Oxidative Coupling of Methane in Solid Oxide Fuel Cell Tubular Membrane Reactor with High Ethylene Yield

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Abstract

A Mn-Ce-Na₂WO₄/SiO₂ catalyst integrated solid oxide fuel cell tubular membrane reactor design is developed for oxidative coupling of methane (OCM). The OCM reaction carried out using the tubular membrane reactor establishes both superb hydrocarbon selectivity and outstanding ethylene-to-ethane ratio over the conventional fixed bed OCM or the button cell reactor. A remarkable performance of 60.7% methane conversion with 41.6% C₂+ selectivity, 5.8 ethylene-to-ethane ratio and 19.4% ethylene yield is achieved using the tubular membrane reactor and the Mn-Ce-Na₂WO₄/SiO₂ catalyst, demonstrating considerable advantages over conventional OCM.

Keywords

OCM, SOFC, methane, ethylene, membrane reactor, Mn-Ce-Na₂WO₄

1. Introduction

The increasing demands in energy along with the expected long-term decline in petroleum reserves require alternative hydrocarbon feedstocks for the production of important industrial chemical intermediates such as ethylene. Methane (CH₄), the major component of natural gas, is a promising starting material because it has the desirable carbon-hydrogen ratio as well as abundant reserves.[1] The efficient conversion of methane, which otherwise is primarily used as fuel for power generation, to value-added chemicals is highly demanded. Conventionally, multiple steps are required to convert methane into value-added chemicals, where methane is first reformed to synthesis gas (CO and H₂), followed by the Fischer-Tropsch process to produce alkenes or the catalytic conversion to produce methanol and the subsequent methanol-to-olefin (MTO) processes. However, the capital and maintenance costs are relatively high in these rather complicated processes. A direct route for the conversion of methane into value-added chemicals is highly demanded.[2,3]

Oxidative coupling of methane (OCM) has been studied for decades[4–13] and is recently being commercialized by Siluria Technologies. In a typical OCM process, methane and pure oxygen are co-fed

through a metal oxide catalyst bed and transformed to ethane, ethylene, and carbon oxides at 500-800 °C. The main reaction proceeds as:

There are several shortcomings of the conventional OCM process, namely, the requirement of air-separation units for the feed of pure oxygen, the unsatisfying yield of ethylene due to the deep oxidation of methane, and the potential explosion hazard from direct mixing of hydrocarbon with pure oxygen.[14] In this communication, we present a solid oxide fuel cell (SOFC) facilitated OCM membrane reactor that simultaneously addresses these problems associated with conventional OCM.

The catalytic membrane reactors have been intensively studied in the last two decades to improve yields of olefin in selective oxidation reactions. A number of comprehensive reviews on this subject are available.[15–21] It is generally accepted that the use of membrane reactors in selective oxidation reactions can benefit olefin selectivity by the distributed feeding of oxygen to suppress deep oxidation. However, these oxygen permeable membrane reactors suffer from the inherent low oxygen flux, resulting in low methane conversion despite of the high selectivity reported and cited in many studies.[22,23] The SOFC membrane reactor introduced here inherits the advantages of conventional catalytic membrane reactor while providing a simple way of tuning the oxygen flux by adjusting the working current of the cell.[24] For instance, Morejudo et al. recently demonstrated a successful integration of a co-ionic conducting SOFC device with the methane dehydroaromatization(MDA) reaction to improve the aromatics selectivity as well as the stability of catalysts.[3] In our study, several OCM catalysts were synthesized and integrated with SOFC, with the purpose to establish advanced SOFC membrane reactors and overcome the problems of traditional OCM process. Through a careful evaluation and optimization of the OCM catalysts, as well as a significant improvement on the SOFC reactor design, we have achieved a very promising catalyst-integrated SOFC tubular membrane reactor demonstrating superior performance, including higher hydrocarbon selectivity and better ethylene-to-ethane ratio, to the conventional OCM process. Our novel process also enables a safer operation with less expensive process cost, making OCM a practical route for producing ethylene from the abundant methane reserves.

2. Experimental

2.1 Catalyst synthesis

All OCM catalysts investigated in this study were synthesized using chemicals from Sigma Aldrich, unless stated otherwise. For instance, MgO-BaCO₃ catalyst was prepared by mixing a stoichiometric 1:1 amount of magnesium nitrate and barium oxalate in water followed by drying at 80 °C and calcining at 800 °C for 4 h.[25] LaAlMgO catalyst was obtained in a similar manner by dissolving the desired amount of lanthanum nitrate, aluminum nitrate and magnesium nitrate in citric acid and evaporating stepwise at 80°C and 100°C. A final calcination at 800°C for 5 h was applied to convert the mixture to the desired composition.[26] Supported Mn-Ce-Na₂WO₄ catalysts were synthesized following the wet impregnation method.[27–29] The desired support was first impregnated with aqueous solutions of Mn(NO₃)₂, Ce(NO₃)₃ and Na₂WO₄ at 80 °C and evaporated, followed by calcination at 850°C for 6 h. Various supports investigated were La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{2.88} (LSCrM),[30] Gd_{0.2}Ce_{0.8}O_{1.9} (GDC,

Fuelcellmaterials.com, SKU: 112102), $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ, Fuelcellmaterials.com, SKU: 312005), SiO_2 particles (0.5-10 μm , Sigma-Aldrich, S5631) and SiO_2 gel (pore size 15 nm, Sigma-Aldrich, 236845), with the corresponding yielded catalysts labelled as Mn-Ce- Na_2WO_4 /LSCrM, Mn-Ce- Na_2WO_4 /GDC, Mn-Ce- Na_2WO_4 /YSZ, Mn-Ce- Na_2WO_4 / SiO_2 NPs and Mn-Ce- Na_2WO_4 / SiO_2 gel, respectively.

2.2 Cell integration

In an effort to integrate the OCM catalyst with the button/tubular cells, the catalyst slurry, made by blending crashed OCM catalyst powders with colloidal gold paste, was coated on the anode side of the Hionic™-electrolyte (scandia stabilized zirconia (ScSZ))/LSM (lanthanum strontium manganite)-GDC (gadolinium doped ceria)/LSM cathode multilayer cell structure (Fuelcellmaterials.com, single electrode cell) and calcined at 1100°C for 2 h (Fig. 1 inset). Gold wire and gold paste were used to complete the electrical contact, and high temperature ceramic sealing paste was used to seal customized cells on the alumina (99.8%) support tube. In the button cell design, button cells with a diameter of 20 mm were mounted on one end of the support tube with the OCM anode facing inward. Additional OCM catalysts of the same kind were added in order to deplete the open space between cell and the lower end of the inner tube (methane inlet), as illustrated in Fig. 1 top. In the tubular geometry design, four rectangular cells of 40 mm x 20 mm were mounted onto a 25.4±1 mm OD alumina (99.8%) support tube with four customized rectangular matching open windows of 42 mm x 21 mm evenly distributed around the tube. The resulted tube after cell mounting is in principle identical to a tubular SOFC (Fig. 1 bottom), with the inner tube surface composed of the OCM-active anode and the outer tube surface of the LSM cathode. Similarly, additional OCM catalysts were packed into the tubular reaction chamber to deplete the open space in the high-temperature cell region to ensure sufficient contact between methane gas, oxygen source and the catalysts.

2.3 Sample characterization

Powder X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were conducted on the as-obtained OCM catalysts to confirm the desired structure and morphology. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the catalyst loading. XRD patterns were recorded on a Bruker D8 powder X-ray diffractometer equipped with Cu K_α as the X-ray source. All SEM images of the OCM catalysts as well as the cross-section micrographs of the cell structure were obtained on a Tescan Mira 3 high resolution scanning electron microscope. An Agilent 7700 spectrometer was used to collect the ICP-MS data.

2.4 Catalytic activity test

Fig. 1 pictures the schematic representation of the two different membrane reactor geometries adopted in our study. An easy-to-fabricate button cell design (Fig. 1 top) is used to screen for the SOFC-compatible best-performing catalyst from a comprehensive database of existing OCM catalysts,[31] and a tubular membrane reactor (Fig. 1 bottom) is designed to evaluate the synergistic effect between OCM and SOFC, utilizing the best OCM catalyst identified. 4 g of OCM catalysts were charged into the button cell reactor 6 g for the tubular reactor. In both scenarios, catalytic testing was conducted by feeding diluted methane gas ($P_{CH_4}=9.2$ kPa) to the inner anode chamber and air directly to the outer cathode

environment. The mixture exiting the anode chamber was analyzed by Agilent 7890, equipped with a natural gas analyzer. During operation, the SOFC unit functions as an internal oxygen pump to selectively transfer oxygen from the air cathode to the anode in the form of oxygen anion, with the amount of oxygen anion transferred per unit time being conveniently tuned by the cell current. As a result, no direct co-feed of methane and pure oxygen is required, featuring reduced operation cost and improved safety.

Fig. 1. Schematic diagrams demonstrating the SOFC-OCM button cell reactor with 4 g catalyst loading (top) and the tubular membrane reactor with 6 g catalyst loading (bottom) used in this study. SEM cross-section image of the multilayer SOFC membrane assembly is illustrated in insert.

3. Results and discussions

3.1 Screening of Catalysts

All OCM catalysts were synthesized following protocols reported in literatures. We firstly evaluated their performance using the button-cell reactor depicted in Fig. 1 top. All tests were conducted at comparable conditions of 800°C, 22 ml/min diluted methane gas flow, 0.37 A cell working current, 1 cm² exposed cell area and the same 4 g catalyst loading, with the corresponding CH_4 -to- O^{2-} molar ratio of 1.9:1. Figure 2 summarizes the results of all catalysts screened in this work. In all experiments, carbon oxides and water are the only detected side products, with no coke deposition. In absence of a proper OCM catalyst, only 8.3% methane is converted at a selectivity of 22.6% towards ethane and ethylene. With a good catalyst, a complete utilization of all delivered oxygen can be achieved with good methane conversion and hydrocarbon selectivity. Particularly, we have identified the porous SiO_2 gel supported Mn-Ce- Na_2WO_4 catalyst to be the best one with a performance of 29.5% methane conversion and 64.6% total hydrocarbon selectivity, which is in good agreement with literature reports on fixed-bed OCM using silica-supported Mn-Ce- Na_2WO_4 . [27]

Fig. 2. Catalytic performance, namely product selectivity and methane conversion, for a variety of OCM catalysts evaluated in this study, using the SOFC-OCM button cell design in Fig. 1 top.

XRD, SEM, and ICP-MS were used to characterize the composition, structure, and the morphology of as-prepared fresh Mn-Ce-Na₂WO₄/SiO₂ catalyst, as shown in Fig. S1 in the supporting information. All of the peaks in the XRD diffractogram (Figure S1A) can be unequivocally indexed to four crystalline phase in the catalyst, namely cristallite SiO₂, Na₂WO₄, MnO₂, and CeO₂, which is in good agreement with previous reports.[27,32]. SEM image (Figure S1B) shows that the metal oxides are loaded on the surface of SiO₂ particles. The loading amount is 2.2% Mn-3.2% Ce-4.9% Na₂WO₄ on the SiO₂ particles which is shown in the supporting Table S1.

In addition, the inset of Fig. 1 presents the cross-sectional SEM micrograph for a typical SOFC structure. The electrolyte, free of cracks and pinholes, is 50 μm in thickness, whereas the porous cathode of lanthanum strontium manganite (LSM) and the customized anode of OCM catalyst-Au composite are approximately 60 μm each. Anode interlayer composed of gadolinium-doped ceria (GDC) and scandium-stabilized zirconia (SSZ), and cathode interlayer of GDC and LSM, are present with a thickness of 20 μm each. The complete cell ranges between 190 μm and 230 μm in total, providing good mechanical strength and no gas permeability.

3.2 Current-tuned catalytic performance

The dependence of catalytic response on cell working current was further investigated using the top performing Mn-Ce-Na₂WO₄/SiO₂ gel catalyst in button cell reactor. Experiments were conducted at 800°C with diluted methane gas flow of 22 ml/min and 1 cm² exposed cell area. This particular cell has an open circuit voltage of 0.670 V with a short circuit current of 0.17 A. Instant response of catalytic activity is observed when cell current is altered hourly, with larger current leading to more transported oxygen and higher methane conversion, enabling a precise tuning of the catalytic performance. Notably,

methane conversion of 50.7% with 44.0% C₂+ selectivity and methane conversion of 59.4% with 35.8% C₂+ selectivity are achieved, representative of the state of the art for OCM catalysts.[27,33,34] No decay in activity is noticed within the hourly window at each current, indicating a stable performance consistent with its coke-free characteristic. In addition, a co-feed of CH₄ and pure oxygen (CH₄:O₂=3:1) experiment, equivalent to the conventional fixed bed test, was conducted at zero current (open circuit) with other parameters being identical. The amount of co-fed oxygen gas chosen is equal to the amount of oxygen source delivered by the SOFC button cell at a current of 0.47 A. Similarly, 36.8% conversion and 57.4% C₂+ selectivity are measured, similar to the results in Fig. 3 at I = 0.47 A, suggesting that in the button cell reactor, the oxygen source provided by SOFC functions in the same manner as the oxygen gas being co-fed in a typical fixed bed reactor. Table 1 summarizes our results as well as results from literature reports for better comparison.

Fig. 3. C₂+ selectivity (A) and methane conversion (B) as a function of reaction time and cell current. Catalyst: Mn-Ce-Na₂WO₄/SiO₂ gel.

Table 1 Comparison of different reactor configuration

	Conversion	C ₂ + selectivity	C+S%	Ethylene: Ethane	Ethylene yield
Fixed bed reactor	36.8%	57.4%	94.2%	1.7	12.6%
Button cell SOFC	37.0%	57.1%	94.1%	1.7	12.5%
Button cell SOFC	59.4%	35.8%	95.2%	2.3	14.1%
Tubular SOFC	34.8%	59.1%	93.9%	3.7	15.3%

Tubular SOFC	60.7%	41.6%	102.3%	5.8	19.4%
Mixed conductor (MIEC)[35]	1.9%	54.4%	56.3%	0.72	0.40%
Mixed conductor (MIEC)[36]	26%	62.5%	88.5%	Not given	Not given
SOFC[24]	1.87%	86.1%	87.97%	Not given	Not given
SOFC[37]	10.0%	70.5%	80.5%	2	7.05%

3.3 Impact of reactor design

With a good understanding of the catalytic performance at a full spectrum of working current for the Mn-Ce-Na₂WO₄/SiO₂ gel catalyst, we implemented the same membrane electrode assembly in the tubular design (Fig. 1 bottom). A distinctive characteristic of the tubular geometry is that, along the methane flow pathway, source of oxygen is introduced into the reaction chamber by SOFC in a distributive manner and consumed instantaneously as it interacts with methane and catalyst without further accumulation. On the contrary, oxygen gas and methane are supplied all at once in a conventional fixed bed reactor or the button cell reactor (Fig. 1 top), where, as a result, the deep oxidation of hydrocarbons to oxides becomes problematic due to the local excess amount of oxygen at the entrance of the reaction zone. Cell operating current was varied in order to investigate the catalytic performance in a wide range of methane conversion. The typical reaction product distribution for a tubular reactor under different operating current is provided in the Table S2 in the supporting information. With increasing conversion of methane, the selectivity of hydrocarbon decreases. Fig. 4 shows the direct comparison of OCM performance between the button and tubular geometries at 800 °C. To account for the different reactor dimensions and catalyst loading amount, the feed rate of dilute methane was adjusted to maintain the same space velocity of GHSV= 6050 ml·g⁻¹·h⁻¹ in both geometries.

Fig. 4. Performance comparison between SOFC-OCM button cell reactor, SOFC-OCM tubular membrane reactor, and fixed bed reactor: Top, Ethylene-to-ethane ratio. Bottom, Total C2+ selectivity, including ethylene, ethane and higher hydrocarbon products.

As evident in Fig. 4, the tubular membrane reactor outperforms the button cell geometry at all conditions explored, featuring greater economic advantages with both better conversion-selectivity profile and higher ethylene-to-ethane ratio. The benefit is more pronounced at higher methane conversions, where the feed of oxygen is higher, consequently more likely to suffer from deep oxidation. With the advantage of the tubular membrane design, even though the total supply of oxygen is the same, the dilution effect by distributing oxygen ion over the entire interior of the tubular membrane effectively reduces the local oxygen concentration at each contact point along the methane pass, lowering the tendency of deep oxidation and shifting the product selectivity towards hydrocarbons. In addition, decent ethylene-to-ethane ratios are observed in the tubular reactor, over 2-fold increase from those in the button-cell reactor (Fig. 4 top) or the conventional fixed-bed reactor.[28] Besides, the ethylene-to-ethane ratio also rises with increasing methane conversion (increasing oxygen-to-methane ratio), in consistency with literature report.[38] The ethane-to-ethylene conversion can occur via two diverse routes, the oxidative and non-oxidative dehydrogenation.[34] The strong dependence of ethylene-to-ethane ratio on the oxygen-to-methane ratio suggests the oxy-dehydrogenation pathway. As a result, the tubular membrane reactor with a continuous oxygen supply along the reaction path enables an effective oxy-dehydrogenation of ethane to ethylene in the entire reaction zone, benefiting a higher ethylene-to-ethane ratio. Hence, the inherent characteristics of the tubular membrane reactor not only improves the C2+ selectivity by suppressing deep oxidation, but also boosts the ethylene-to-ethane ratio by supplying continuous oxygen source along the reaction zone. All combined, a remarkable ethylene yield, one of the most crucial indicators determining the economic merit of a given OCM process, can be achieved. In particular, with the dual benefits of the tubular membrane reactor, a

methane conversion of 60.7% with 41.6% C₂⁺ selectivity, 5.8 ethylene-to-ethane ratio and 19.4% ethylene yield is successfully demonstrated, highlighting the best performance among OCM reactions.

4. Conclusions

We have demonstrated an SOFC-OCM tubular membrane reactor design with the use of an optimized Mn-Ce-Na₂WO₄/SiO₂ catalyst. OCM reaction carried out using the tubular membrane reactor establishes both superb hydrocarbon selectivity and outstanding ethylene-to-ethane ratio over the conventional fixed-bed OCM and the SOFC-OCM in the button cell design. A remarkable performance of 60.7% methane conversion with 41.6% C₂⁺ selectivity, 5.8 ethylene-to-ethane ratio and 19.4% ethylene yield is successfully achieved using the SOFC-OCM tubular membrane reactor. The use of an oxygen-selective SOFC membrane eases the cost and safety concerns of conventional fixed bed OCM reactions by eliminating the requirement of an expensive air separation unit as well as preventing the direct co-feed of explosive methane-oxygen mixture. Moreover, comparing with the mixed ionic electronic conductor (MIEC) reactor which generally provides limited oxygen flux, the tubular SOFC reactor design offers the flexibility of precisely controlled oxygen delivery and tunable product distribution. We believe our work presents encouraging results to overcome the hurdles associated with conventional OCM processes.

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