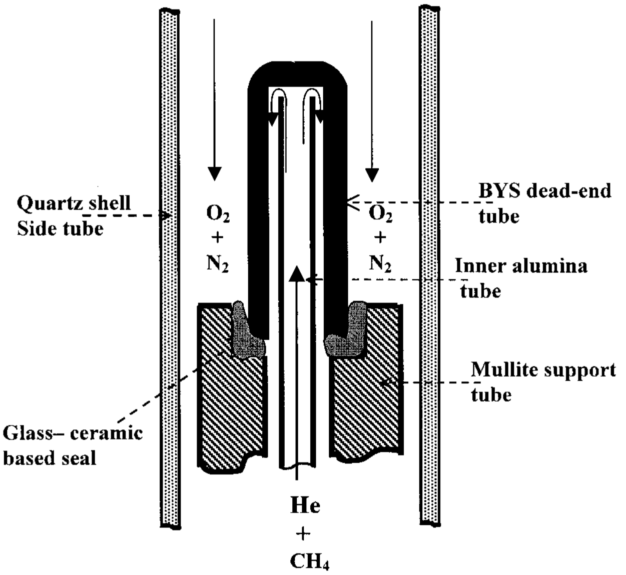

Figure 1. Schematic diagrams showing (a) dead-end tubular membrane and the central part of the membrane reactor and (b) flow chart of BYS membrane reactor operation. The open-end side of the $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) membrane tube is sealed on top of a dense mullite tube of 13 mm OD and 5 mm ID. The seal used is a home-made ceramic–glass composite consisting of the BYS powder (45 wt%), $SrCe_{0.95}Tb_{0.05}O_3$ powder (25 wt%), Pyrex glass (10 wt%), $Na_2Al_2O_3$ (10 wt%) and B_2O_3 (10 wt%). Inside the mullite support tube is a smaller dense alumina tube of 3.1 mm OD. The BYS membrane tube on the mullite support is placed inside a larger quartz tube of 15 mm ID.

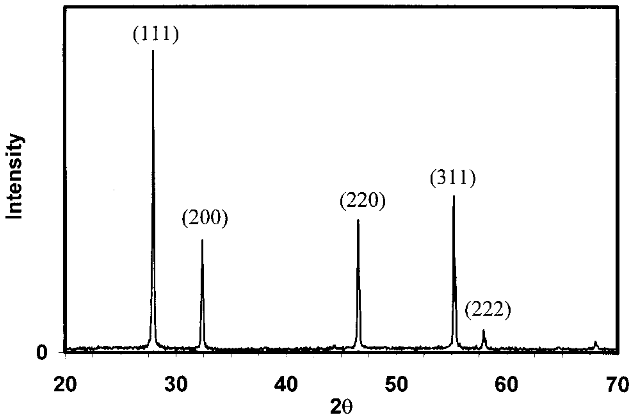

Figure 2. XRD pattern of the BYS membrane showing fcc fluorite structure (Siemens Kristalloflex D500, Cu Kα radiation).

1050 °C for 20 h and then annealed at 850 and 650 °C respectively for 2 h. The membrane has a fcc fluorite structure, as confirmed by XRD shown in figure 2, with a lattice constant of $a = 0.555$ nm, and a real density of 8.0 g/cm^3. A helium permeation test showed that the membranes were hermetic to helium (permeance lower than 1×10^{-10} mol s^{-1} m^{-2} Pa^{-1} based on the detection limit of the helium permeation set-up).

For OCM experiments, the open-end side of the BYS membrane tube was vertically placed and hermetically sealed on top of a medium sized mullite tube, as shown in figure 1(a). Inside the mullite support tube was a smaller dense alumina tube through which He or He/CH_4 mixture was introduced to the dead-end side of the BYS membrane tube (referred to as downstream, or tube side). The BYS membrane tube on the mullite support was placed inside a larger quartz tube. O_2–N_2 mixture was passed through the annulus between the larger quartz and medium mullite tubes (referred to as the upstream, or shell side). The influent compositions and flow rates were controlled by mass flow controllers. The effluent flow rates and compositions were measured respectively by a bubble flow meter and gas chromatography. The oxygen partial pressure in the non-reducing effluents was also determined by an yttria-stabilized-zirconia oxygen sensor. The oxygen permeation flux was calculated from the oxygen concentration and flow rate of the downstream effluent when helium was used as the purge gas, or from the compositions of the oxygen-containing species in the downstream effluent when CH_4–He was used as the feed to the downstream side. The membrane module was heated by a temperature programmable tubular furnace with a maximum temperature of 1000 °C. Typical experimental conditions for OCM are summarized in table 1.

Table 1
BYS membrane reactor dimension and typical OCM reaction conditions

Parameter	Value
BYS membrane inner diameter (mm)	3.8
BYS membrane outer diameter (mm)	6.25
BYS inner tube length (mm)	29
BYS membrane inner surface area (cm^2)	3.1
Cross-sectional area of downstream side (mm^2)	2.8
Cross-sectional area of upstream side (mm^2)	144
Membrane surface to reaction volume ratio (1/cm)	27
Reaction temperature (°C)	900
Downstream CH_4-He feed flow rate (cm^3/min)	7
Upstream air feed flow rate (cm^3/min)	40
Total pressure (kPa)	103
P_{CH_4} in feed (methane side) (kPa)	2
P_{O_2} in feed (oxygen side) (kPa)	21

3. Results and discussion

Figure 3 shows the OCM results at different tube side P_{CH_4} with other experimental parameters fixed under the optimum conditions (listed in table 1). The gas chromatogram of the effluent from the tube side of the reactor at the best C_2 yield is shown in figure 4. As shown, the C_2 selectivity and yield increases with decreasing P_{CH_4}. A 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 BYS membrane

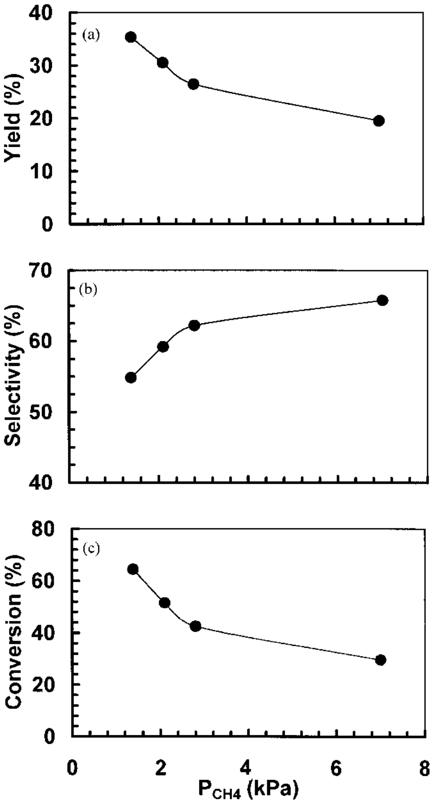

Figure 3. Results of OCM in the BYS membrane reactor at different P_{CH_4} in the membrane mode. Conditions: $T = 900\,°C$, $P_{O_2} = 19.6\,kPa$, $F_{shell} = 40\,ml/min$, $F_{tube} = 7 \pm 0.02\,ml/min$.

reactors, as shown in figure 5. The BYS membrane reactors could be continuously operated for about 1 week until the seal used in this study became ineffective.

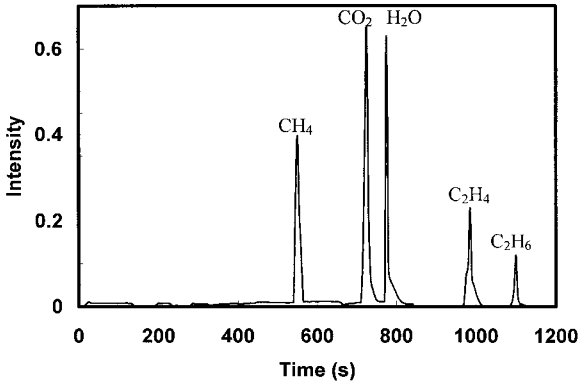

Figure 4. Gas chromatogram of effluent from the tube side under the conditions with the highest C_2 yield. GC: Perkin–Elmer Model 8500; Column: 80–100 mesh molecular sieve column of 1/8 in OD and 10 ft long (Alltech); Conditions: Oven-temperature program from 32 °C to 225 °C with a ramp rate of 20 °C/min; HWD detector at 275 °C; Sample injection port at room temperature; He carrier gas flow rate 20 ml/min. Influent composition: $CH_4 = 1.38\,kPa$; effluent composition: $CH_4 = 0.48\,kPa$, $CO_2 = 0.4\,kPa$, $C_2H_4 = 0.33\,kPa$, $C_2H_6 = 0.15\,kPa$.

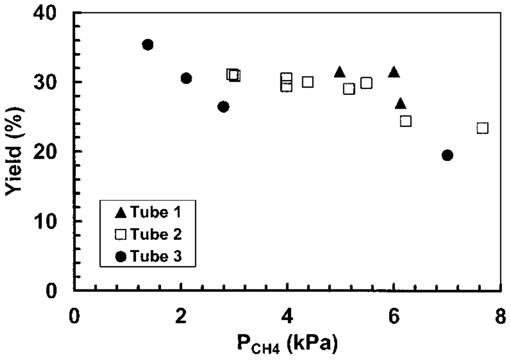

Figure 5. Results of OCM in three different BYS membrane reactors at different P_{CH_4} in the membrane mode. Conditions: Reaction surface area/reaction volume = 27–29 (1/cm), $F_{tube} = 6\text{–}7\,ml/min$, $F_{shell} = 30\text{–}40\,ml/min$, $P_{O_2} = 10\text{–}20\,kPa$, $T = 900\,°C$.

The BYS is known to be a good oxygen ionic conductor with an electronic conductivity of about 2 orders of magnitude lower than its ionic conductivity (~0.5 S/cm at 900 °C). The electron conduction in the bismuth oxide is dominated by a *p*-type mechanism in a large P_{O_2} range (down to 10^{-21} atm) [16]. It is known that for OCM on metal oxide catalysts the *p*-type electronic mechanism favors the formation of methyl radicals (C_2 selectivity), and high mobility and concentration of the nonstoichiometric oxygen enhance the activity of the reaction (CH_4 conversion) [16,17]. Mechanistically, the reaction on the BYS membrane surface exposed to methane can be described by (in Kroger–Vink notation):

$$2CH_4 + O_O^x + 2h^\bullet \Rightarrow 2CH_3{}^\bullet + V_O^{\bullet\bullet} + H_2O$$

The oxygen vacancies transfer across the membrane to the other side of the BYS membrane, and electron-holes move across the membrane wall in the opposite direction. The reaction on the BYS membrane surface exposed to O_2–N_2 is expressed by:

$$O_2 + 2V_O^{\bullet\bullet} \Leftrightarrow 2O_O^x + 4h^\bullet$$

The BYS can have up to 25% oxygen sites vacant, much larger than the perovskite and brownmillerite type oxide catalysts. This ensures a large number of nonstoichiometric oxygen present on the BYS surface, giving rise to a high activity for OCM reaction (with a turnover frequency as high as 625 1/s) [14]. For OCM in the BYS membrane reactor, the C_2 formation rate per unit membrane surface under the conditions of the highest C_2 yield is $0.1\,mmol/m^2\,s$, larger than those on the perovskite type ceramic membrane surfaces under similar conditions with a lower C_2 selectivity and yield.

The present membrane reactor design gives a membrane surface to reactor volume ratio of 29 1/cm, much larger than those of the membrane reactors studied previously for OCM. This reactor configuration is required for achieving higher C_2 yield for OCM with a heterogeneous and homogeneous mechanism. Although pure bismuth oxide is not chemically stable in a reducing environment, the BYS has an improved chemical stability due to the doping of more stable samarium and yttrium oxides. Figure 6 compares conversion versus

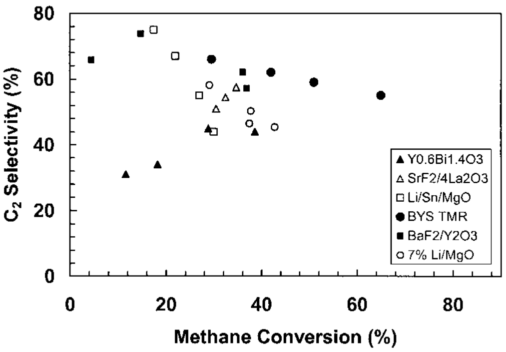

Figure 6. Comparison of C_2 selectivity *versus* methane conversion for OCM in the BYS tubular membrane reactor (TMR) with various catalyst systems (Y0.6Bi1.4O3 [18], SrF2/4La2O3 [19], Li/Sn/MgO [20], BaF2/Y2O3 [21], 7% Li/MgO [22]).

selectivity data for various catalysts operated in a fixed-bed reactor [18–22] with those obtained in this study using a BYS dead-end dense ceramic membrane reactor. It is difficult to make a strict comparison between these systems since the operating conditions are very different, so only the best results obtained with these catalysts are included in the plot. As can be seen from figure 6, at the same conversion, the highest selectivities are obtained in the BYS dead-end dense ceramic membrane reactor. Membrane reactors provide a unique medium for partial oxidation reactions. Their main advantage is to avoid direct contact between the reactant and molecular oxygen, yielding much higher selectivity than the conventional packed-bed reactors. Improvement in conversion was achieved by increasing the catalytically active surface area to reaction volume ratio to promote the surface methyl radical formation and coupling reactions and optimize the gas-phase reactions [23].

Conclusions

BYS dead-end tubes in fcc fluorite structure were successfully synthesized by the citrate method and processed by CIP with green machining. The dead-end tubes were used in a membrane reactor for OCM. The oxygen permeation fluxes through tubular BYS membrane reactors under OCM reaction conditions are approximately 1.5–3.5 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. High C_2 yields were obtained at low methane partial pressures. The results are reproduced in three different membrane reactors, and repeatability of the high yields is demonstrated.

Acknowledgment

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